CHE 1000 – Introduction to Chemistry

Lecture notes on Stoichiometry and Gases

LECTURE 1

Stoichiometry – What is Stoichiometry?

Stoichiometry is a term derived from the Greek term *Stoicheion* meaning *element* and *metron* meaning *measure*.

Its used in chemistry to describe all quantitative aspects of chemical composition and reaction.

Measurements

A quantitative observation, or measurement, always consists of two parts: a number and a scale (called a unit). Both parts must be present for the measurement to be meaningful.

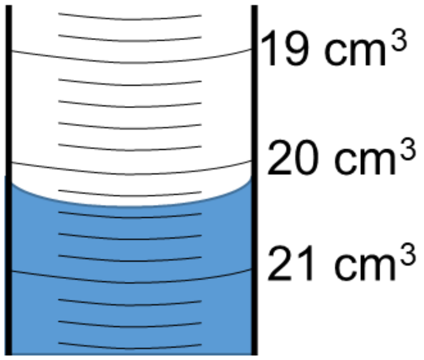
We measure volume, mass, temperature length, time electric current, amount of substance etc.

Elements in measured physical quantity

[Physical quantity] = [measurement] [prefix if necessary] [Unit]

Example volume of water is V= 25.00 mL

1.1 Significant figures in a measurement are a number of digits that are known with some degree of confidence
A burette reading 20.25 cm^3 can be reported as 20.24, 20.25, 20.26 cm^3 by 3 different students.



Student A 20.25 cm^3

Student B 20.24 cm^3

Student C 20.26 cm^3

The first 3 digits remain the same regardless of which student takes the reading. These are called CERTAIN and the last digit UNCERTAIN. We customarily report a measurement by recording all the certain digits plus the first uncertain digit.

Rules of significant figures

Rule 1

1.1 Digits 1-9 are always significant

1.2 Zeroes to the right of the significant digit after a decimal place are significant,.e.g. 25.00

1.3 Zeroes the right of significant digit are not significant e.g.2500

Rule 2

When adding or subtracting numbers, your answer can only have as many decimal places as the measurement having the least number of decimal places,

Example 2.2 + 4.53 = 6.73 and final answer = 6.7

Rule 3

When multiplying or dividing, your answer may only show as many significant figures showing the least number of significant digits.

Example number of mol n = 0.033 mol/L x 0.002500 L

= 0.00082500 mol

= 0.00083 mol to 2 sig fig.

Rule 4

The number in the conversion factors, molar masses, atomic masses, physical constants are considered to be exact, have more significant figures than shown and are not included in establishing the number of significant figures.

Example number of moles n= 0.2512 g/1.01g/ mol
= 0.2487129 mol
= 0.2487 mol

Rule 5
Rounding of Rule
If the digit next to the significant digit is smaller than 5, the significant digits is unchanged.
If the digit next to the significant digit is greater than 5, the significant digit is increased by one

Example 5.042 mol/L = 5.04 mol/L to 3 sig fig or 6. 47 g = 6.5 g to 2 sig fig

1.2 **Fundamental SI Unites (Base quantities and base Units)**

Base quantity	Symbol	Base unit	Symbol
1. length	l	meter	m
2. mass	m	kilogram	kg
3. time	t	second	s
4. Thermodynamic temperature	T	Kelvin	K
5. Electric current	I	ampere	A
6. Amount of substance	n	mole	mol
7. Luminous intensity	I_v	candela	cd

1.3 Non- SI Physical quantities in common use

Physical quantity	Symbol	Unit	Symbol	Conversion
Volume	V	Litre	L	$1L=10^{-3} m^3$
Length	l	angstrom	Å	$1Å=10^{-10}$ m
Pressure	P	atmosphere	atm	1 atm =101325Pa
		bar	bar	1bar= 100000 Pa
		torr	torr	1torr =133.24 Pa
		mmHg	mmHg	1 mmHg =133.25 Pa
Energy	E	Electron volt	eV	1 eV =1.601 $x10^{-19}$J
Temperature	t	Degree centigrade	°C	1°C= T-273.15 K
Concentration	c	Molarity	M	mol/L

1.4. Prefixes

Because the fundamental units are not always convenient (expressing the mass of a pin in kilograms is awkward), prefixes are used to change the size of the unit.

Exponential notation	Name	Symbol	Expanded form and meaning	US name
10^{12}	tera	T	1 000 000 000 000	trillion
10^{9}	giga	G	1 000 000 000	billion
10^{6}	mega	M	1 000 000	million
10^{3}	kilo	k	1 000	thousand
10^{2}	hecto	h	100	hundred
10^{1}	deca	da	10	ten
10^{0}			1	one
10^{-1}	deci	d	0.1	tenth
10^{-2}	centi	c	0.01	hundredth
10^{-3}	milli	m	0.001	thousandth
10^{-6}	micro	µ	0.000 001	millionth
10^{-9}	nano	n	0.000 000 001	billionth
10^{-12}	pico	p	0.000 000 000 001	trillionth
10^{-15}	femto	f	0.000 000 000 000 001	quadrillionth

Example Convert 5.01 mg to g expressing it in scientific notation

= 5.01 $x10^{-3}$ g.

Volume is very important in chemistry. Its not an SI unit but is derived from the SI unit, length (v = l x w x h).

Express 1L in dm^3, cm^3 m^3

10 cm = 1 dm, therefore $(10)^3$ cm^3 = $(1)^3$ dm^3

1L = $1dm^3$ =1000 cm^3

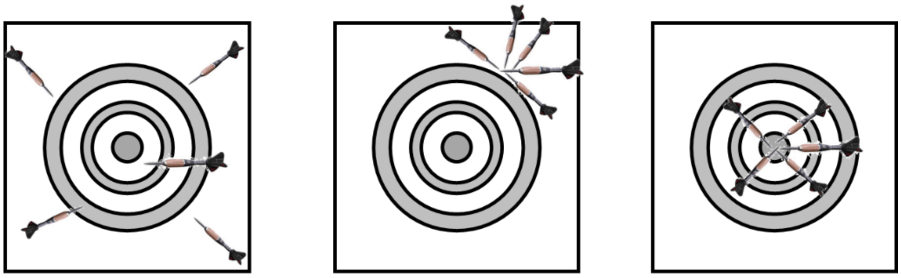
1m = 10 dm, therefore $1m^3$ = $(10)^3$ dm^3 = 1000 dm^3

$1dm^3$= 1L = 1x 10^{-3} m^3

1.5 Precision and Accuracy

Precision indicates how close together or how repeatable the results of the measurement are to each other

Accuracy indicates the closeness of a measurement to a true value



Poor precision	Good precision	Good precision
Poor Accuracy	Poor accuracy	Good accuracy

1.6 Dimensional analysis

Dimensional analysis is used to convert units to other units. We use the equivalence statement

Example

Convert 10 km to miles

Solution

We need to know the equivalence statements

1km = 1000 m, 1 m = 1.094 yards, 1 mi = 1760 yards (usually given)

Convert km to m i.e. $10\text{ km} \times \frac{1000\text{ m}}{\text{km}} = 1\times 10^{4}\text{ m}$

Convert m to yards $1\times 10^{4}\text{ m} \times \frac{1.094\text{ yard}}{\text{m}} = 1.094\times 10^{4}\text{ yards}$

Finally, convert yards to miles $1.094\times 10^{4}\text{ yards} \times \frac{1\text{ mi}}{1760\text{ yards}} = 6.22\text{ mi}$

LECTURE 2

2.1 Elementary idea of atoms, molecules and ions

All substances are made of atoms, molecules, and ions

2.2 Atomic structure

Each atom has a nucleus which consists of protons (p) and neutrons (n). Part of the mass of p, and n are used up as binding energy. Surrounding the nucleus are electrons in different shells.

Masses of p, n, e in kg and u(amu)

Particle	Mass in grams	Mass in unified mass unit, u
Electron	9.10956×10^{-28}	0.00054859
Proton (P)	1.67261×10^{-24}	1.007277
Neutron (N)	1.67492×10^{-24}	1.008665

1u = 1/ N_A =1.6605×10^{-24} g by definition

2.3 Isotopes, Atomic and molecular masses

Symbol for isotopes of element X, $^{A}_{Z}X$ A= Z +N

A= mass number

Z= number of protons = atomic number

N= number of neutrons

2.4 Isotopic mass, A_i,

Because of loss of mass to binding energy isotopic masses and % abundance are measured using a Mass Spectrometer (MS)

Atomic mass (u)

The units of atomic mass are in u (formerly a.m.u)

Physical scale of atomic masses of elements are based on the ${}^{12}_{6}C$, where the MS is calibrated to read the ${}^{12}_{6}C$ peak at exactly 12.0000 u

2.5 **Atomic mass (or atomic weight or relative atomic mass)**

The atomic mass, A, of an element is calculated as $A = \sum_{i=1}^{n} A_i f_i$ where f_i = % abundance/100 %

The atomic mass is the mass of **one** element

Example

The mass values for ^{63}Cu (69.09 %) and ^{65}Cu (30.91%) are 62.93 amu and 64.93 amu, respectively . Calculate the average atomic mass of copper

Solution

Average atomic mass = $\frac{69.09}{100} \times 62.93u + \frac{30.91}{100} \times 64.93u = 63.55$ u

2.6 Molecular mass (or molecular weight) is sum of the atomic masses of all the atoms in a molecule

2.7 **Definition of Avogadro number and Avogadro constant**

2.8 Avogadro constant

The Avogadro constant, N_A, is defined as the number of atoms or molecules, in one mole, that is the number of carbon in 12.0000 g of carbon-12.

N_A = 6.022 141 79 x10^{23} mol^{-1} to 9 sig. fig.

$N_A = 6.022 \times 10^{23} mol^{-1}$ to 4 sig. fig.

2.9 Formula for calculating mass of one atom of an element

$$m = 1.6605x10^{-24} \frac{g}{u} xA(u) = 1.6605x10^{-24} A\ g$$

Example

Calculate the mass of 6 atoms of Americium (Am)

Solution

1 atom of Am weighs 243 u

6 atoms = 6 x 243u/atom = 1.46×10^3 u

1 u= 1.6605×10^{-24}g

Mass = 1.66×10^{-24} g/u x 1.46×10^3 u = 2.42×10^{-21} g

2.10 Formula for calculating mass of one mole of atoms

$$M = 1.6605x10^{-24} \frac{g}{u} xA(u)x6.22141x10^{23} mol^{-1} = A\,g\,mol^{-1}$$

M is called the **molar mass** with units of g mol^{-1}.

For molecules the molecular mass, M(u) is used in the above expressions

2.11 Ions

Ionic compounds such as NaCl exist as ion in solution

$NaCl(aq) = Na^+(aq) + Cl^-(aq)$

LECTURE 3

Mole and Mole concept

3.1 The Mole

The mole is defined as the amount of a substance that contains as many entities (such as atoms, molecules, ions, electrons, photons, protons etc) as there are in exactly 12 g of carbon-12 isotope.

One mole of something consists of 6.022 x 10^{23} units of that substance.

The following formulas can be used to calculate the number of moles, n, of a substance

1. $n = \frac{N}{N_A}$
2. $n = \frac{m}{M}$, m = mass in grams, M = molar mass in g mol^{-1}.
3. $n = MV$ M = molarity in mol/L, V= volume in L for solutions
4. $n = \frac{PV}{RT}$ for ideal gases
5. $n = \frac{It}{F}$ I = current in ampre (C s^{-1}, t =time in s , F =96485 $Cmol^{-1}$ under Electrolysis

Examples

Calculate the number of moles for 5.00 x 10^{20} Co atoms

$$n=\frac{N}{N_A}=\frac{5.00 \times 10^{20} \text{ atoms}}{6.02 \times 10^{23} \text{ atoms/mol}}=8.30\times 10^{-4} \text{ mol Co}$$

How many mole are in 0.2512 g of hydrogen atoms sample

$$n = \frac{m\ (g)}{\text{molar mass g/mol}} = \frac{0.2512\ g}{1.01\ g/mol} = 0.2487\ mol$$

Calculate the number of moles of a gas at 1.5 atm in 8.56 L volume at 273 K.

$$n = \frac{PV}{RT} = \frac{1.5\ atm \times 8.56\ L}{0.08206\ L.\frac{atm}{K.mol} \times 273\ K} = 0.57\ mol$$

Home practice

Calculate the number of moles of 0.033 mol/L acid in 0.025 L solution

3.2 Mole concept

Mole concept provides a simple mole-mole relationship in:

1. Species in a molecular formula
2. Species in a balanced chemical reaction

Example

$$aA + bB \rightarrow cC + dD$$

Small letters a, b, c and d are the stoichiometric coefficient on the chemical species A, B, C and D respectively in a balanced chemical reaction (atoms on the LHS =atoms on RHS consequently mass is conserved)

$$\frac{n_A}{a} = \frac{n_B}{b} = \frac{n_C}{c} = \frac{n_D}{d}$$

Example 2

Calculate the number of moles of aluminum in 10 g sample

1 mol Al = 26.98 g

x mol $\longrightarrow$ 10 g

cross multiply and make x the subject of the formula

$$x = \frac{1\,mol\,Al\ \times 10g}{26.98\ g} = 0.371\,mol$$

Calculate the number of atoms in 10 g Al

10 g Al = 0.371 mol

1 mol Al atoms = 6.022x 10^{23} atoms

0.371 mol $\longrightarrow$ x atoms

Cross multiply and make x the subject = 2.23 x 10^{23} atoms

How many Si atoms are present in 10 mg Si

1 mol Si = 6.022 x 10^{23} atoms = 28.09 g

28.09 g = 6.022 x 10^{23} atoms

10/1000 g $\longrightarrow$ x atoms

Cross multiply and solve for x = 2.14 x 10^{20} atoms

LECTURE 4

Chemical formula: Empirical, Molecular and Structural formulae

4.1 Empirical shows the simplest ratios of atoms in a chemical formula

Molecular formula shows the actual number of number of atoms in a given molecule

Structural formula shows spatial or geometric representation of a molecule in which the relative positions of the atoms are shown and the bonds are indicated by lines.

4.2 Determination of empirical, molecular formulae

One of the method of the empirical formula is determine products produced in a chemical reaction by gravimetric method or combustion reaction

The molecular formula is determined by performing an additional experiment on determining the molecular mass of the analyte.

Example

Cumene is a compound containing C and H that is used in the production of acetone and phenol in the chemical industry. Combustion of 47.6 mg of cumene produced some CO_2 and 42.8 mg water. The molar mass cumene is 125 g/mol. Determine the empirical and molecular formulas of cumene.

Solution

$$\mathrm{C_xH_y + O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O}$$

Stoichiometric equivalents

x atoms C y atoms H or on a mole ration x mol C and y mol H

molar mass of water 18.02 g/mol

Number of moles of water in 42.8mg = $n = \frac{\frac{42.8}{1000}g}{18.02g/mol} = 0.0023575\, mol$

1mol of H_2O yields 2mol H.

So 0.0023575 yields 2 x 0.002375 = 0.00475 mol.

Total number of moles of H = 0.00475 in cumene.

1mol H= 1.01 g so 0.00475mol = 0.00479g.

Mass of Carbon is total mass of cumene used minus mass of hydrogen i.e 0.0476-0.00478=0.04281 g

Moles of carbon = 0.04281/12.01 = 0.00356

	C	H
Mass in g	0.04281 g	0.00479 g
Mol	0.00356	0.00475
Mole ratio	1	1.333
Factor (3)	3	3.99≈4

Therefore, empirical formula is C_3H_4

Molecular formula is $(E.F)_n$=molar mass where n is a small whole number

$(C_3H_4)n=125$ $(40.07)n=125$

n= 125/40.07= 3.11 ≈3 therefore molecular formula is

C_9H_{12}

Molecular formulae from percentage composition

Percent composition

This is the quantitative approach to know the relative masses of elements in a compound.

% by mass of element=$\frac{mass\ of\ element}{mass\ of\ whole\ sample} \times 100\%$

Mass of element X=$\frac{A_X S_X}{M_Y} \times m_Y$

Where A_X= atomic mass of element X

S_X= stoichiometric coefficient of the element X

M_Y= molar mass of compound

m_Y= mass of compound

e.g in the combustion of m_{cpd} of $C_rH_sO_t$:

For product H_2O: m_Y = mass of H_2O produced, X= H, S_X =2 ,M_Y =18.02 u, A_X = 1.01 u

For product CO_2: m_Y = mass of CO_2 produced, X= C, S_X =1 ,M_Y =44.01 u, A_X = 12.01 u

For O: m_O= m_{cpd} - m_H + m_C

$$\%C = \frac{m_C}{m_{cpd}} \times 100\%$$

$$\%H = \frac{m_H}{m_{cpd}} \times 100\%$$

$$\%O = \frac{m_O}{m_{cpd}} \times 100\%$$

Example

A sample of a liquid with mass 8.657 g was decomposed into its elements and gave 5.217 g of carbon, 0.9620 g of hydrogen and 2.478 g of oxygen. What is the percentage composition and empirical formula for the compound?

Solution

$$\%C = \frac{m_C}{m_{cpd}} \times 100\% \Longrightarrow \frac{5.217\ g}{8.657\ g} \times 100\% = 60.263\%\ C$$

$$\%H = \frac{m_H}{m_{cpd}} \times 100\% \Longrightarrow \frac{0.9620\ g}{8.657\ g} \times 100\% = 11.112\%\ H$$

$$\%O = \frac{m_O}{m_{cpd}} \times 100\% \Longrightarrow \frac{2.478\ g}{8.657\ g} \times 100\% = 28.624\%\ O$$

Total is 99.999% which if rounded off to 4 sig fig is 100.00%

Choosing a mass of 100 g, percentages are numerically equal to masses hence

	C	H	O
Mass in g	60.263 g	11.112 g	28.624 g
mol ($n = \frac{m\ (g)}{M\ (\frac{g}{mol})}$	$\frac{60.263\ g}{12.01\ g/mol} = 5.0177$	$\frac{11.112\ g}{1.01\ g/mol} = 11.0019$	$\frac{28.624\ g}{16.00\ g/mol} = 1.789$
Mole ratio	$\frac{5.0177\ mol}{1.789\ mol} = 2.80$	$\frac{11.0019\ mol}{1.789\ mol} = 6.149$	$\frac{1.789\ mol}{1.789\ mol} = 1$
Factor (round off easily)	3	6	1

E.F = C_3H_6O

Percent yield

$$\% \, yield = \frac{actual \ yield \ from \ experiment}{Theoretical \ yield \ from \ balanced \ equation} \times 100\%$$

When potassium chromate (K_2CrO_4) is added to a solution containing 0.500 g silver nitrate ($AgNO_3$), solid silver chromate (Ag_2CrO_4) is formed.

a) Determine the theoretical yield of the silver chromate precipitate.

b) If 0.455 g of silver chromate is obtained, calculate the percent yield.

Solution

a) First write a balanced chemical equation

$K_2CrO_4(aq)$ + **2**$AgNO_3(aq) \rightarrow Ag_2CrO_4(s)$ + **2**$KNO_3(aq)$

$$n = \frac{0.5 \ g}{169.9 \frac{g}{mol}} = 2.943 \ \times 10^{-3} molAgNO_3$$

2 mol $AgNO_3$ $\rightarrow$ 1 mol Ag_2CrO_4

2.943×10^{-3} mol $AgNO_3$ $\rightarrow$ *x* mol Ag_2CrO_4

Cross multiply and make *x* the subject = 1.47×10^{-3} mol Ag_2CrO_4

Theoretical yield = mol Ag_2CrO_4 x molar mass of Ag_2CrO_4

1.47×10^{-3} mol x 331.7 g/mol = **0.488 g**

b)

$$\% \, yield = \frac{0.455}{0.488} \times 100\% = 93.2 \ \%$$

LECTURE 5

Limiting and Excesses reagent

5.1 Limiting reagent and excess reagent

A limiting reagent is a reactant that will be exhausted in a chemical reaction and the reaction will stop.
The limiting reagent determines how much part of the excess reagent will be used up and how much of the products are to be formed.

An excess reagent is a reactant that will remain in excess after the reaction has stopped

5.2 Finding the limiting reagent in a reaction below

$aA + bB \rightarrow cC + dD$

1. From data given in the question calculate, n_A and n_B
2. Calculate $R_A = n_A/a$ and $R_B = n_B/b$
3. If $R_A < R_B$ then A is a limiting reagent
4. Perform mole concept based on the limiting reagent

Example

Hydrogen cyanide is produced industrially from the reaction of gaseous ammonia, oxygen and methane:

$$2NH_3(g) + 3O_2(g) + 2CH_4(g) \rightarrow 2HCN(g) + 6H_2O(g)$$

If 5.00 x 10^3 kg each NH_3, O_2 and CH_4 are reacted, what mass of HCN and of H_2O will be produced, assuming 100% yield?

$$n_{NH_3} = \frac{5.00 \times 10^3\ kg \times 10^3 g/kg}{17.04\ g/mol} = 2.934 \times 10^5\ mol$$

$$R_{NH_3} = \frac{n_{NH_3}}{2} = \frac{2.934 \times 10^5}{2} = 1.467 \times 10^5$$

$$n_{O_2} = \frac{5.00 \times 10^3\ kg \times 10^3 g/kg}{32.00\ g/mol} = 1.5625 \times 10^5\ mol$$

$$R_{O_2} = \frac{n_{O_2}}{3} = \frac{1.5625 \times 10^5}{3} = 5.2083 \times 10^4$$

$$n_{CH_4} = \frac{5.00 \times 10^3\ kg \times 10^3 g/kg}{16.05\ g/mol} = 3.115 \times 10^5\ mol$$

$$R_{CH_4} = \frac{n_{CH_4}}{2} = \frac{3.115 \times 10^5}{2} = 1.5575 \times 10^5$$

- $R_{O_2} < R_{NH_3} < R_{CH_4}$

O_2 is the limiting reagent and must be used for calculating other amounts

3 mol O_2 → 2 mol HCN

1.5625×10^5 mol → x

$$x = \frac{2\ mol\ HCN \times 1.5625 \times 10^5\ \cancel{mol\ O_2}}{3\ \cancel{mol\ O_2}} = 1.0416 \times 10^5\ mol\ HCN$$

Mass of HCN = 1.0416 x 10^5 x27.03 g/mol = 2.815x10^6 g

3 mol O_2 → 6 mol H_2O

1.5625×10^5 mol → y

$$y = \frac{6\ mol\ H_2O \times 1.5625 \times 10^5\ \cancel{mol\ O_2}}{3\ \cancel{mol\ O_2}} = 3.125 \times 10^5\ mol\ H_2O$$

Mass of HCN = 3.125 x 10^5 x 18.02 g/mol = 5.631x10^6 g

LECTURE 6

Solution stoichiometry

Molarity is defined as the number of moles of a substance in 1 liter or solution

$$M = \frac{moles\ (n)}{Volume\ (mol/L)}$$

Units of M is mol L^{-1}.

Dilution= changing concentration from high to low in a given volume

$$n_i = M_iV_i = M_dV_d = n_d$$

Reactions in solutions

1. Acid-base reactions

Bronsted-Lowry definition of acids and bases

An acid is a proton donor

A base is a proton acceptor

Acid-base reaction always occurs together, as in the example below:

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

2. Precipitation reactions

$Na_2SO_4(aq) + BaCl_2(aq) = BaCl_2(s) + 2NaCl(aq)$ molecular rxn

$2Na^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2Cl^-(aq) \rightarrow BaSO_4(s) + 2Na^+(aq) + 2Cl^-(aq)$ ionic rxn

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ net ion rxn

3. Reduction-oxidation (Redox) reaction

A Reduction-oxidation reaction or Redox reaction is an electron transfer reaction between electrons in one half-reaction to the other half reaction.

Oxidation reaction and reduction reactions always occurs together.

Redox reaction involves change in oxidation number of one of the atoms in each half-reaction.

In a reduction reaction the oxidation number of one of the atoms in the half-reaction decreases. The reactant in the reduction reaction is called an oxidant or oxidizing reagent.

In an oxidation reaction, the oxidation number of one of the atoms in the half-reaction increases. The reactant in the oxidation reaction is called a reductant or reducing reagent.

Rules for Assigning Oxidation numbers

Compound	**Oxidation number = ON**	**Exception**
1, Pure elements	+0	
2. Monoatomic ion	±z, z = charge on the ion	
3. Polyatomic ion	Sum of ON = ±z	
4. F in compounds	-1	
5. H in compounds	+1	H^- = -1
6. O in compounds	-2	H_2O_2 = -1
7. Neutral molecules	Sum of ON= 0	
8. Diatomics, Cl_2,O_2,N_2, etc.	0	
9. Group I element	+1	
10 Group II element	+2	
11. C in compounds	-4 to +4	

Steps for balancing Redox reactions by Ion-electron method

Example

Balance the following redox reaction in an acidic media

$$Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) \rightarrow Cr^{3+}(aq) + CO_2(g) + H_2O(l)$$

Step 1: Divide reaction into half reactions, and assign the oxidation numbers

+6 -2 +3
$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$ Reduction half reaction

-2 +1 -2 +1 -2 +1 +2 -2 +1 -2
$C\ H_3\ C\ \ H_2\ O\ \ H(aq) \rightarrow C\ \ O_2(g) + H_2\ O(l)$ Oxidation half reaction

The number in bracket is the ON, and outside the bracket is the coefficient on the element

Step 2: Balance atoms other than H and O

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

$$CH_3CH_2OH(aq) \rightarrow 2CO_2(g) + H_2O(l)$$

Step 3: Balance O by adding H_2O on the side deficient with O

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(\mathrm{l})$$

$$CH_3CH_2OH(aq) + 4H_2O(\mathrm{l}) \rightarrow 2CO_2(g) + H_2O(l)$$

$$CH_3CH_2OH(aq) + 3H_2O(\mathrm{l}) \rightarrow 2CO_2(g)$$

Step 4: Balance H by adding H^+

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O$$

$$CH_3CH_2OH(aq) + 3H_2O(\mathrm{l}) \rightarrow 2CO_2(g) + 12H^+(aq)$$

Step 5: Balance net charge by adding electrons to the side with more positive charges

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$$

(-2)1 (+1)14 (-1)6 = (+3)2

$$CH_3CH_2OH(aq) + 3H_2O(\text{l}) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-$$

0 0 0 (+)12 (-1)12

Step 6: Balance electron gain = electron loss, and add the two half-reactions

$$2 \times [Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O]$$

$$1 \times [CH_3CH_2OH(aq) + 3H_2O(\text{l}) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-]$$

$$2Cr_2O_7^{2-}(aq) + 28H^+(aq) + 12e^- \rightarrow 4Cr^{3+}(aq) + 14H_2O$$

$$CH_3CH_2OH(aq) + 3H_2O(\text{l}) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-$$

$$\mathbf{2}Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + \mathbf{28}H^+(aq) + \mathbf{3}H_2O(l) \rightarrow \mathbf{4}Cr^{3+}(aq) + \mathbf{2}CO_2(g) + \mathbf{14}H_2O(l) + \mathbf{12}H^+(aq)$$

Step 7: Cancel anything that is common on both sides of the equation

$$2Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l)$$

Steps for balancing Redox reaction in basic media

Follow steps 1- 7 and add the following additional steps:

Step 8: Add on both sides of the equation the same number of OH^- to eliminate H^+ in step 7

$$2Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + 16H^+(aq) + 16OH^-(aq) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l) + 16OH^-(aq)$$

Step 9: Combine OH^- and H^+ to form water

$$2Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + 16H_2O(l) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l) + 16OH^-(aq)$$

Step10: Cancel any water that you can.

$$2Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + 5H_2O(l) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 16OH^-(aq)$$

Take home practice questions

Balance the following in acidic media

$$MnO_4^-(aq) + ClO_3^-(aq) \rightarrow ClO_4^-(aq) + Mn^{2+}(aq) + H_2O(l)$$

Solution

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

$$5ClO_3^-(aq) + 5H_2O(l) \rightarrow 5ClO_4^-(aq) + 10H^+(aq) + 10e^-$$

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

Balance the following in basic media

$$Ag(s) + CN^-(aq) + O_2(g) \rightarrow Ag(CN)_2^-(aq)$$

Solution

$$4Ag(s) + 8CN^-(aq) \rightarrow 4Ag(CN)_2^-(aq) + 4e^-$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l)$ as in acidic media

$$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H^+(aq) + 4OH^-(aq) \rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l) + 4OH^-(aq)$$

$$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H_2O(l) \rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l) + 4OH^-(aq)$$

$$\mathbf{4Ag(s) + 8CN^-(aq) + O_2(g) + 4H_2O(l) \rightarrow 4Ag(CN)_2^-(aq) + 4OH^-(aq)}$$

Students should ask tutors if they fail

LECTURE 7

TITRATIONS

7.1 Titration is a chemical analysis method in which the quantity of the sample (analyte) is determined by placing it in the conical flask and after stepwise addition of a standardized solution from the burette, the end-point is reached.

The end point is determined by adding an indicator to the analyte solution. Some redox titration reactions are self-indicating. The molarity of the standardized solution, M_s, is known, and the volume of the titre, V_s, is found at the end-point.

7.1 Forward or Normal Titration

They are of two types:

1. Single reaction

Here the analyte and the titrant are in a single reaction

$$\underset{\text{standard}}{MnO_4^-(aq)} + \underset{\text{analyte}}{5Fe^{2+}(aq)} + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

2. Sequence of reactions

Here the analyte and the titrant are in separate reaction reactions

$$\underset{\text{analyte}}{Mn_2O_7(s)} + H_2O(l) \rightarrow MnO_4^-(aq) + 2H^+(aq)$$

$$MnO_4^-(aq) + \underset{\text{standard}}{5C_2O_4^-(aq)} + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O + 10CO_2(g)$$

Note that the molarity of the std $M_{C_2O_4^{2-}}$ and the volume of the titre $V_{C_2O_4^{2-}}$ found at the end-point are known

Steps in the calculation are:

1. $n_{C_2O_4^{2-}} = M_{C_2O_4^{2-}} V_{C_2O_4^{2-}}$

2. $\frac{n_{C_2O_4^{2-}}}{5} = \frac{n_{MnO_4^-}}{1}$

3. $\frac{n_{MnO_4^-}}{1} = \frac{n_{Mn_2O_7((s)}}{1}$

7.2 Back Titration

Back titration is carried on the excess moles of the excess reagent left after the completion of the reaction.

Here the analyte is the limiting reagent.

The excess reagent left after the completion of the reaction is titrated using a suitable standard.

Example

A 0.2719 g sample containing $CaCO_3$ reacted with 20.00 mL of 0.2254 M HCl. The excess HCl required exactly 20.00 mL of 0.1041 M NaOH to reach the phenophalene end point. Determine percent $CaCO_3$ in the sample. The reaction involved is

$$\underset{\text{lim iting resgent}}{CaCO_3(s)} + \underset{\text{excess reagent}}{2HCl(aq)} \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

The titration reaction is

$$\underset{\text{excess left}}{HCl(aq)} + \underset{\text{s tan dard}}{NaOH(aq)} \rightarrow NaCl(aq) + H_2O(l)$$

1. Start calculation from the titration rxn

$$\frac{n_{HCl,excess}}{1} = \frac{n_{NaOH}}{1}$$

2. Calculate the initial moles of HCl

$n_{HCl,initial}$

3. Calculate moles of HCl that reacted with $CaCO_3$

$$n_{HCl,reacted} = n_{HCl,initial} - n_{HCl,excess}$$

4. $\dfrac{n_{HCl,reacted}}{2} = \dfrac{n_{CaCO_3}}{1}$

5. From n_{CaCO_3} calculate mass of $CaCO_3$ and percent

Oxidation-Reduction Reactions

Academic Resource Center

Introduction

- Oxidation-reduction reactions are also known as redox reactions
- Def: Redox reactions describe all chemical reactions in which there is a net change in atomic charge
- It is a class of reactions that include:
  - formation of a compound from its elements
  - all combustion reactions
  - reactions that generate electricity
  - reactions that produce cellular energy

Terminology

- The key idea is the net movement of electrons from one reactant to the other
- *Oxidation* is the loss of electrons
- *Reduction* is the gain of electrons
- *Oxidizing agent* is the species doing the oxidizing
- *Reducing agent* is the species doing the reducing

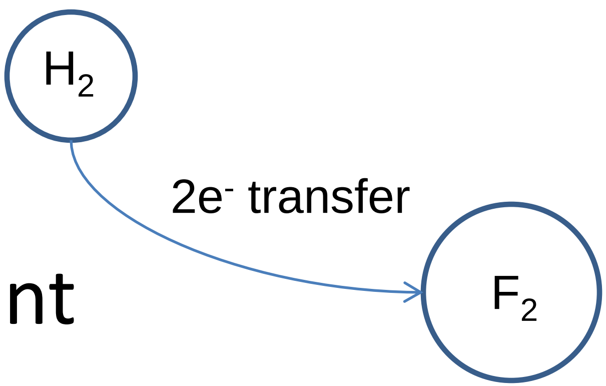
Redox Illustration

- $H_2 + F_2 \longrightarrow 2HF$
- Oxidation (electron loss by H_2)
  - $H_2 \longrightarrow 2H^+ + 2e^-$
- Reduction (electron gain by F_2)
  - $F_2 + 2e^- \longrightarrow 2F^-$

H_2

- Oxidized

- Reducing agent



F_2

- Reduced

- Oxidizing agent

Oxidation Number

- Oxidation number (O.N.) is also known as oxidation state
- It is defined as the charge the atom would have if electrons were not shared but were transferred completely
- For a binary ionic compound, the O.N. is equivalent to the ionic charge
- For covalent compounds or polyatomic ions, the O.N. is less obvious and can be determined by a given set of rules

Rules for Assigning an Oxidation Number

General Rules

1. For an atom in its elemental form (Na, O_2): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals to zero. (equals to the ion's charge if it is a polyatomic ion)

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1A(1): O.N. = +1 in all compounds
2. For Group 2A(2): O.N. = +2 in all compounds
3. For hydrogen: O.N. = +1 in combination with nonmetals
   O.N. = -1 in combination with metals and boron
4. For fluorine: O.N. = -1 in all compounds
5. For oxygen: O.N. = -1 in peroxides
   O.N. = -2 in all other compounds (except with F)
6. For Group 7A(17): O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

Example 1

- Determine the oxidation number (O.N.) of each element in these compounds:
  a) CaO (s)
  b) KNO_3 (s)
  c) $NaHSO_4$ (aq)
  d) $CaCO_3$ (s)
  e) N_2 (g)
  f) H_2O (l)

Solution to Example 1

Simply apply the rules for assigning an oxidation number as described earlier

a) $\overset{+2}{Ca}\overset{-2}{O}$ (s)

b) $\overset{+1}{K}\overset{+5}{N}\overset{-2}{O_3}$ (s)

N = 0-(+1)-3(-2) = +5

c) $\overset{+1}{Na}\overset{+1}{H}\overset{+6}{S}\overset{-2}{O_4}$ (aq)

S = 0-(+1)-(+1)-4(-2) = +5

d) $\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O_3}$ (s)

C = 0-(+2)-3(-2) = +4

e) $\overset{0}{N_2}$ (g)

f) $\overset{+1}{H_2}\overset{-2}{O}$ (l)

Example 2

- Identify the oxidizing agent and reducing agent in each of the following:

a) $2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(g)$

b) $Cu\,(s) + 4HNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2NO_2\,(g) + 2H_2O\,(l)$

Solution to Example 2

Assign oxidation numbers and compare.

Oxidation is represented by an increase in oxidation number

Reduction is represented by a decrease in oxidation number

a) $$2\overset{0}{H}_2\,(g) + \overset{0}{O}_2\,(g) \longrightarrow 2\overset{+1}{H}_2\overset{-2}{O}\,(g)$$

- O_2 was reduced (O.N. of O: 0 -> -2); O_2 is the oxidizing agent
- H_2 was oxidized (O.N. of H: 0 -> +1); H_2 is the reducing agent

b) $$\overset{0}{Cu} + 4\overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3 \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O}_3)_2 + 2\overset{+4}{N}\overset{-2}{O}_2 + 2\overset{+1}{H}_2\overset{-2}{O}$$

- Cu was oxidized (O.N. of Cu: 0 -> +2); Cu is the reducing agent
- HNO_3 was reduced (O.N. of N: +5 -> +4); HNO_3 is the oxidizing agent

Balancing Redox Equations

- When balancing redox reactions, make sure that the number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent

- Two methods can be used:

1. Oxidation number method
2. Half-reaction method

Balancing Redox Equations

Method 1: Oxidation number method

1. Assign oxidation numbers to all elements in the reaction
2. From the changes in O.N., identify the oxidized and reduced species
3. Compute the number of electrons lost in the oxidation and gained in the reduction from the O.N. changes
4. Multiply one or both of these numbers by appropriate factors to make the electrons lost equal the electrons gained, and use the factors as balancing coefficients
5. Complete the balancing by inspection, adding states of matter

Example 3

- Use the oxidation number method to balance the following equations:

a) $Al(s) + H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + H_2(g)$

b) $PbS(s) + O_2(g) \longrightarrow PbO(s) + SO_2(g)$

Part a: Solution to Example 3

- Step 1. Assign oxidation numbers to all elements

$$\overset{0}{Al}(s) + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4}(aq) \longrightarrow \overset{+3}{Al_2}(\overset{+6}{S}\overset{-2}{O_4})_3(aq) + \overset{0}{H_2}(g)$$

- Step 2. Identify oxidized and reduced species
  - Al was oxidized (O.N. of Al: 0 -> +3)
  - H_2SO_4 was reduced (O.N. of H: +1 -> 0)
- Step 3. Compute e^- lost and e^- gained
  - In the oxidation: $3e^-$ were lost from Al
  - In the reduction: $1e^-$ was gained by H

Part a: Solution to Example 3

- Step 4. Multiply by factors to make e^- lost equal to e^- gained, and use the factors as coefficients
  - Al lost $3e^-$, so the $1e^-$ gained by H should be multiplied by 3. Put the coefficient 3 before H_2SO_4 and H_2.

$$Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

- Step 5. Complete the balancing by inspection

$$2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

Part b: Solution to Example 3

- Step 1. Assign oxidation numbers to all elements

$$\overset{+2}{Pb}\overset{-2}{S}(s) + \overset{0}{O_2}(g) \longrightarrow \overset{+2}{Pb}\overset{-2}{O}(s) + \overset{+4}{S}\overset{-2}{O_2}(g)$$

- Step 2. Identify oxidized and reduced species
  - PbS was oxidized (O.N. of S: -2 -> +4)
  - O_2 was reduced (O.N. of O: 0 -> -2)
- Step 3. Compute e^- lost and e^- gained
  - In the oxidation: $6e^-$ were lost from S
  - In the reduction: $2e^-$ were gained by each O

Part b: Solution to Example 3

- Step 4. Multiply by factors to make e^- lost equal to e^- gained, and use the factors as coefficients
  - S lost $6e^-$, O gained $4e^-$ ($2e^-$ each O). Thus, put the coefficient 3/2 before O_2.

$$PbS(s) + 3/2O_2(g) \longrightarrow PbO(s) + SO_2(g)$$

- Step 5. Complete the balancing by inspection

$$2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$$

Balancing Redox Equations

Method 2: Half-reaction method

1. Divide the skeleton reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species
2. Balance the atoms and charges in each half-reaction
   - Atoms are balanced in order: atoms other than O and H, then O, then H
   - Charge is balanced by adding electrons
     - To the left in reduction half-reactions
     - To the right in oxidation half-reactions
3. If necessary, multiply one or both half-reactions by an integer to make the number of e^- gained equal to the number of e^- lost
4. Add the balanced half-reactions, and include states of matter
5. Check that the atoms and charges are balanced

Example 4

- Use the half-reaction method to balance the following equations:

a) $ClO_3^-(aq) + I^-(aq) \longrightarrow I_2(s) + Cl^-(aq)$ [acidic]

b) $Fe(OH)_2(s) + Pb(OH)_3^-(aq) \longrightarrow Fe(OH)_3(s) + Pb(s)$ [basic]

Part a: Solution to Example 4

- Step 1. Divide the reaction into half-reactions

  $ClO_3^-(aq) \longrightarrow Cl^-(aq)$ $I^-(aq) \longrightarrow I_2(s)$

- Step 2. Balance atoms and charges in each half-reaction
  - Atoms other than O and H

    $ClO_3^-(aq)$ -> $Cl^-(aq)$ Cl is balanced

    $2I^-(aq)$ -> $I_2(s)$ I now balanced

  - Balance O atoms by adding H_2O molecules

    $ClO_3^-(aq)$ -> $Cl^-(aq) + 3H_2O(l)$ Add $3H_2O$

    $2I^-(aq)$ -> $I_2(s)$ No change

Part a: Solution to Example 4

- Balance H atoms by adding H^+ ions

$ClO_3^-(aq) + 6H^+ \rightarrow Cl^-(aq) + 3H_2O(l)$	Add $6H^+$
$2I^-(aq) \rightarrow I_2(s)$	No change

- Balance charge by adding electrons

$ClO_3^-(aq) + 6H^+ + 6e^- \rightarrow Cl^-(aq) + 3H_2O(l)$	Add $6e^-$
$2I^-(aq) \rightarrow I_2(s) + 2e^-$	Add $2e^-$

- Step 3. Multiply each half-reaction by an integer to equalize number of electrons

$ClO_3^-(aq) + 6H^+ + 6e^- \rightarrow Cl^-(aq) + 3H_2O(l)$	x 1
$3[2I^-(aq) \rightarrow I_2(s) + 2e^-]$	x 3

Part a: Solution to Example 4

- Step 4. Add the half-reactions together

$$ClO_3^-(aq) + 6H^+ + 6e^- \rightarrow Cl^-(aq) + 3H_2O(l)$$

$$6I^-(aq) \rightarrow 3I_2(s) + 6e^-$$

$$ClO_3^-(aq) + 6H^+(aq) + 6I^-(aq) \longrightarrow Cl^-(aq) + 3H_2O(l) + 3I_2(s)$$

- Step 5. Check that atoms and charges balance
  - Reactants (Cl, 3O, 6H, 6I, -1) -> products (Cl, 3O, 6H, 6I, -1)

- ClO_3^- is the oxidizing agent
- I^- is the reducing agent

Part b: Solution to Example 4

- The only difference in balancing a redox equation that takes place in basic solution is in Step 4.
- At this point, we add one OH^- ion to both sides of the equation for every H^+ ion present
- The H^+ ions on one side are combined with the added OH^- ions to form H_2O, and OH^- ions appear on the other side of the equation

Part b: Solution to Example 4

- Step 1. Divide the reaction into half-reactions

  $Pb(OH)_3^-(aq) \rightarrow Pb(s)$ $Fe(OH)_2(s) \rightarrow Fe(OH)_3(s)$

- Step 2. Balance atoms and charges in each half-reaction
  - Atoms other than O and H

    $Pb(OH)_3^-(aq) \rightarrow Pb(s)$ Pb is balanced

    $Fe(OH)_2(s) \rightarrow Fe(OH)_3(s)$ Fe is balanced
  - Balance O atoms by adding H_2O molecules

    $Pb(OH)_3^-(aq) \rightarrow Pb(s) + 3H_2O$ Add $3H_2O$

    $Fe(OH)_2(s) + H_2O \rightarrow Fe(OH)_3(s)$ Add H_2O

Part b: Solution to Example 4

- Balance H atoms by adding H^+ ions

$Pb(OH)_3^-(aq) + 3H^+ \rightarrow Pb(s) + 3H_2O$ Add $3H^+$

$Fe(OH)_2(s) + H_2O \rightarrow Fe(OH)_3(s) + H^+$ Add H^+

- Balance charge by adding electrons

$Pb(OH)_3^-(aq) + 3H^+ + 2e^- \rightarrow Pb(s) + 3H_2O$ Add $2e^-$

$Fe(OH)_2(s) + H_2O \rightarrow Fe(OH)_3(s) + H^+ + e^-$ Add e^-

- Step 3. Multiply each half-reaction by an integer to equalize number of electrons

$Pb(OH)_3^-(aq) + 3H^+ + 2e^- \rightarrow Pb(s) + 3H_2O$ x 1

$2[Fe(OH)_2(s) + H_2O \rightarrow Fe(OH)_3(s) + H^+ + e^-]$ x 2

Part b: Solution to Example 4

- Step 4. Add the half-reactions together

$Pb(OH)_3^-(aq) + 3H^+ + 2e^- \rightarrow Pb(s) + 3H_2O$

$2Fe(OH)_2(s) + 2H_2O \rightarrow 2Fe(OH)_3(s) + 2H^+ + 2e$

$Pb(OH)_3^-(aq) + H^+(aq) + 2Fe(OH)_2(s) \longrightarrow Pb(s) + H_2O(l) + 2Fe(OH)_3(s)$

- Step 4(basic). Add OH^-
  - Here, we add 1 OH^-

$Pb(OH)_3^-(aq) + H^+(aq) + OH^- + 2Fe(OH)_2(s) \rightarrow Pb(s) + H_2O(l) + 2Fe(OH)_3(s) + OH^-$

$Pb(OH)_3^-(aq) + 2Fe(OH)_2(s) \longrightarrow Pb(s) + 2Fe(OH)_3(s) + OH^-(aq)$

- Step 5. Check
  - Reactants (Pb, 7O, 7H, 2Fe, -1) -> products (Pb, 7O, 7H, 2Fe, -1)
- $Pb(OH)_3^-$ is the oxidizing agent
- $Fe(OH)_2$ is the reducing agent

Practice Problem

1. Identify the oxidizing and reducing agents in the following:

a) $8H^+(aq) + 6Cl^-(aq) + Sn(s) + 4NO_3^-(aq) \longrightarrow SnCl_6^{2-}(aq) + 4NO_2(g) + 4H_2O(l)$

b) $2MnO_4^-(aq) + 10Cl^-(aq) + 16H^+(aq) \longrightarrow 5Cl_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Practice Problem

2. Use the oxidation number method to balance the following equations and then identify the oxidizing and reducing agents:

a) $HNO_3(aq) + C_2H_6O(l) + K_2Cr_2O_7(aq) \longrightarrow KNO_3(aq) + C_2H_4O(l) + H_2O(l) + Cr(NO_3)_3(aq)$

b) $KClO_3(aq) + HBr(aq) \longrightarrow Br_2(l) + H_2O(l) + KCl(aq)$

Practice Problem

3. Use the half-reaction method to balance the following equations and then identify the oxidizing and reducing agents:

a) $Mn^{2+}(aq) + BiO_3^-(aq) \longrightarrow MnO_4^-(aq) + Bi^{3+}(aq)$ [acidic]

b) $Fe(CN)_6^{3-}(aq) + Re(s) \longrightarrow Fe(CN)_6^{4-}(aq) + ReO_4^-(aq)$ [basic]

References

- Silberberg, Martin. Chemistry The Molecular Nature of Matter and Change. New York: McGraw-Hill Science/Engineering/Math, 2008.

CHE 1000 e-LEARNING

RECAP ON TITRATIONS

LECTURERS: DR. J NYIRENDA
MRS M. XAVIER
2019 ACADEMIC YEAR

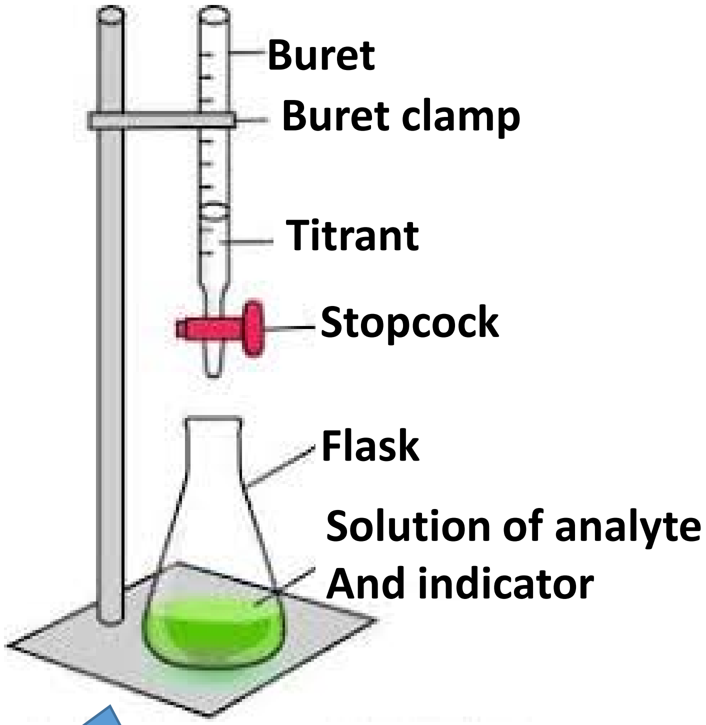
- Titration is a chemical analysis method in which the quantity of the sample (analyte) is determined by placing it in the conical flask and by stepwise addition of a standardized solution from the burette until the end-point is reached.
- The end point is determined by adding an indicator to the analyte solution.
- Some redox titration is self-indicating.
- The molarity of the standardized solution, M_s, is known, and the volume of the titre, V_s, is found at the end-point.

Remember this statement please

- In **titration,** a solution of accurately known concentration, called a **standard solution,** is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete.

- If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution.

This is the main objective of any titration



Typical Titration setup

Standardization of solutions

- Before we use a solution in titrations, it must be standardized.
- There are two types of standard solutions in titrations:
  - Primary standard
    - A **primary standard** is a reference chemical used to measure an unknown concentration of another known chemical. It can be used directly when performing **titrations** or used to calibrate **standard** solutions. A **primary standard** is of **known purity and stability** that can be measured accurately and used in its entirety requiring no additional measurements.
  - Secondary standard
    - A **secondary standard** is a chemical that has been standardized (whose concentration has been accurately determined) against a **primary standard** for use in a specific analysis. **Secondary standards** are commonly used to calibrate analytical methods.

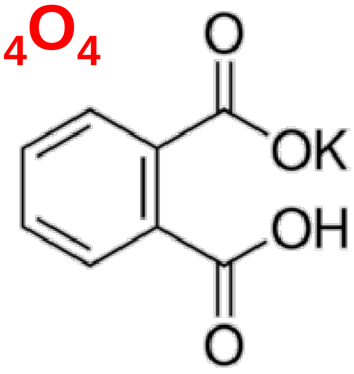
Four Characteristics of a Primary Standard

- It must be pure (99.999 % purity)
- It must be cheap and readily available
- It must be very stable (remain unchanged during storage and weighing)
- It must have a known formula

Remember these characteristics

Example of a primary standard that fits these characteristics a white crystalline acidic chemical compound called **Potassium hydrogen phthalate** (KHP) which **$KHC_8H_4O_4$**

It has the following structural formula



Examples of primary and secondary standards

- **Standardization of a secondary standard using a primary standard**
- This is the titration of secondary standard using accurate concentration (Molarity) of a primary standard
- Primary std/ secondary std

  Na_2CO_3(aq)/HCl(aq) 1:2 rxn

  KHP(aq)/NaOH(aq) 1:1 rxn
- KHP ($KHC_8H_4O_4$, 204.23 g/mol)

Example:

How do you prepare 0.1000 M Na_2CO_3 in a 250.00 mL volumetric flask

Solution

First calculate the number of moles using the formula or relationship between moles, volume and concentration

- n_{Na2CO3} = 0.1000 mol/L x 0.2500L=0.02500 mol

Remember M is moles per liter so volume must be in liters

Next, convert the moles to mass. Recall that n= m/mol/g

- m_{Na2CO3} = 0.02500 mol x 105.99 g/mol =2.6498 g

- So finally weigh 2.6498 g Na_2CO_3 and dissolve all of it in a little water and transfer into 250 mL volumetric flask and add more water up to the lower meniscus of the mark.

Types of titrations

There are two main types of titration: Forward or Normal Titration and Back Titration

Forward or Normal Titration

They are of two types:

1. Single reaction

   Here the analyte and the titrant are in a single reaction

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

standard   Analyte

2. Sequence of reactions

Here the analyte and the titrant are in separate reaction reactions

Mn_2O_7 (l) + H_2O(*l*)→ $2MnO_4^-$(*aq*) +$2H^+$(*aq*)

Analyte

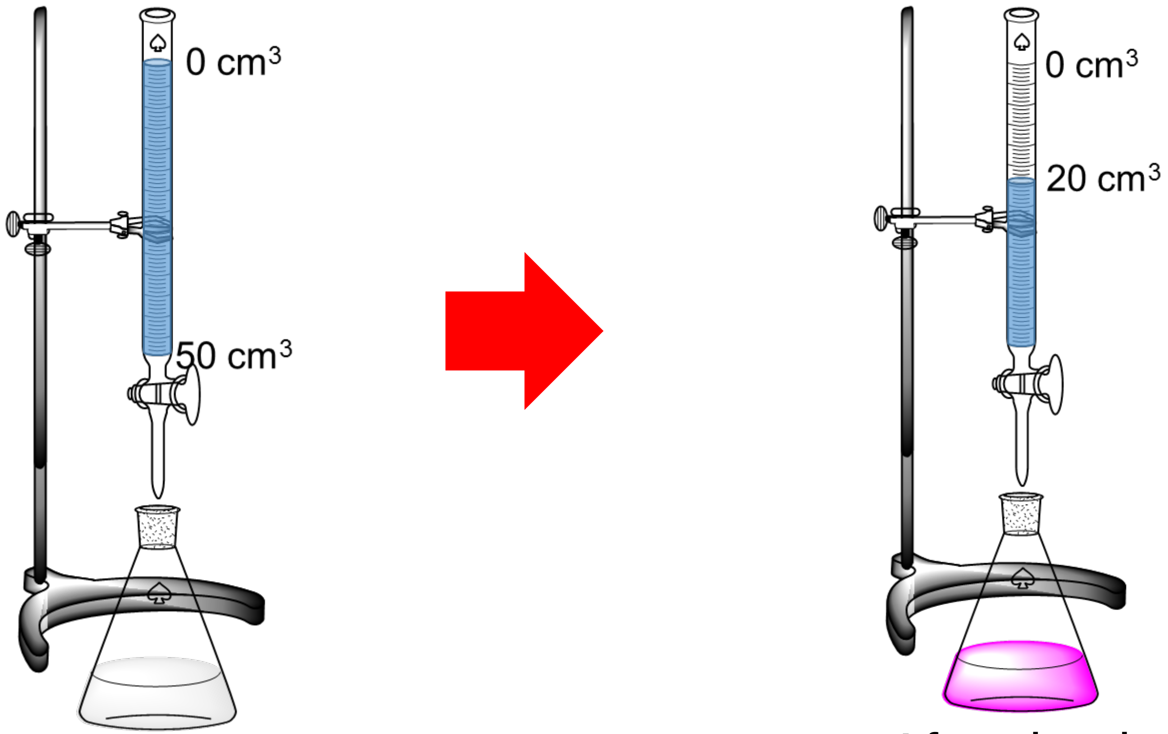
$2MnO_4^-$(*aq*) + $5C_2O_4^{2-}$(*aq*) + $16H^+$(*aq*) → $2Mn^{2+}$(aq) + $8H_2O$(*l*)+ $10CO_2$(*g*)

Standard

Example

A 5.00 g sample of manganese (VII)oxide (di-manganese heptoxide- a very volatile liquid) was dissolved in distilled water and volume made up to 250 cm^3. 25.0 cm^3 of this solution required exactly 20 cm^3 of a 0.5 molar oxalic acid at the phenolphthalein end point. Calculate the percent manganese in the original sample.

NOTE that the molarity of the standard $M_{C_2O_4^{2-}}$ is known and the volume of the titre $V_{C_2O_4^{2-}}$ is found at the end of the titration by reading off the buret



Before titration
Initial volume= 0 cm^3

After titration
Final volume= 20 cm^3

To calculate the volume of the titrant used in the titration, subtract initial volume from final volume 20 cm^3 – 0 cm^3= 20 cm^3 = titre

Steps in the Calculations in Sequence rxns

- First calculate the number of moles of titrant. Why are we first calculating these moles? Its because we know the concentration of the titrant and now after titration, we know the volume hence its easy to calculate the moles.

REMEMBER THAT IN CHEMISTRY, ALL REACTIONS OCCUR ON A MOLE TO MOLE RATIO HENCE THINK IN TERMS OF MOLES NOT VOLUMES OR MASSES n $_{C_2O_4^{2-}}$ =M$_{C_2O_4^{2-}}$ x V$_{C_2O_4^{2-}}$ remembering that volume must be in Liters

n $_{C_2O_4^{2-}} = 0.5\ {}^{mol}/_{L} \times 20\ cm^3 \times \frac{1\ L}{1000\ cm^3} = 0.01\ mol$

Next check the reaction ratio in the balanced equation.

5 mol $C_2O_4^{2-}$ reacts with 2 mol MnO_4^{2-}

0.01 mol $C_2O_4^{2-}$ $\longrightarrow$ x

Cross multiply and solve for x.

5 mol $C_2O_4^{2-}$ reacts with 2 mol MnO_4^{2-}

0.01 mol $C_2O_4^{2-}$ $\longrightarrow$ x

$$0.01\ mol\ C_2O_4^{2-}\ \times 2\ mol\ MnO_4^- = x\ \times 5\ mol\ C_2O_4^{2-}$$

$$x = \frac{0.01\ mol\ C_2O_4^{2-}\ \times 2\ mol\ MnO_4^-}{5\ mol\ C_2O_4^{2-}}$$

$$x = \frac{0.01\ \cancel{mol\ C_2O_4^{2-}}\ \times 2\ mol\ MnO_4^-}{5\ \cancel{mol\ C_2O_4^{2-}}}$$

Cancel out common items

$$x = 0.004\ mol\ MnO_4^-$$

Now, these moles are in 25 cm^3 so in 250 cm^3 we have

$$\frac{250\ cm^3 \times 0.004\ molMnO_4^-}{25\ cm^3} = 0.04\ molMnO_4^-.$$

Next check the reaction ratio in the balanced equation.

2 mol MnO_4^- are produced by 1 mol Mn_2O_7

0.04 mol MnO_4^- ⟶ y

Cross multiply and solve for y as in the previous step.

$$y = 0.02\ mol\ Mn_2O_7$$

Now 1 mol Mn_2O_7 contains 2 mol Mn

0.02 mol Mn_2O_7 will have 0.02 x 2 mol Mn = 0.04 Mn

Now 1 mol Mn weighs 54.94 g

So 0.04 mol Mn will weigh 0.04 x 54.94 g= 2.1992 g

$$Percent\ Mn = \frac{2.1992\ g}{5.0\ g} \times 100\% = 43.98\% = 44.0\ \%$$

Back Titration

- Back titration is carried on the excess moles of the excess reagent left after the completion of the reaction.
- Here the analyte is the limiting reagent.
- The excess reagent left after the completion of the reaction is titrated using a suitable standard.

Example

A 1.25 g sample OF LIMESTONE was added to 50.00 mL of 1.00 M HCl. When reaction stopped, the solution was made up to 250 mL with distilled water. A 25.00 mL of this sample was pippetted into a conical flask and titrated with 0.100 M NaOH in presence of Methyl orange indicator. It required exactly 30.00 mL of NaOH. Determine percent $CaCO_3$ in the sample.

The reaction involved is

$$CaCO_3(s) + 2HCl(aq) = CaCl_2(aq) + 2H_2O(l)$$

The titration reaction is

$$HCl(aq) + NaOH(aq) = NaCl(aq) + H_2O(l)$$

Solution

Start the calculation from the titration reaction (last or back reaction)
As usual, check the reaction or mol ratio. In this case its 1mol HCl reacts with 1 mol NaOH = 1:1

$$n_{HCl,in\ 25cm^3} = n_{NaOH} = 0.100\frac{mol}{L} \times 30\ cm^3 \times \frac{1L}{1000\ cm^3} = 3.00 \times 10^{-3}\ mol$$

$$n_{HCl,in\ 250cm^3} = 3.00 \times 10^{-3}\ mol \times \frac{250cm^3}{25cm^3} = 3.00 \times 10^{-2}\ mol$$

$$n_{HCl,initial\ or\ original} = 1.0\frac{mol}{L} \times 50\ cm^3 \times \frac{1L}{1000\ cm^3} = 5.00 \times 10^{-2}\ mol$$

Mol of HCl that reacted with limestone = initial – excess mol in 250 cm^3

$$= 5.00 \times 10^{-2}\ mol - 3.00 \times 10^{-2}\ mol = 2.00 \times 10^{-2}\ mol$$

Next calculate the amount of calcium carbonate. Remember that in back titration, analyte is limiting. Check the equation and make appropriate mol ratios.

2 mol HCl reacts with 1 mol $CaCO_3$

2.00×10^{-2} mol $\longrightarrow$ z

Cross multiply and solve for z.

$$x_{CaCO_3} = 2.00 \times 10^{-2}\, mol\ (HCl\ reacted) \times \frac{1\ molCaCO_3}{2\ mol\ HCl} = 1.00 \times 10^{-2}\, mol$$

$$mass_{CaCO_3} = 1.00 \times 10^{-2}\, mol \times 100.09\ \frac{g}{mol} = 1.009\ g$$

$$Percent\ CaCO_3 = \frac{1.009\ g}{1.25\ g} \times 100\% = 80.07\%$$

CHE 1000-e LEARNING

RECAP ON BALANCING REDOX REACTIONS

LECTURERS: DR. J NYIRENDA
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2019 ACADEMIC YEAR

Overview of Redox Reactions

Oxidation is the ***loss*** of electrons and ***reduction*** is the ***gain*** of electrons. These processes occur ***simultaneously***.

Oxidation Number (ON) is defined as the imaginary charge a species will acquire when an electron or electrons are added to it or subtracted from it.

Oxidation results in an ***increase*** in O.N. while reduction results in a ***decrease*** in O.N.

The ***oxidizing agent*** takes electrons from the substance being oxidized. The oxidizing agent is therefore reduced.

The ***reducing agent*** takes electrons from the substance being oxidized. The reducing agent is therefore oxidized.

Rules for Assigning Oxidation Numbers

Compound	Oxidation Number = ON	Exception
1, Pure elements	= 0	
2. Monoatomic ion	ON= charge (z) on the ion (e.g. Cl^- ; ON= -1, Cu^{2+}; ON= +2)	
3. Polyatomic ion	Sum of ON = ±z e.g. SO_4^{2-} $ON_S + 4xON_O = -2$	
4. F in compounds	-1	
5. H in compounds	+1	H^- = -1 (metal hydrides
6. O in compounds	-2	Peroxides (H_2O_2 = -1)
7. Neutral molecules	Sum of ON= 0	
8. Diatomics, Cl_2,O_2,N_2, etc.	=0	
9. Group I element	+1	
10 Group II element	+2	
11. C in compounds	-4 to +4	

Steps for Balancing Redox reactions by Ion-Electron Method

Case 1=(Acidic Media)

- **Step 1:** Divide reaction into half reactions, and assign the oxidation numbers
- **Step 2:** Balance atoms other than H and O
- **Step 3:** Balance O by adding H_2O on the side deficient with O
- **Step 4:** Balance H by adding H^+ on the side deficient with H
- **Step 5:** Balance net charge
- **Step 6:** Balance electron gain = electron loss, and add the two half-reactions
- **Step 7:** Cancel anything that is common on both sides of the equation

Case 2=(Basic Media)

- (Additional steps)
- **Step 8:** Add on both sides of the equation the same number of OH^- to eliminate H^+ in step 7
- **Step 9:** Combine OH- and H+ to form water
- **Step10:** Cancel any water that you can.

- Example: See examples in this topic

Half-Reaction Method for Balancing Redox Reactions

The ***half-reaction method*** or ion pair electron method divides a redox reaction into its oxidation and reduction ***half-reactions***.

- This reflects their physical separation in electrochemical cells.

The half-reaction method is easier to apply to reactions in acidic or basic solutions.

Steps in the Half-Reaction Method Summary

- Divide the skeleton reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species.
- Balance the atoms and charges in each half-reaction.
  - First balance atoms other than O and H, then O, then H.
  - Charge is balanced by ***adding*** electrons (e^-) to the ***left side*** in the ***reduction*** half-reaction and to the ***right side*** in the ***oxidation*** half-reaction.
- If necessary, multiply one or both half-reactions by an integer so that
  - number of e^- gained in reduction = number of e^- lost in oxidation
- Add the balanced half-reactions, and include states of matter.

Balancing Redox Reactions in Acidic Solution

Example: balance the following redox reaction in acid media

$$Cr_2O_7^{2-}(aq) + I^-(aq) \rightarrow Cr^{3+}(aq) + I_2(s)$$

Step 1: *Divide the reaction into half-reactions and assign ON.*

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

$For\ the\ Cr_2O_7^{2-}\ species, let\ Cr = x$

$2x + 7(-2) = -2.$ $Remember\ that\ we\ know\ more\ about\ oxygen\ than\ Cr$

$2x - 14 = -2 \quad giving\ 2x = 12\ and\ x = 6$

So oxidation number for chromium = 6 on the left hand side while on the right hand side its +3 since it's a monoatomic ion.

ON=+6 -2 +3

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

Solving for the other half reaction which is straight forward we have

ON=- 1 0

$$I^- \rightarrow I_2$$

Balancing Redox Reactions in Acidic Solution

ON=+6 -2 +3

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

ON of Cr has reduced from 6 to 3 hence it's a REDUCTION half reaction

ON=- 1 0

$I^- \rightarrow I_2$

ON of I has increased from -1 to 0 hence it's an OXIDATION half reaction

Steps 2-5: *Balance the atoms and charges in each half-reaction.*

For the $Cr_2O_7^{2-}/Cr^{3+}$ half-reaction:

Balance atoms other than O and H:

$$Cr_2O_7^{2-} \rightarrow \mathbf{2}Cr^{3+}$$

Balance O atoms by adding H_2O molecules:

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

Balance H atoms by adding H^+ ions:

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

Balance charges by adding electrons:

$$\mathbf{6e^-} + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

Remember, this is the ***reduction*** half-reaction. $Cr_2O_7^{2-}$ is reduced, and is the oxidizing agent. The O.N. of Cr decreases from +6 to +3.

For the I^-/I_2 half-reaction:

Balance atoms other than O and H:

$$\mathbf{2}I^- \rightarrow I_2$$

There are no O or H atoms, so we balance charges by adding electrons:

$$2I^- \rightarrow I_2 + \mathbf{2e^-}$$

Remember, this is the *oxidation* half-reaction. I^- is oxidized, and is the reducing agent. The O.N. of I increases from -1 to 0.

Step 6: *Multiply each half-reaction, if necessary, by an integer* so that the number of e^- lost in the oxidation equals the number of e^- gained in the reduction.

The reduction half-reaction shows that $6e^-$ are gained; the oxidation half-reaction shows only $2e^-$ being lost and must be multiplied by 3:

$$\mathbf{3}(2I^- \rightarrow I_2 + 2e^-)$$
$$\mathbf{6}I^- \rightarrow \mathbf{3}I_2 + \mathbf{6}e^-$$

Step 7: *Add the half-reactions*, canceling substances that appear on both sides, and include states of matter. Electrons must always cancel.

$$\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
$$6I^- \rightarrow 3I_2 + \cancel{6e^-}$$

$$6I^-(aq) + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3I_2(s) + 7H_2O(l) + 2Cr^{3+}(aq)$$

Balancing Redox Reactions in Basic Solution

An acidic solution contains H^+ ions and H_2O. We use H^+ ions to balance H atoms.

A basic solution contains OH^- ions and H_2O. To balance H atoms, we proceed as if in acidic solution, and then add one OH^- ion to ***both*** sides of the equation.

For every OH^- ion and H^+ ion that appear on the ***same*** side of the equation we form a H_2O molecule.

Excess H_2O molecules are canceled in the final step, when we cancel electrons and other common species.

Example

Balancing a Redox Reaction in Basic Solution

PROBLEM: Permanganate ion reacts in basic solution with oxalate ion to form carbonate ion and solid manganese dioxide. Balance the skeleton ionic equation for the reaction between $NaMnO_4$ and $Na_2C_2O_4$ in basic solution:

$MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow MnO_2(s) + CO_3^{2-}(aq)$ [basic solution]

PLAN: We follow the numbered steps as described in the text, and proceed through step 7 as if this reaction occurs in acidic solution. Then we add the appropriate number of OH^- ions and cancel excess H_2O molecules.

SOLUTION:

Step 1: *Divide the reaction into half-reactions.*

$MnO_4^- \rightarrow MnO_2$ $C_2O_4^{2-} \rightarrow CO_3^{2-}$

Steps 2-5: *Balance the atoms and charges in each half-reaction.*

Balance atoms other than O and H:

$MnO_4^- \rightarrow MnO_2$ $\quad$ $C_2O_4^{2-} \rightarrow \mathbf{2}CO_3^{2-}$

Balance O atoms by adding H_2O molecules:

$MnO_4^- \rightarrow MnO_2 + \mathbf{2H_2O}$ $\quad$ $\mathbf{2H_2O} + C_2O_4^{2-} \rightarrow 2CO_3^{2-}$

Balance H atoms by adding H^+ ions:

$\mathbf{4H^+} + MnO_4^- \rightarrow MnO_2 + 2H_2O$ $\quad$ $2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + \mathbf{4H^+}$

Balance charges by adding electrons:

$\mathbf{3e^-} + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$ [reduction]

$2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + 4H^+ + \mathbf{2e^-}$ [oxidation]

Practice on assigning oxidation numbers or states

We will use the same example of oxalate and permanganate

$MnO_4^- \rightarrow MnO_2$

$C_2O_4^{2-} \rightarrow CO_3^{2-}$

$Let\ Mn = x$

$x + 4(-2) = -1 \ \ and\ x + 2(-2) = 0$

$x = +7 \ \ and\ x = +4$

$Let\ C = y$

$2y + 4(-2) = -2 \ \ and\ y + 3(-2) = -2$

$y = +3 \ \ and \ \ y = +4$

ON= +7 -2 +4 -2

$MnO_4^- \rightarrow MnO_2$

ON= +3 -2 +4 -2

$C_2O_4^{2-} \rightarrow CO_3^{2-}$

Recall what an increase in ON signifies and a decrease in the same signifies. This is going to help you understand which reaction is undergoing oxidation or reduction

Step 6: *Multiply each half-reaction, if necessary, by an integer* so that the number of e^- lost in the oxidation equals the number of e^- gained in the reduction.

x 2 $\quad \mathbf{6}e^- + \mathbf{8}H^+ + 2MnO_4^- \rightarrow \mathbf{2}MnO_2 + \mathbf{4}H_2O$

x 3 $\quad \mathbf{6}H_2O + \mathbf{3}C_2O_4^{2-} \rightarrow \mathbf{6}CO_3^{2-} + \mathbf{12}H^+ + \mathbf{6}e^-$

Step 7: *Add the half-reactions***,** canceling substances that appear on both sides.

$$\cancel{6e^-} + \cancel{8H^+} + 2MnO_4^- \rightarrow 2MnO_2 + \cancel{4H_2O}$$

$$\mathbf{2}\ \cancel{6H_2O} + 3C_2O_4^{2-} \rightarrow 6CO_3^{2-} + \mathbf{4}\ \cancel{12H^+} + \cancel{6e^-}$$

$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+$$

Steps 8 and 9, basic media. Add OH^- to both sides of the equation to neutralize H^+, and cancel H_2O.

$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + [4H^+ + 4OH^-]$$

$$2MnO_4^- + \cancel{2H_2O} + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + \mathbf{2}\ \cancel{4H_2O}$$

Step 10

Including states of matter gives the final balanced equation:

$$2MnO_4^-(aq) + 3C_2O_4^{2-}(aq) + 4OH^-(aq) \rightarrow 2MnO_2(s) + 6CO_3^{2-}(aq) + 2H_2O(l)$$

CHE 1000 e-LEARNING

GASES

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2019 ACADEMIC YEAR

Lecture 1- Gases

- Matter exists in three states namely , solids, liquids and gases.
- The difference between gases and the other two states of matter is that gas particles have very large distances between them.
- A pure gas may be made up of individual atoms (e.g. a noble gas like neon), elemental molecules made from one type of atom (e.g. oxygen), or compound molecules made from a variety of atoms (e.g. carbon dioxide).

Characteristics of gases

Gases:

i. are highly compressible

   You can pump a bicycle tyre or a ball etc

ii. are thermally expandable

   When heated, gases expand- hot air balloons get filled this way

iii. have low viscosity

   Compared to liquids gases have no friction and flow easily

iv. have relatively low density

   Compared to solids and liquids, gases are very light

v. infinitely miscible

   Gases mix in all proportions at all concentrations

Gases exert pressure on the walls of the container. This pressure can be measured using a **barometer** or a **manometer**

Gas Laws

- Gases obey the following physical laws
- Boyle’s Law
- Charles's Law
- Avogadro’s Law
- Gay-Lussac’s Law and
- Ideal gas Law
- Combined Law

Remember BCA or ABC to memorize names of these laws and relationships between variables. The others are combinations of the three.

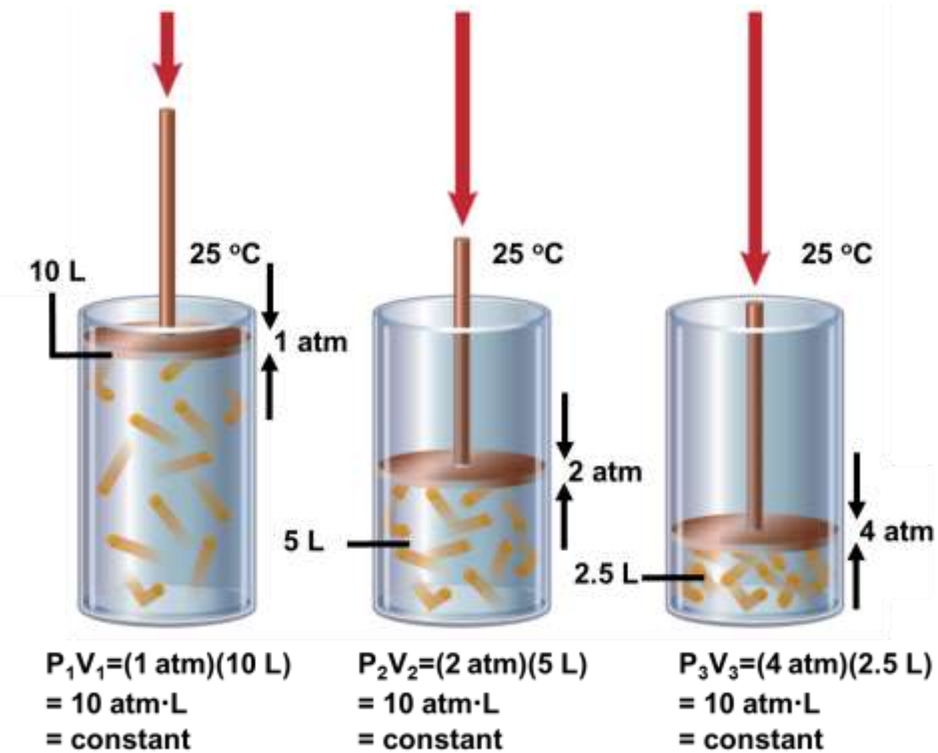
Boyles Law states that:

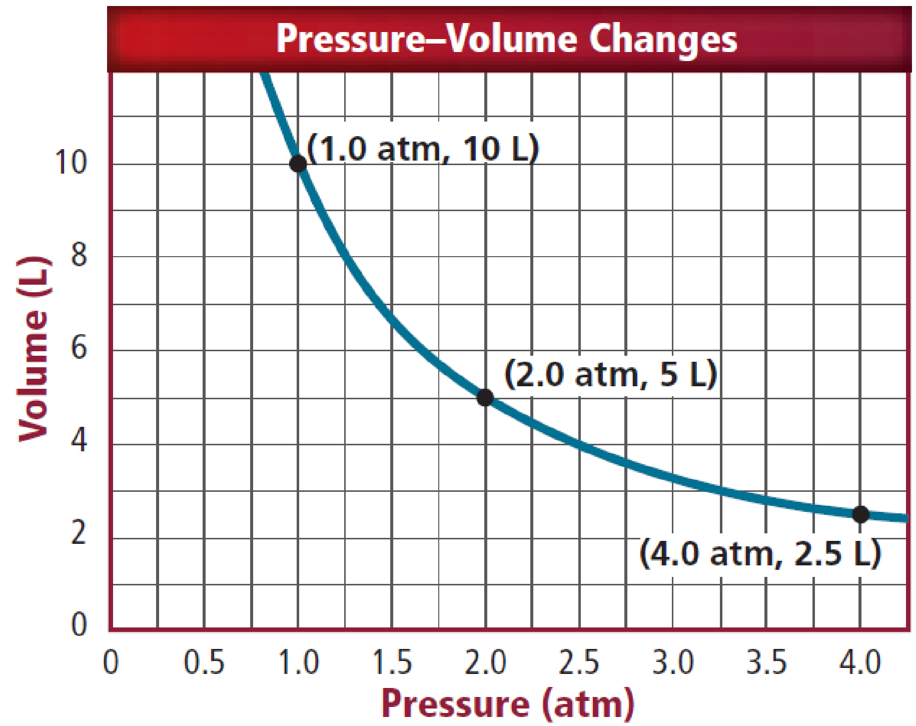
- the **volume** of a fixed amount of gas held at a constant **temperature** varies inversely with the **pressure**.
- Mathematically, $V \propto \frac{1}{P}$ or $P = \frac{1}{V}$
- Introducing a proportionality constant k, we have an equation
- $V = \frac{k}{P} = k\frac{1}{P}$ hence **$PV=k$** where P=Pressure, V=Volume and k=proportionality constant
- Plotting volume against pressure yields a graph which decreases exponentially as shown

Summary of Boyle's Law **$P_1V_1=P_2V_2$**

Practice and memorize these mathematical expressions

Plot of volume against pressure





An increase in pressure reduces the volume or vice versa

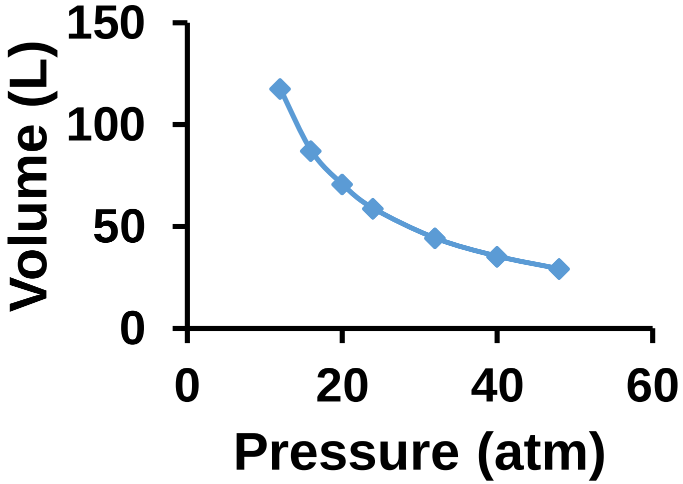
Example

The following data was obtained at constant temperature. Plot volume against pressure and also volume against 1/pressure

Volume (L)	117.5	87.2	70.7	58.8	44.2	35.3	29.1
Pressure (atm)	12.0	16.0	20.0	24.0	32.0	40.0	48.0
Pressure x Volume (atm x L)	14.0 x 10^2	14.0 x10^2	14.0 x 10^2	14.0 x 10^2	14.0 x 10^2	14.0 x 10^2	14.0 x 10^2

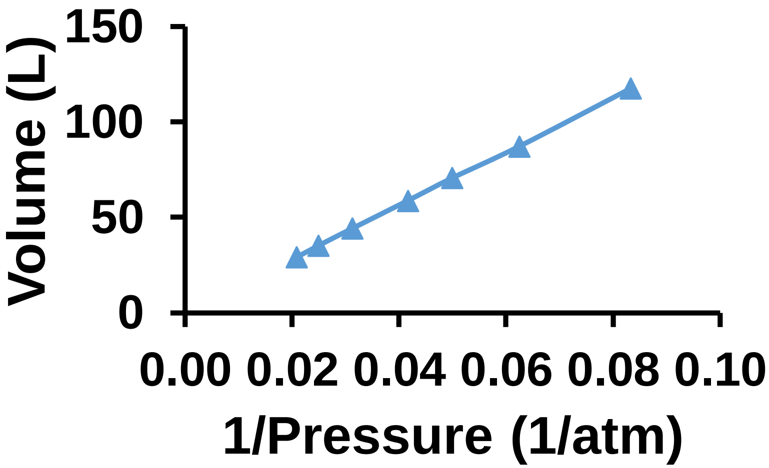
Solution

A plot of volume against pressure yields a curve with decreasing gradient while



Solution

A plot of volume against 1/pressure yields a straight line with positive gradient



Example

1. A gas has volume of 255 mL at 725 torr. What volume will it occupy at 365 torr?

Solution

First, understand what we want! It's the volume. What we have is pressure 1, volume 1 and pressure2.What is missing is volume 2

$P_1V_1 = P_2V_2$
=725 torr x 255 mL = 365 torr x V_2 .Make V_2 the subject and solve
V_2 = 506.5 mL

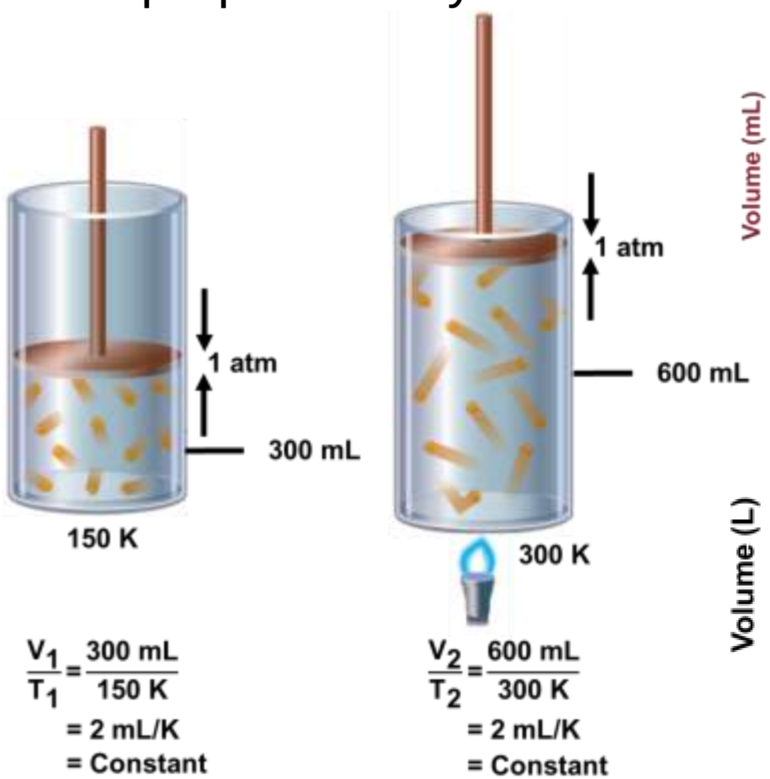
2. A diver blows a 0.75-L air bubble 10 m under water. As it rises to the surface, the pressure goes from 2.25 atm to 1.03 atm. What will be the volume of air in the bubble at the surface?

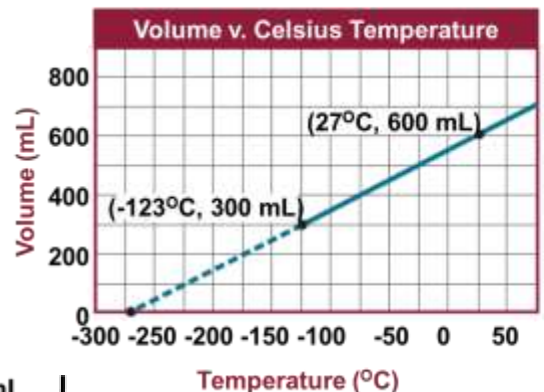
Solution

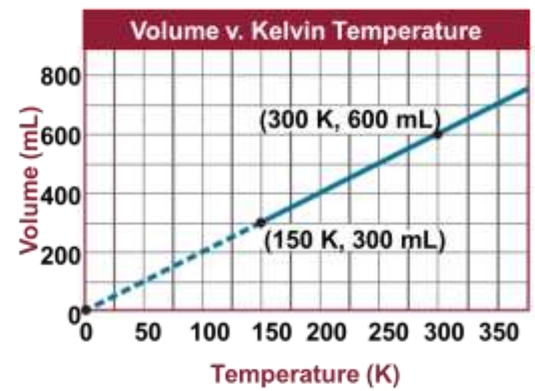
$P_1V_1 = P_2V_2$
=2.25 atm x 0.75 L = 1.03 atm x V_2 .Make V_2 the subject and solve
V = 1.64 L

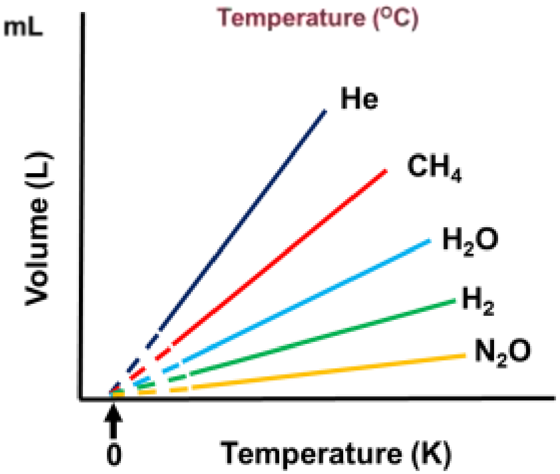
Charles's Law states that:

- the **volume** of a given amount of gas is directly proportional to its **Kelvin temperature** at constant **pressure**. In other words, the volume of a fixed mass of gas at constant pressure increases linearly with the increase in temperature.
- Mathematically, $v \propto T$ or **$V = b\,T$** T = Temperature in K, V = volume b = proportionality constant









A plot of various gases at constant pressure yields a straight line. Slopes of these lines INDICATE different number of moles for each gas.

A very interesting feature of these plots is that the volumes of all the gases extrapolate to zero at the same temperature, -273^{O}C. On the Kelvin temperature scale this point is defined as 0 K, which leads to the following relationship between the Kelvin and Celsius scales: K= ^{O}C +273

Example

1. A gas has volume of 3.86 L at temperature of 45 ^{O}C. What will be volume at 80 ^{O}C?

Solution

We have V_1=3.86 L , T_1=45 ^{O}C and T_2=80 ^{O}C. We need V_2.

REMEMBER TO CHANGE TEMPERATURE TO KELVINS ALWAYS

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \quad \frac{3.86\ \text{L}}{318\ \text{K}} = \frac{V_2}{353\ \text{K}} = \qquad V_2 = \frac{3.86\ \text{L} \times 353\ \text{K}}{318\ \text{K}} = 4.28\ \text{L}$$

Example

2. A helium balloon in a closed car occupies a volume of 2.32 L at 40.0°C. If the car is parked on a hot day and the temperature inside rises to 75.0°C, what is the new volume of the balloon, assuming the pressure remains constant?

Solution

Again let us convert Celsius temperature to Kelvin temperature

40.0°C= 273 +40.0 = 313 K and 75.0°C= 273 + 75=348 K

We have V_1=2.32 L , T_1=313 K and T_2=348 K. We need V_2.

We replace the values and make V_2 the subject of the formula and solve for V_2

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{2.32\ \text{L}}{313\ \text{K}} = \frac{V_2}{348\ \text{K}} = \qquad V_2 = \frac{2.32\ \text{L} \times 348\ \text{K}}{313\ \text{K}} = 2.58\ \text{L}$$

Lecture 2- Avogadro's Law

Avogadro's Law or principle states that equal **volumes** of gases at the same temperature and pressure contains equal number of **particles** (moles).

Mathematically, $V \propto n$ or **V= an** where V = volume, n = number of moles, a = proportionality constant

- Recall that 1 mol contains 6.02×10^{23} particles.
- The **molar volume** of a gas is the volume that 1 mol occupies at 0.00°C (273 K) and 1.00 atm pressure. The conditions of 0.00°C and 1.00 atm are known as standard temperature and pressure (STP).
- Avogadro showed experimentally that 1 mol of any gas occupies a volume of 22.4 L at STP.

Example

The main component of natural gas used for home heating and cooking is methane (CH_4). Calculate the volume that 2.00 kg of methane gas will occupy at STP.

Solution

What do we know ? Pressure= 1atm, temperature 273 K (remember STP), mass= 2.00 kg. What we are looking for is volume.

Lets revise calculations of molar mass by determinig molar mass of methane from first principles

$$M_r = 1\ \text{C}\ \cancel{\text{atom}}\left(\frac{12.01\ \text{amu}}{1\ \text{C}\ \cancel{\text{atom}}}\right) + 4\ \text{H}\ \cancel{\text{atoms}}\left(\frac{1.01\ \text{amu}}{1\ \text{H}\ \cancel{\text{atom}}}\right)$$

Cancel out common units

M_r=12.01 amu + 4.04 amu= 16.05 amu = 16.05 g/mol

Next we will determine the number of moles of methane gas from mass and molar mass

$$\text{number of moles } n = \frac{\text{mass in grams}}{\text{molar mass in g/mol}}$$

Please, don't forget this formula

$$\text{number of moles } n = \frac{2.00 \times 10^3 \text{ g}}{16.05 \text{ g/mol}} = 124.61 \text{ mol}$$

Also recall that the unit for mole is mol

Recall that the linking conversion factor is 22.4 L/mol at STP and using our usual relationship using arrows we have

1 mol → 22.4 L

124.61 mol → x L

Cross multiply and make x the subject of the formula

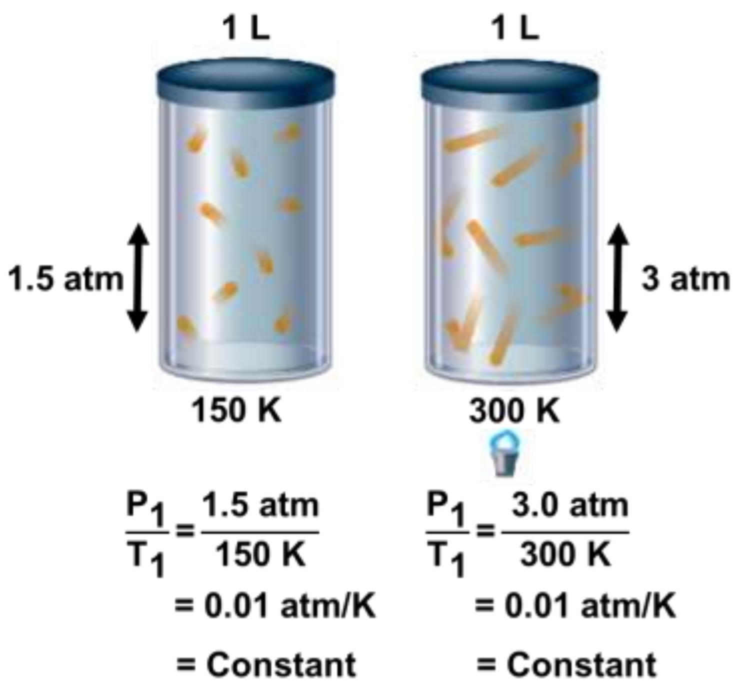
$$x = \frac{22.4 \text{ L} \times 124.61 \cancel{\text{mol}}}{1 \cancel{\text{mol}}} = 2791.264 \text{ L} = 2.8 \times 10^3 \text{ L}$$

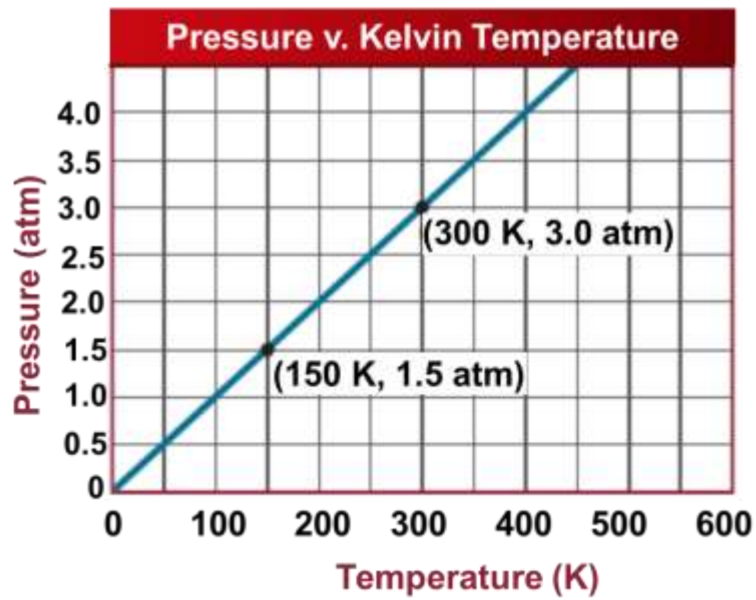
Gay-Lussac's Law

Gay-Lussac's law states that the **pressure** of a fixed amount of gas varies directly with the Kelvin **temperature** when the **volume** remains constant. It can be expressed mathematically as follows.

$P \propto T$ or $P = dT$ where P= pressure, T=Kelvin temperature and d = proportionality constant

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





Example

The pressure of the oxygen gas inside a canister is 5.00 atm at 25.0°C. The canister is located at a camp high on Mount Everest. If the temperature there falls to -10.0°C, what is the new pressure inside the canister?

Solution

What do we know ? P_1= 5 atm, T_1= 298 K, T_2= 263 K. What we are looking for is P_2.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{5\text{ atm}}{298\text{ K}} = \frac{P_2}{263\text{ K}}$$

Make P_2 the subject of the formula and solve

$$P_2 = \frac{5\text{ atm} \times 263\text{ K}}{298\text{ K}} = 4.41\text{ atm}$$

Combined law and Ideal Gas Law

In a number of applications involving gases, such as the weather balloons, pressure, temperature, and volume might all change. Boyle's, Charles's, and Gay-Lussac's laws can be combined into a single law. This **combined gas law** states the relationship among pressure, temperature, and volume of a fixed amount of gas. All three variables have the same relationship to each other as they have in the other gas laws: pressure is inversely proportional to volume and directly proportional to temperature, and volume is directly proportional to temperature. The combined gas law can be expressed mathematically as follows.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Example

A gas at 110 kPa and 30.0°C fills a flexible container with an initial volume of 2.00 L. If the temperature is raised to 80.0°C and the pressure increases to 440 kPa, what is the new volume?

Solution

As in previous examples, we need to have a quick look at what information we have and what is being asked for. Remember this approach to solve many questions

So we have P_1=110 kPa , T_1= 30.0°C , V_1=2.00 L and T_2= 80.0°C, P_2= 440 kPa. We need V_2.

Remember temperature is always to be in KELVINS

$K = {}^{O}C + 273$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{110 \text{ kPa} \times 2.0 \text{ L}}{303 \text{ K}} = \frac{440 \text{ kPa} \times V_2}{353 \text{ K}}$$

So work out the rest and make sure your solution is 0.58 L

Recap on the three laws (ABC)

Avogadro's Law $V = an$

Boyle's Law $PV = k$ or $V = \frac{k}{P}$

Charles's Law $V = b\,T$

So combining all these laws expressed as volume we have

$$V = \frac{k}{P} = b\,T = a\,n$$

$$V = \frac{(k\,b\,a)n\,T}{P} = R\frac{nT}{P}$$ or $PV = n\,RT$

Where R = k b a = combined proportionality constant called Universal gas constant. R value depends on pressure units used so be conversant with various values given for this constant.

$PV = n\,RT$ is called the IDEAL GAS LAW

It is important to recognize that the ideal gas law is an empirical equation—it is based on experimental measurements of the properties of gases. A gas that obeys this equation is said to behave *ideally.*

Example

Calculate the number of moles of ammonia gas (NH_3) contained in a 3.0-L vessel at 3.00×10^2 K with a pressure of 1.50 atm.

Solution

PV = n RT   Make n the subject of the formula and solve for it

$$n = \frac{PV}{RT} \Rightarrow \frac{1.50 \text{ atm} \times 3.0 \text{ L}}{0.0821 \frac{\text{L.atm}}{\text{mol.K}} \times 3.00 \times 10^2 \text{ K}} = 0.18 \text{ mol}$$

Make sure you understand the dimension analysis of units and cancel out appropriately.

Kinetic molecular theory of gases

Postulates of kinetic theory:

(i) Gases consist of small particles called molecules. These moles are constant motion.

(ii) Moles collide with each other and the walls of the container.

(iii) These collisions are elastic collisions (No energy is lost)

(iv) Gas exert pressure due to the collision with the walls of the container.

(v) Particles are assumed to exert no forces of attraction on each other.

(vi) The average kinetic energy is assumed to be directly proportional to the Kelvin temperature of the gas.

What does the word Postulate mean?

From KMT and definitions of momentum, volume and velocity, pressure of a sample of gas is given by

$$P = \frac{2}{3}\left[\frac{nN_A\left(\frac{1}{2}m\bar{u}^2\right)}{V}\right]$$ where $N_A\left(\frac{1}{2}m\bar{u}^2\right) = (KE)_{avg}$ = average kinetic energy of one mole of gas

Then the pressure of the gas, $P = \frac{2}{3}\left[\frac{n(KE)_{avg}}{V}\right]$ Or $\frac{2}{3}(KE)_{avg} = \frac{PV}{n}$

We know temperature is the measure of average KE (from physics 5124 or 5070 thermodynamics topic at high school).

$$\frac{PV}{n} = \frac{2}{3}(KE)_{avg} \propto T \quad \text{or} \quad \frac{PV}{n} \propto T$$ from Kinetic Molecular Theory

In short average kinetic energy is directly proportional to temperature which is directly proportional to pressure and volume. Revise this fundamental principle

Compare this with Ideal gas law $\frac{PV}{n} = R\,T$ from experiment

FOR PRACTICE QUESTIONS REFER TO ZUMDHAL AND ZUMDHAL

CHE 1000 e-LEARNING

GASES

LECTURERS: DR. J. NYIRENDA
MRS M. XAVIER
2019 ACADEMIC YEAR

Lecture 3- Gas Stoichiometry

Recall that Molar volume of a gas at STP = 22.4 L (1 atm, 0 °C)

$$\text{Molar volume of gas} = \frac{nRT}{P} = \frac{1\ \text{mol} \times 0.08206\ \text{atm L mol}^{-1}\text{K}^{-1} \text{x}\ 273.15\ \text{K}}{1.00\ \text{atm}}$$

$$= 22.414689\ \text{L} = 22.4\ \text{L}$$

Remember 22.4 L/mol

Remember that this was stated at high school as 1 mol of any gas occupies 22.4 L at STP OR 24.0 L at RTP

Example

If a sample of nitrogen occupies 1.75 L at STP. How many moles of nitrogen are present?

Solution

$$\text{Number of moles in 1.75 L} = \frac{PV}{RT} = \frac{1.00\ \text{atm} \times 1.75\ \text{L}}{0.08206\ \text{atm L mol}^{-1}\text{K}^{-1} \text{x}\ 273.15\ \text{K}}$$

$$= 0.07807 = 7.81 \times 10^{-2}\ \text{mol}$$

Example

What mass of sodium azide is required to inflate an airbag to 70.0 L at STP?

Balanced reaction is: $2\ NaN_3(s) \rightarrow 2\ Na(s) + 3\ N_2(g)$

Solution

$$n_{N_2} = \frac{PV}{RT} = \frac{1.00\ \text{atm} \times 70\ \text{L}}{0.08206\ \text{atm L mol}^{-1}\text{K}^{-1} \text{x}\ 273.15\ \text{K}} = 3.1229\ \text{mol}$$

$3\ \text{mol}\ N_2 \rightarrow 2\ \text{mol}\ NaN_3$

$3.1229\ \text{mol}\ N_2 \rightarrow x\ \text{mol}\ NaN_3$

Cross multiply, make x the subject and solve

$$x\ \text{mol}\ NaN_3 = \frac{2\ \text{mol}\ NaN_3 \times 3.1229\ \text{mol}\ N_2}{3\ \text{mol}\ N_2} = 2.08\ \text{mol}$$

$$m_{\ NaN3} = n_{NaN_3} \times M = 2.082\ \text{mol} \times 65.02\text{g/mol} = 135\ \text{g}$$

Example

Consider the reaction between 50.0 mL of liquid Methanol, CH_3OH, (density 0.850 g/ mL) and 22.8 L of oxygen at a pressure of 2.00 atm and $27^{O}C$. The products of the reaction are CO_2 and H_2O. Calculate the number of moles of water formed if the reaction goes to completion.

Solution

First write a balanced chemical equation and find the number of moles for each reactant and ultimately the number of moles of water. REMEMBER OTHER CONCEPTS LIKE LIMITING REAGENT HERE AND ELSEWHERE.

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

$$n_{CH3OH} = \frac{mass}{M} = \frac{50.0\,mL \times 0.850\ g/mL}{12.01 + (4 \times 1.01) + 16.00} = \frac{42.5\ g}{32.05\ g/mol} = 1.326\ mol$$

$$n_{O_2} = \frac{PV}{RT} = \frac{2.00\ atm \times 22.8\ L}{0.08206\ \left(\frac{atm\ L}{mol\ K}\right)(273.15 + 27)K} = 1.851 mol$$

Let us learn another way of determining the limiting reactant by using mole ratios. From the balanced equation, 3 mol O_2 reacts with 2 mol CH_3OH expressed as

$$\frac{n_{O_2}}{3} = \frac{n_{CH_3OH}}{2} \quad \text{which translates to} \quad \frac{1.851}{3} = \frac{1.326}{2}$$

$0.613\ O_2 : 0.663\ CHE_3OH$

Therefore the Limiting reactant is oxygen since 0.613 is less than 0.663.

Remember, the limiting reagent determines how much product forms so all of the products will depend on the moles of oxygen.

$$\frac{n_{O_2}}{3} = \frac{n_{H_2O}}{4} \quad \text{which translates to} \quad \frac{1.851}{3} = \frac{n_{H_2O}}{2}$$

Therefore moles of water = n_{H_2O}=2.47 mol

See how we apply other concepts we learnt earlier to different problems. So learnt to link all these other concepts

Molar mass of gases

Ideal gas law can be used to determine the molar mass of a gas or a volatile liquid. The volatile liquid sample is placed in the previously weighted flask. This flask is then heated in a water bath. The liquid evaporates and the vapour completely fills the flask at 100 °C. The flask is cooled and weighed again. The mass of the vapour is given by the difference in mass. The volume of the gas is the volume of the flask and the pressure is atmospheric pressure. Molecular weight can be calculated from ideal gas equation as follows:

$$\text{Number of moles, } n = \frac{\text{mass}}{\text{molar mass}}$$

Don't forget this formula. Learn it by heart

$$\text{And from Ideal gas law } n = \frac{PV}{RT} = \frac{\text{mass}}{\text{molar mass}}$$

$$\text{Molar mass} = \frac{\text{mass} \times RT}{PV} \text{ and } \frac{\text{mass}}{V} = \text{density}$$

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

Example

A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36 ^{O}C and 2.88 atm. Calculate the molar mass of the compound.

Solution

We can calculate the molar mass of a gas if we know its density, temperature, and pressure. The molecular formula of the compound must be consistent with its molar mass. What temperature unit should we use if you can remember?

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

Develop the habit of stating the formula you are going to use. This costs marks!

$$\text{Molar mass} = \frac{7.71\ \text{g/L} \times 0.08206\ \text{L.atm K}^{-1}.\text{mol}^{-1} \times \text{T}309.15\ \text{K}}{2.88\ \text{atm}} = 67.9\ \text{g/mol}$$

Try using the ideal gas equation to solve this problem given the information above. You should arrive at the same solution.

Dalton's Law of Partial Pressure

States that for a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.

$P_{total} = P_1 + P_2 + P_3 + P_4 + \ldots P_x$ (where P_x = partial pressure of gas x)

$P_1 = n_1 RT/V$, $P_2 = n_2 RT/V$, $P_3 = n_3 RT/V$, $P_4 = n_4 RT/V$, $P_x = n_x RT/V$

$$P_{total} = n_1\frac{RT}{V} + n_2\frac{RT}{V} + n_3\frac{RT}{V} + n_4\frac{RT}{V} + \ldots n_x\frac{RT}{V}$$

$$P_{total} = (n_1 + n_2 + n_3 + n_4 + ..n_x)\left(\frac{RT}{V}\right)$$

Note that RT/V is constant for all gases as they occupy the same container, experience the same temperature and have the same R

Partial Pressure: Partial pressure refers to the pressure exerted by an individual gas in a mixture of gasses. OR The **partial pressure** of a gas is the pressure that gas would exert if it occupied the container by itself.

Mole fraction = $\frac{number\ of\ moles\ of\ a\ gas}{total\ number\ of\ moles\ of\ gases\ in\ the\ mixture}$

Partial pressure = $\frac{number\ of\ moles\ of\ a\ gas}{total\ number\ of\ moles\ of\ gases\ in\ the\ mixture} \times Total\ pressure$

Example:

Mixture of Helium and oxygen can be used in scuba diving tanks to help prevent “the bends”. For a particular dive, 46 L of He at 25 °C and 1.0 atm and 12 L of oxygen at 25 °C and 1.0 atm were pumped into the tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25 °C.

Solution:

Moles of helium = $\frac{PV}{RT} = \frac{1.0\ atm \times 46.0\ L}{0.08206 L.atm\ K^{-1} mol^{-1} \times 298.15\ K} = 1.9\ mol$

Moles of oxygen = $\frac{PV}{RT} = \frac{1.0\ atm \times 12.0\ L}{0.08206 L.atm\ K^{-1} mol^{-1} \times 298.15\ K} = 0.49\ mol$

Pressure exerted by He = $\frac{nRT}{V} = \frac{1.9 \times 0.08206 L.atm\ K^{-1} mol^{-1} \times 298.15\ K}{5.0\ L}$ = 9.29 atm

Pressure exerted by O_2 = $\frac{nRT}{V} = \frac{0.49 \times 0.08206 L.atm\ K^{-1} mol^{-1} \times 298.15\ K}{5.0\ L}$ = 2.398 atm

Total pressure = 9.3 + 2.4 = 11.7 atm

Lecture 4- Collecting a gas over water

Dalton's law of partial pressures is most commonly encountered when a gas is collected by displacement of water. Because the gas has been bubbled through water, it contains some water molecules and is said to be "wet." The total pressure of this wet gas is the sum of the partial pressure of the gas itself and the partial pressure of the water vapor it contains. The partial pressure of water vapors is called **the vapor pressure** of water. It depends only on the temperature of the experiment.

Example

A sample of solid potassium chlorate was heated in a test tube and decomposed as follows:

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

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

Total pressure = partial pressure of oxygen + vapour pressure of water

$$P_{Total} = P_{O_2} + P_{H_2O}$$

partial pressure of oxygen = 754 – 21 =733 torr

$$n_{O_2} = \frac{P_{O_2} \times V}{RT} = \frac{733\ \text{torr} \times 0.650\ \text{L}}{62.364\ \text{L.torr K}^{-1}\text{mol}^{-1} \times 295.15}$$

=0.02588 mol = 2.59 x 10^{-2} mol

$$\frac{n_{O_2}}{3} = \frac{n_{KClO_3}}{2}$$ which translates to $$\frac{0.0259}{3} = \frac{n_{KClO_3}}{2}$$

n_{KClO_3}=0.0173 mol

Mass = 0.0173 mol x 122.6 g mol^{-1}= 2.12 g of potassium chlorate

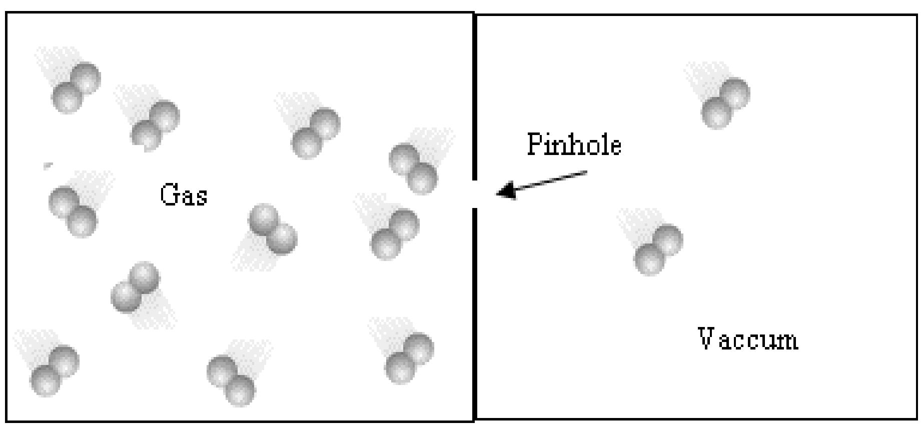
Other important application

Gas exchange between living organisms and the environment depends on the properties of gases, in particular, partial pressure and solubility. Gaseous exchange during RESPIRATION in lungs also depends on Partial pressure.

Diffusion and effusion

Diffusion: Inter mixing of two or more gases to form a homogeneous mixture without any chemical change is called "DIFFUSION OF GASES". Diffusion is purely a physical phenomenon. Gases diffuse very quickly due to large empty spaces among molecules. Different gases diffuse with different rates (depending on velocities). It takes relatively long time to complete.

Effusion: is the term used to describe the passage of a gas through a tiny orifice into an evacuated chamber, as shown in the figure below.



The **rate of effusion** measures the **speed** at which the gas travels through the tiny hole into a vacuum.

Root Mean Square Velocity

Root Mean Square (rms) Velocity is defined as the square root of the average of the squares$(\overline{u^2})$ of velocities of particles. See that the u has a bar on top to signify average velocity

$$u_{rms}=\sqrt{\bar{u}^2}$$

We can get expression of u_{rms} from the KMT equation by making $\bar{u}^2$ the subject

$$(KE)_{avg}=N_A\left(\frac{1}{2}m\bar{u}^2\right) = \frac{3}{2}R\,T$$

$$\bar{u}^2 = \frac{3}{2}R\,T\times\frac{2}{m\,N_A}=\frac{3RT}{m\,N_A}$$

Then take square root on both sides

$$\sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{m\,N_A}}=\sqrt{\frac{3RT}{M}}$$

Where m = mass in kilograms of a single gas particle and $M=N_A$ x *m* to give the mass of a *mole* of gas particles in *kilograms*.

Example

Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in m/s at 25°C.

Solution

To calculate u_{rms}, the units of *R* should be 8.314 JK^{-1} mol^{-1} and, because 1 J =1 kg m^2 /s^2 , the molar mass must be in kg/mol. The molar mass of He is 4.003 g/mol, or 4.003 $\times 10^{-3}$ kg/mol.

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314\, kg\frac{m^2}{s^2}.K^{-1}.mol^{-1} \times 298\, K}{4.003 \times 10^{-3}\, kg/mol}} = 1362\, m/s$$

Do the same for N_2 and prove that the U_{rms}= 515 m/s

Graham's Law: Rate of effusion is inversely proportional to the square root of the mass of the particles (density of the gas) under the same conditions.

$r \qquad \frac{1}{\sqrt{d}}$ Or for two gases $\frac{Rate\ of\ diffusion\ of\ gas\ 1}{Rate\ of\ diffusion\ of\ gas\ 2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$

Derivation from Kinetic Molecular Theory:

Rate of effusion of gas depends on the velocity of the gas molecules at any temperature. Gases at the same temperature have same average kinetic energy.

$KE_1 = KE_2$ or $\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$ which simplifies to $\frac{v_2^2}{v_1^2} = \frac{m_1}{m_2}$

$$\frac{Rate\ of\ effusion\ of\ gas\ 1}{Rate\ of\ effusion\ of\ gas\ 2} = \frac{u_{rms}of\ gas\ 1}{u_{rms}of\ gas\ 2} = \frac{\sqrt{\frac{3RT}{M_1}}}{\sqrt{\frac{3RT}{M_2}}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

This is same as Graham's Law.

Graham's law provides a basis for separating isotopes by diffusion.

Example

A given volume of N_2 requires 68.3 seconds to effuse from a hole into a vacuum chamber. Under the same conditions another unknown gas required 85.6 seconds for the same volume to effuse. What is the molar mass of the unknown gas and what is the gas?

$$\frac{Rate\ of\ effusion\ of\ unknown\ gas}{Rate\ of\ effusion\ of\ N_2} = \frac{t_{N_2}}{t_x} = \frac{\sqrt{M_{N_2}}}{\sqrt{M_x}}$$

This is another form of Graham's law expressed in time units. See that the ratios are making sense i.e rate is *inversely* proportional to the time required for diffusion

$$\frac{t_{N_2}}{t_x} = \frac{\sqrt{M_{N_2}}}{\sqrt{M_x}} \Longrightarrow \frac{68.3\ s}{85.6\ s} = \frac{\sqrt{28.2\ \frac{g}{mol}}}{\sqrt{\mathrm{M_X}}}$$

Taking squares on either side and making M_x the subject, we have

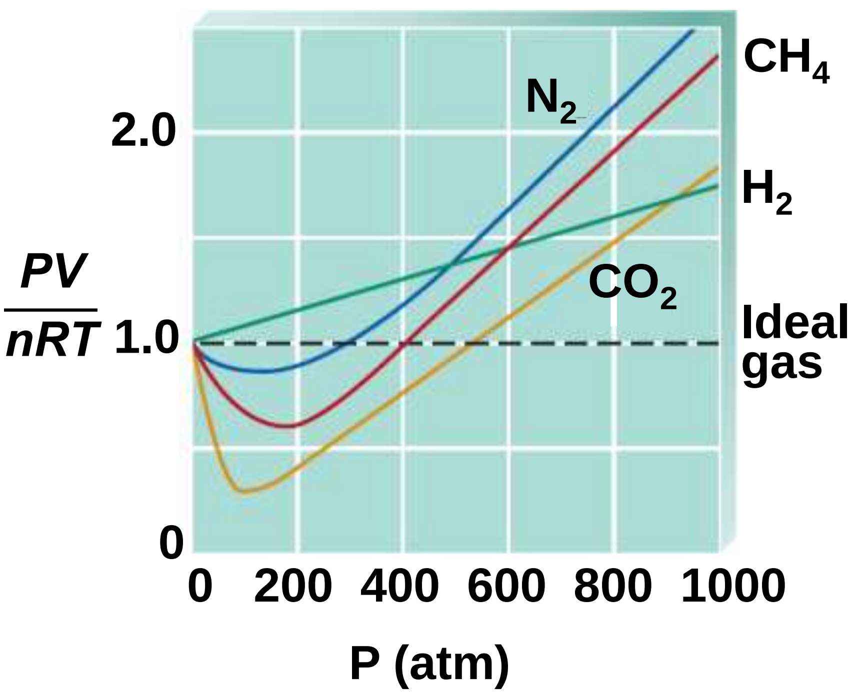
$$(0.79789)^2 = \frac{28.2\ \frac{g}{mol}}{\sqrt{\mathrm{M_X}}} \Longrightarrow M_x = \frac{28.2\frac{g}{mol}}{0.63663} = 44.02\ g/mol$$

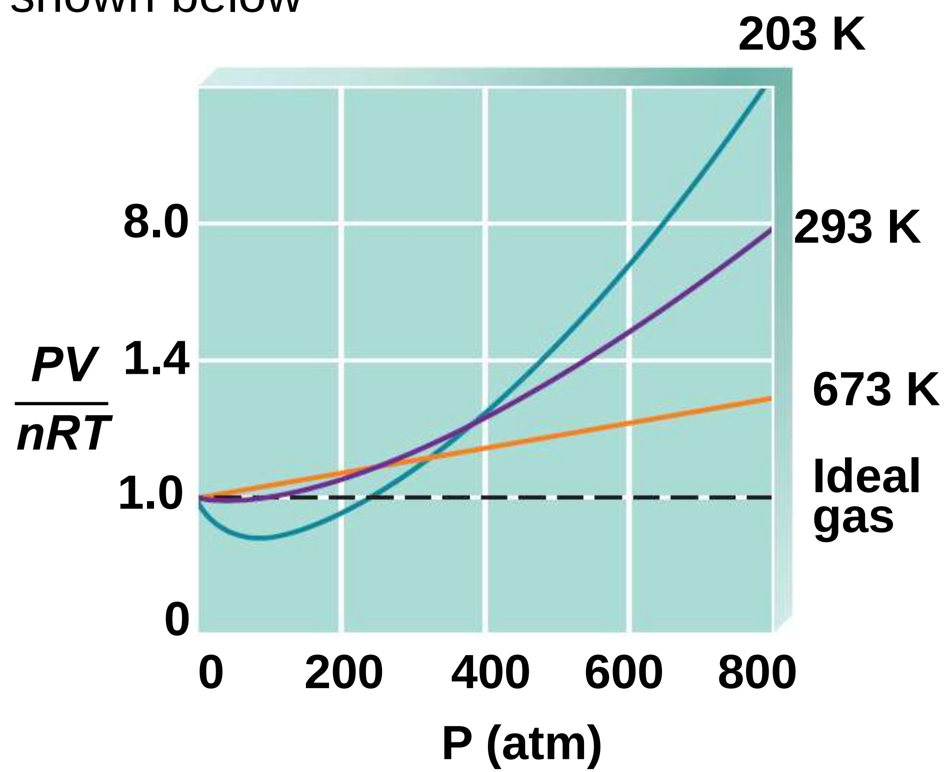
The gas is carbon dioxide

Lecture 5-Real Gases

Ideal gas is a hypothetical concept in which gas molecules do not interact with each other, and do not occupy any space. These assumptions are not always valid for real gases. Real gases follow these ideal gas laws at low pressure and high temperature.

Experimentally observed graphs are shown below





Adopted from Zumdhal and Zumdhal 8th ed

Real gases consist of atoms or molecules which occupy space and attract each other. van der Waals made the following correction in pressure and the volume.

Effect of pressure:

In real gases at low temperatures molecules attract each other which causes a delay in reaching the walls of the container. This also reduces the number of collisions in a given time. The impact is further reduced due to the attraction by other molecules.

$$P_{obs} = P_{ideal} - a\left(\frac{n}{V}\right)^2$$

Effect of Volume:

According to KMT gas molecules are so small that the volume of gas is volume of the container. However at high pressure the volume of the molecules is significant fraction of the volume. Therefore, the free volume for the molecules is less than the volume of the container.

Memorize this formula

$V_{container} = V_{ideal} + nb$

$V_{ideal} = V_{container} - nb$

If we substitute in ideal gas equation

$$[P_{obs} + a\left(\frac{n}{V}\right)^2] \times (V_{container} - nb) = nRT$$

where a and b are constants for a gas. This equation is called van der Waal's equation. The values of a and b are determined experimentally.

Example

Calculate the pressure exerted by 10.000 mol of helium gas at 25^{O}C in a volume of 1.00 L using van der Waals equation. Also calculate the pressure deal gas would exert under these condition.

Non ideal behavior.

$$[P_{obs} + a\left(\frac{n}{V}\right)^2] \times (V - nb) = nRT$$

a =0.034 L^2 atm/ mol^2 and b = 0.0237 L/ mol

P_{obs} + 0.034 L^2 atm/ $mol^2$$[\left(\frac{10.000\ mol}{1.00\ L}\right)^2]$(1.00 – 10.00x 0.0237 L/ mol) = nRT

(P_{obs} + 3.4) x 0.768 = 10.0 x 0.08206 x 298.15/1.00

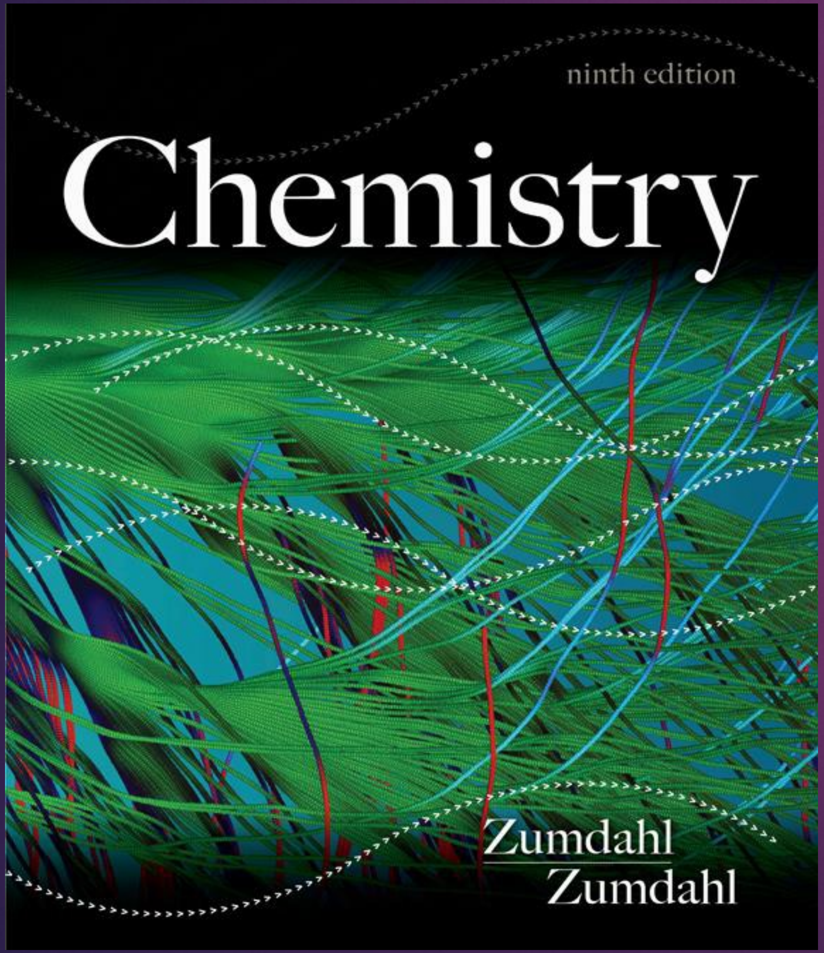
P_{obs} = 316 atm

Ideal pressure P = nRT/V

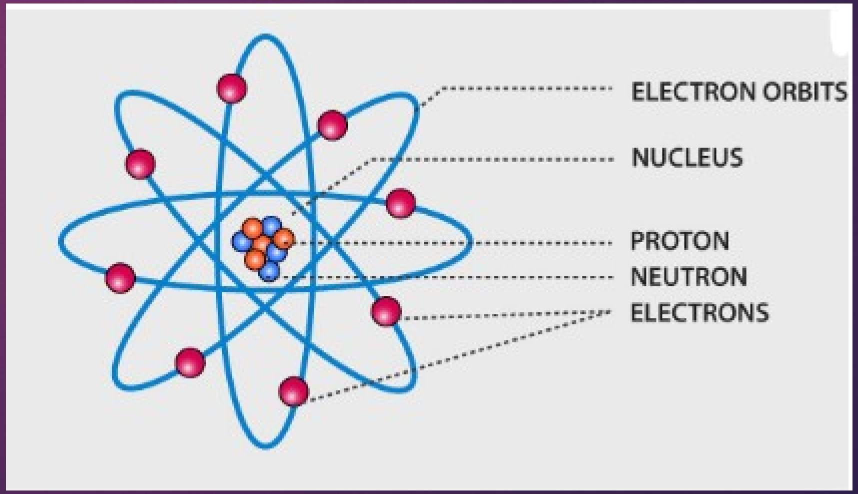
P = 10.0 mol x 0.08206 L.atm.K^{-1}.mol^{-1} x
298.15 K/1.00 L

Pressure = 245 atm

PRACTICE WITH MORE EXAMPLES IN ZUMDHAL AND ZUMDHAL.



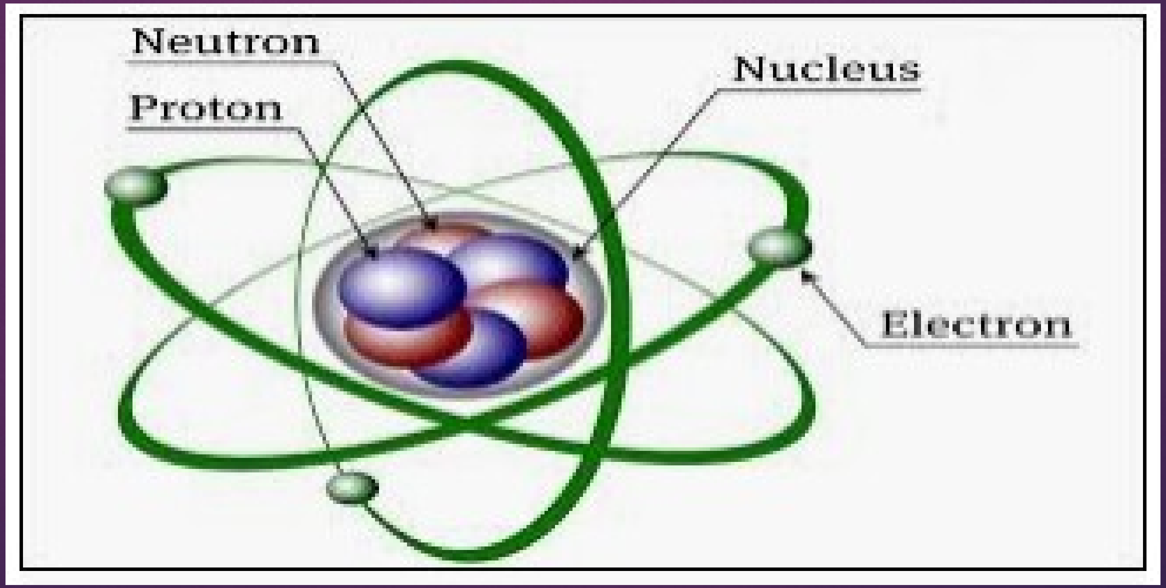
The Atomic Structure



Atomic Structure and Periodicity
Objectives

- What is the evidence of the atom and its structure
- Describe the properties of electromagnetic radiation.
- Explain the relationship between energy, frequency, and wavelength.
- Describe the origin of light emitted by excited atoms and its relationship to atomic structure.
- Describe the evidence for particle-wave duality.
- Define the Bohr atomic model and explain how it is flawed.
- Identify the principles of the quantum mechanical model of the atom.
- Define the four quantum numbers(n, l, ml, and ms) and recognize their relationship to electronic structure.
- Write the electron configuration for atoms and monatomic ions.
- How do we explain the trends in the periodic table
- Explain trends in atom and ion sizes, ionization energy, and chemical properties

Atomic Structure



Atoms

- Everything is made up of atoms!
- Here we will try to understand matter (composed of indivisible **tiny units**) in the most basic manner.**An atom!!..**
- All Matter is Made of Atoms





Dalton’s Atomic Theory (1808)

- John Dalton’s theory of the atom started out as a solid sphere with no charges

- Proposed the atomic theory by investigating atomic weights of atoms

- formulated a **precise definition** of the indivisible building blocks of matter that we call atoms.

John Dalton (1766–1844)

Hypotheses of Dalton’s theory

1. Elements are composed of extremely small particles, called **atoms.**

2. All atoms of a given element are identical, having the same size, mass, & chemical properties.

- ✓ The atoms of one element are different from the atoms of all other elements.

Hypotheses of Dalton’s theory

3. Compounds are composed of atoms of more than one element. Chemical compounds are formed when atoms of different elements combine with each other.

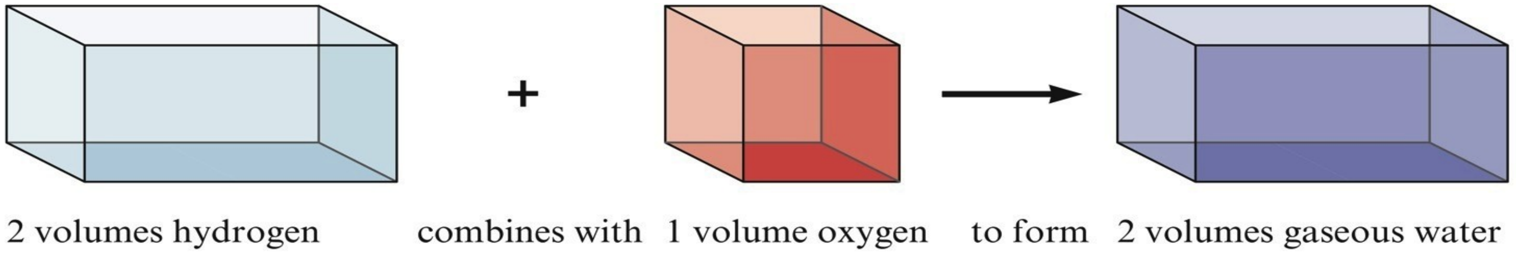
- A given compound always has the same relative numbers and types of atoms.
  - ✓ In any compound, the ratio of the numbers of atoms of any two of the elements present is either an integer or a simple fraction.

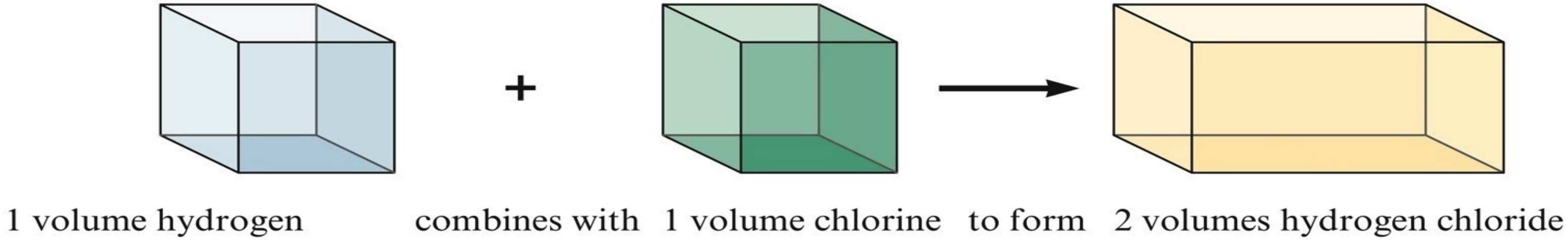
Hypotheses of Dalton's theory

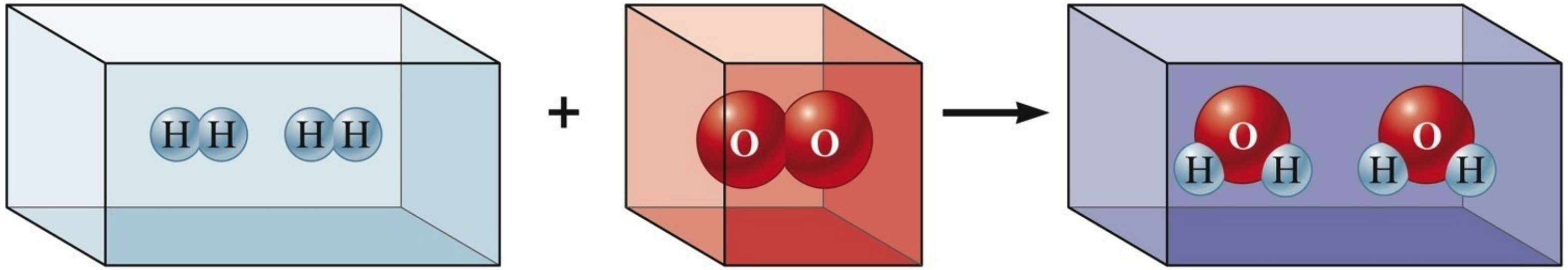
4. A chemical reaction involves only the separation, combination, or rearrangement of atoms; it does not result in their creation or destruction.
   - ✓ *Chemical reactions involve reorganization of the atoms*—changes in the way they are bound together.
   - ✓ The atoms themselves are not changed in a chemical reaction.

Representing Gay—Lussac's Results

Following the Dalton theory



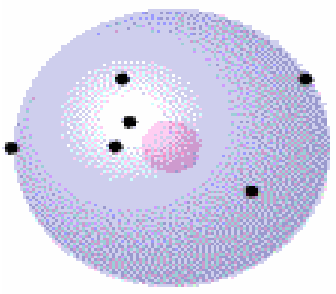


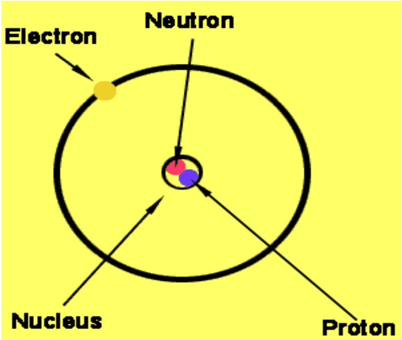


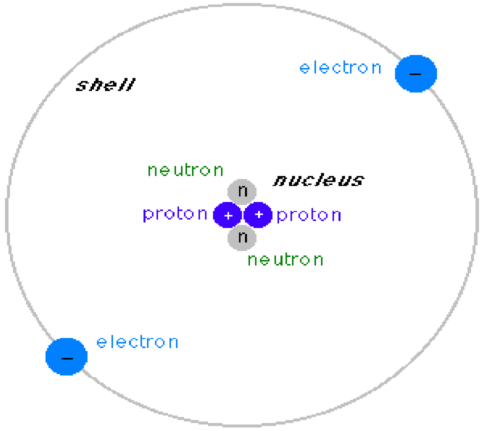
The Modern view of Atomic Structure

Atoms

- The smallest particle of an element that has the properties of the element
- made of 3 basic subatomic particles
- *there are now many more subatomic particles - theoretical physics*

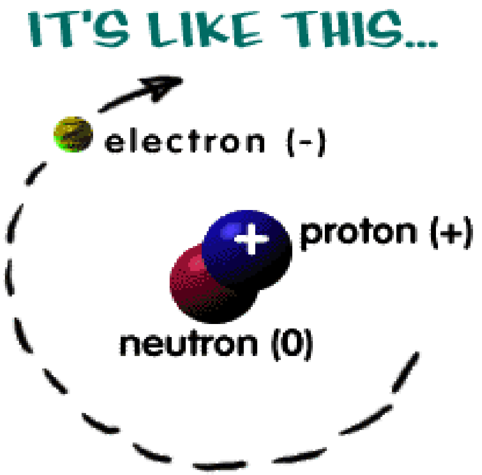






The atom contains:

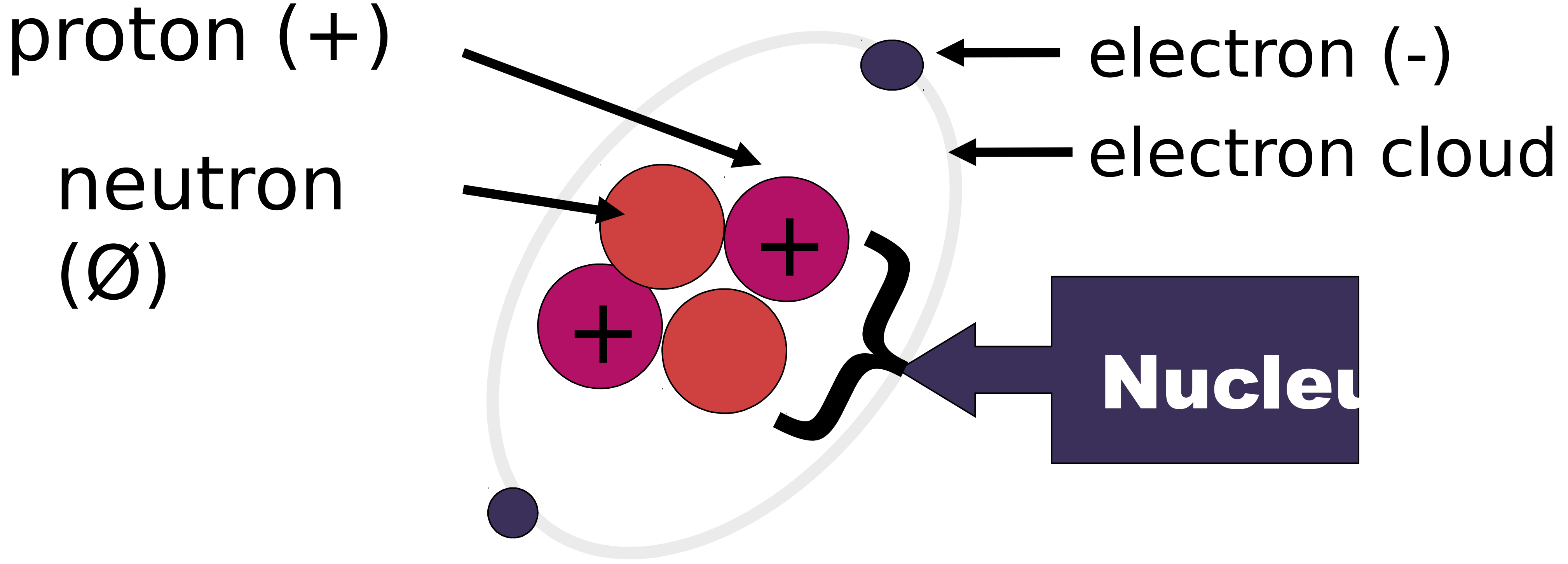
- ***Electrons*** – found outside the nucleus; negatively charged.
- ***Protons*** – found in the nucleus; positive charge equal in magnitude to the electron's negative charge.
- ***Neutrons*** – found in the nucleus; no charge; virtually same mass as a proton.



Subatomic Particles Properties

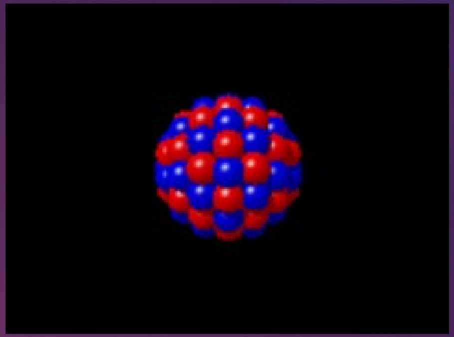
Name	Protons (p or +)	Neutrons (n)	Electrons (e^-)
Charge	+1	No charge	-1
Location	in nucleus	in nucleus	in shells around nucleus
Mass	≈ 1 amu	≈ 1 amu	≈ 2000 x smaller
"Job"	Determines identity of element	Supplies proper mass to hold nucleus together	Determines bonding/ how it reacts
Number	**Atomic #**	**Atomic mass – atomic # = # of neutrons**	**Same as # of protons**

Atom Basic Structure

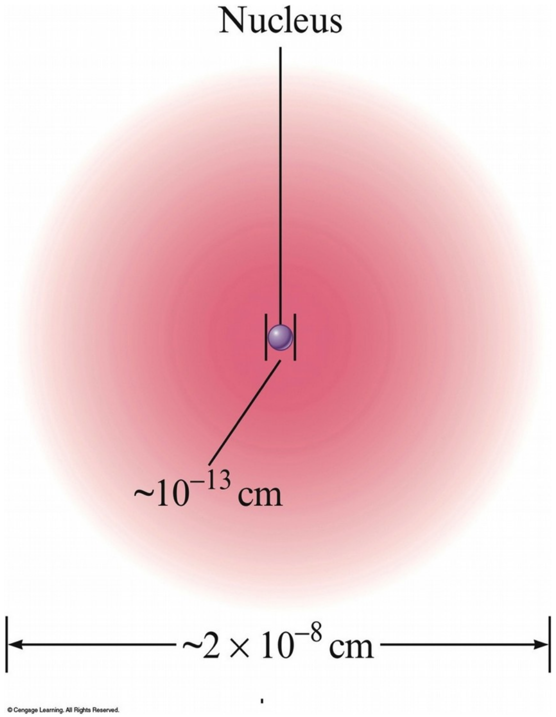


Nucleus: smallest yet heaviest part of the atom

The nucleus:



- Consist of protons & neutrons
- Small compared with the overall size of the atom.
- Extremely dense; accounts for almost all of the atom's mass.
- Every different atom has a characteristic number of protons in the nucleus called the **Atomic Number**.
- The **mass number** is the total number of protons and neutrons in the nucleus of an atom

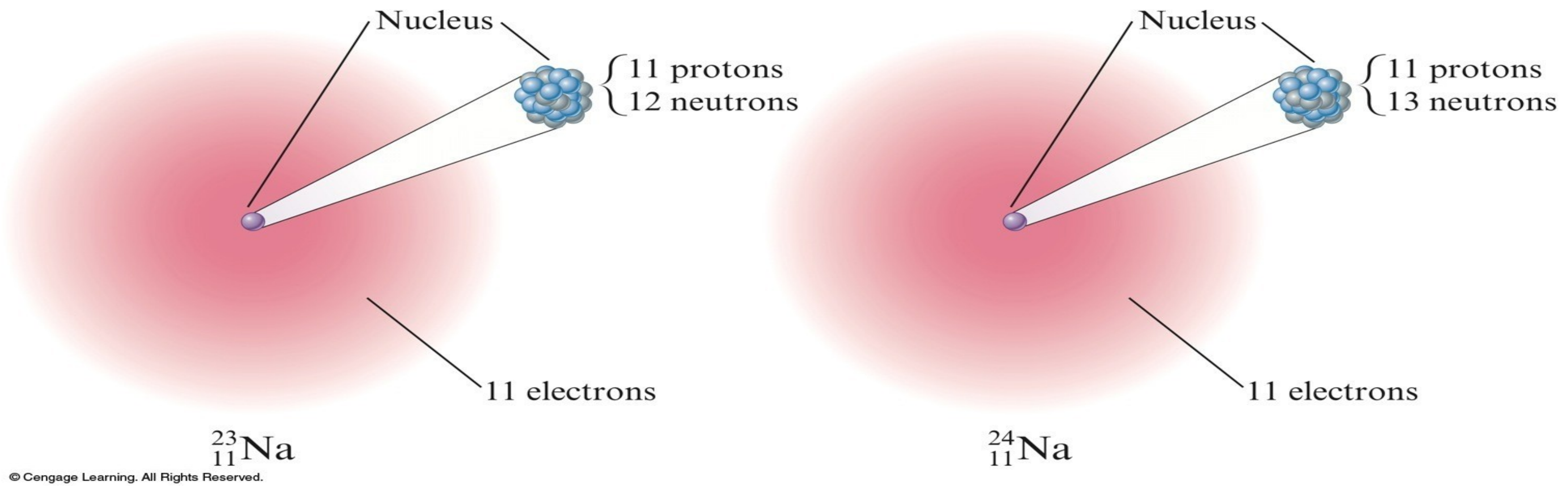


Nuclear Atom Viewed in Cross Section

Isotopes

- Atoms with the same number of protons but different numbers of neutrons.
- Show almost identical chemical properties; chemistry of atom is due to its electrons.
- In nature most elements contain mixtures of isotopes.

Two Isotopes of Sodium



Isotopes are identified by:

Mass number (A)

the number of protons and neutrons in an atom

$$^{A}_{Z}X$$

Atomic number (Z)

the number of protons in an atom

Element

Example: Sodium $^{23}_{11}Na$

EXAMPLE!

A certain isotope X contains 23 protons and 28 neutrons.

- What is the mass number of this isotope?
- Identify the element.

Mass Number = 51

Vanadium

Why atomic structure?

Some questions associated with it

- World consist of many substances made out of elements, about 100 natural occurring elements.

So…

- How is that so few elements can lead to such a diverse number of substances?
- Why does each element have unique physical &chemical properties?

In atomic structure we attempt to answer these questions! !!

Electromagnetic radiation & atomic structure

- In the 1890s many scientists became caught up in the study of **radiation...**
  - the **emission** & transmission of energy **(E)** through space in the form of waves.

- Information gained from this contributed **greatly** to understanding of **atomic structure.**

Electromagnetic radiation & atomic structure

- Much information about the **electronic structure of atoms** comes from observation of the ***action of visible light & atoms on each other.***

- Once it was established that the atom is not indivisible, the scientists made attempts to ***understand the structure of the atom***

Electromagnetic Radiation

Questions to Consider

- Why Different Colored Fireworks?
- Why do we get colors?
- Why do different chemicals give us different colors?

Important points

- Physical & chemical properties of compounds are influenced by the structure of the atoms that they consist of.

- Chemical structure depends, in turn, on how electrons are arranged around atoms & how electrons are shared among atoms in molecules.

Important points

- Properties of compounds & atoms relie on a detailed understanding of the arrangement of electrons

- Arrangement of electrons has been studied by observing how electromagnetic radiation (emr) interacts with atoms.

- To appreciate the interaction, we ought to understand the nature of emr.!

Electromagnetic radiation

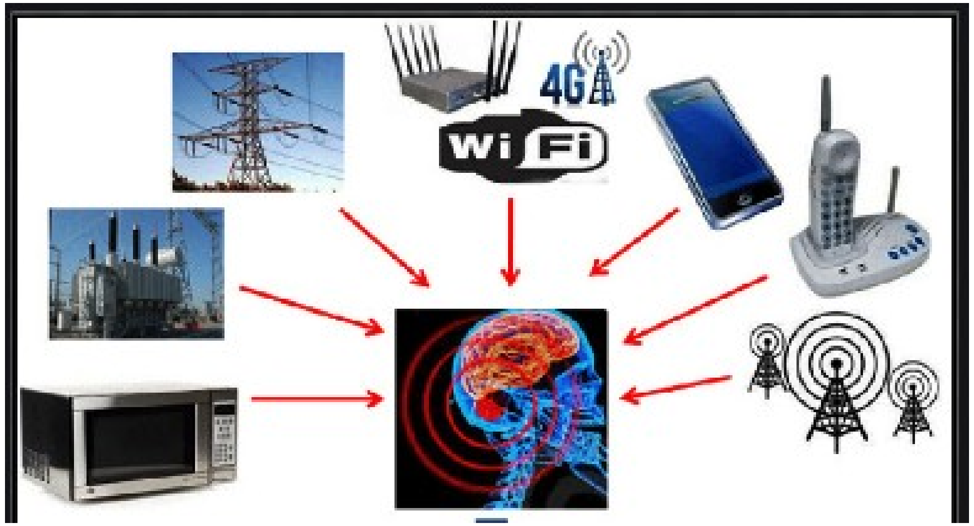
What is EMR?

- Energy that travels through space as waves, is made up of magnetic & electric fields oscillating at right angles to one another.
- type of energy that is commonly known as *light!!*
- *Light is an electromagnetic wave, consisting of oscillations in electric & magnetic fields traveling through space*

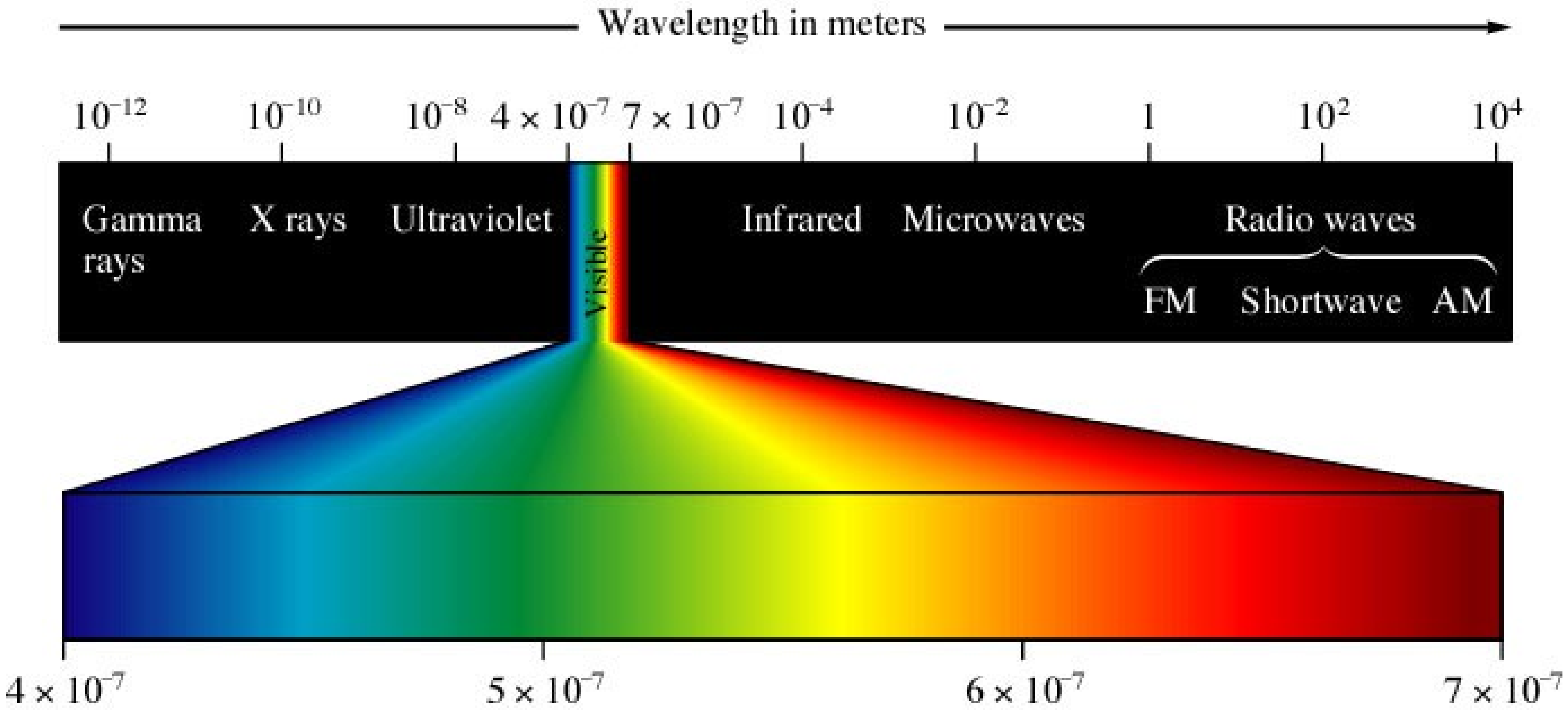
Electromagnetic radiation

EMR is a form of energy that is all around us & takes many forms, such as

- ✓ sunlight,
- ✓ radio waves used by mobile phones,
- ✓ microwaves ovens ,
- ✓ X-rays and gamma rays used in Medicine

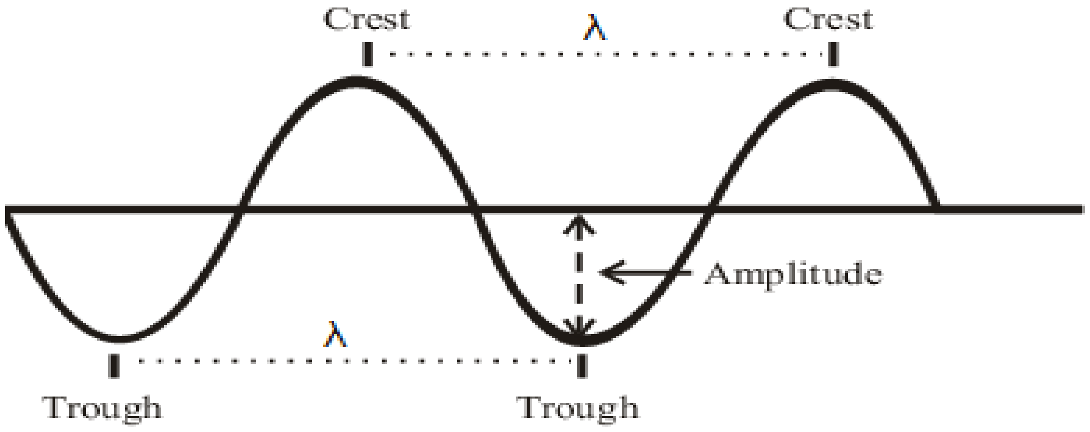


Classification of Electromagnetic Radiation



Waves

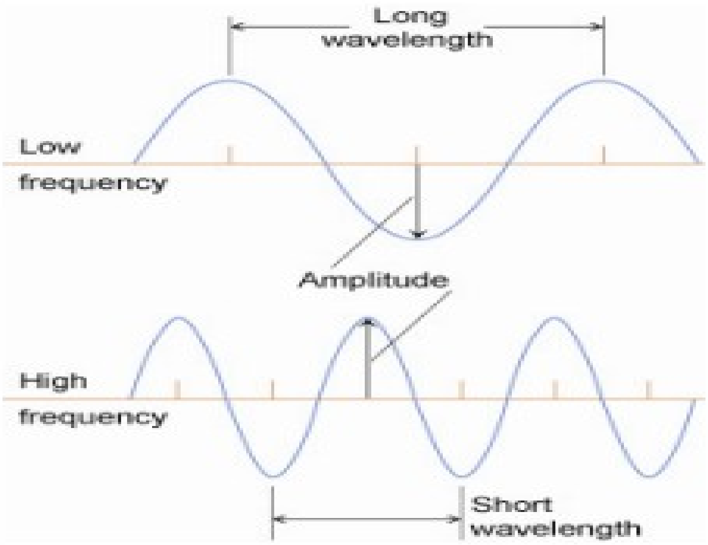
- Radiant energy - *exhibits wavelike characteristics*, travels through space at the speed of light in a vacuum.
- A wave is a continuously repeating change or oscillation in matter or in a physical field.
- A wave consists of repeating units called *cycles*.



Main wave characteristics:

Wavelength (λ) – the distance between two successive crests/peaks (or bottom of two troughs).

Understand the properties of waves.



Wavelength, frequency, and amplitude

Main wave characteristics:

Frequency (υ,nu) – # of crests or troughs that pass through a given point per unit time.

- ✓ has units of time^{-1}, usually per second (s^{-1}) or Hertz.

1Hz=1/s or 1Hz=1 s^{-1}

$\bar{\nu}$:

Amplitude : refers to the maximum height to which the wave oscillates.

- ✓ It equals the height of the crests or depth of the troughs.

Main wave characteristics:

Wave number (ṽ): # of waves per unit length. It is denoted as (nu bar, ṽ)

It is equal to the reciprocal of the wavelength.

- ✓ The SI unit of is m^{-1}. Sometimes expressed as cm^{-1}

Main wave characteristics:

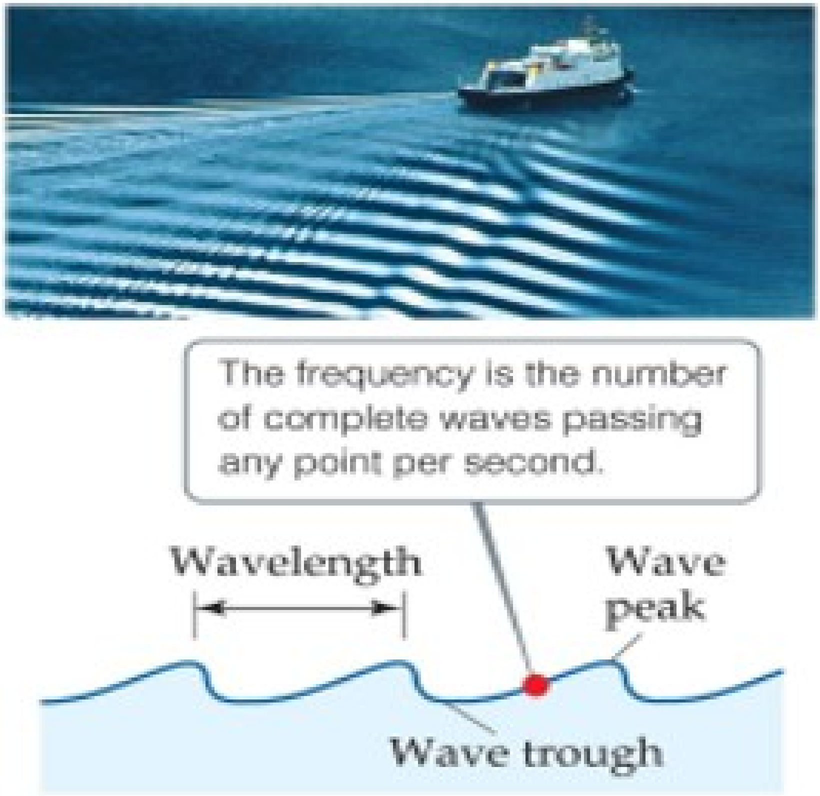
Velocity: it is defined as the linear distance travelled by the wave in 1 sec.

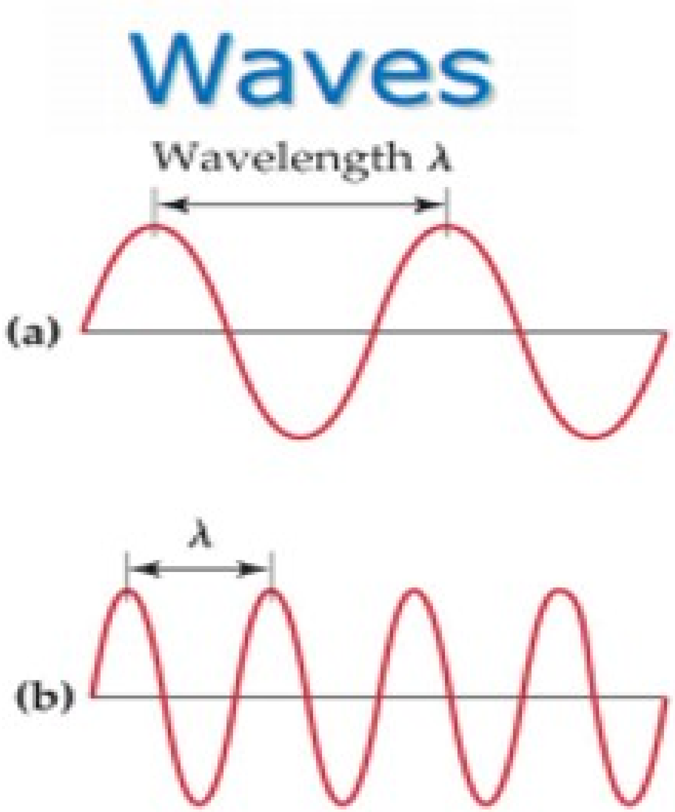
- ✓ The velocity of a radiation depends on the medium.
- ✓ In a vacuum the velocity is equal to 2.998×10^8 m s^{-1}.

Electromagnetic radiation

have 3 primary characteristics:

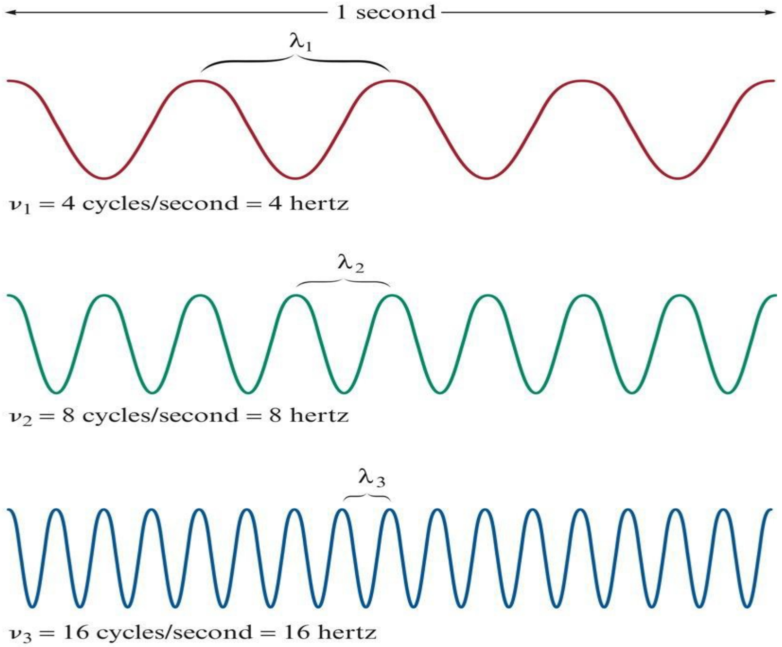
1. **Wavelength (λ)**: distance between two consecutive peaks in a wave.
2. **Frequency (ν)** number of waves (cycles) per second that pass a given point in space.
3. **Speed**: speed of light is 2.9979 x 10^8m/s. We will use 3.00 x10^8 m/s.


The frequency is the number of complete waves passing any point per second.
Wavelength
Wave peak
Wave trough


Waves
Wavelength λ
(a)
λ
(b)

Properties of waves

- **Wave with shortest λ has the highest frequency**
- Wave with longest λ has the lowest frequency,
- *Hence* *λ is inversely proportional to frequency* *(ν)*



Wavelength & frequency can be interconverted & they have an inverse relationship

$$\nu = c/\lambda$$

ν = frequency (s^{-1})

λ = wavelength (m)

c = speed of light (m s^{-1}). All types of electromagnetic radiation travel at the same speed, 2.998 X 108 m/s

- Wavelength is also given in nm (1 nm = 10^{-9} m) and Angstroms (Å) (1 Å = 10^{-10} m).
- The frequency value of s̃1 or 1/s is also called "hertz (Hz)" like KHz on the radio.

EXAMPLE!

When green light is emitted from an oxygen atom it has a wavelength of 558 nm. What is the frequency?

We know,

$\nu = c/\lambda$ where, c = speed of light

= 3.00 x 10^8m/s

λ = wavelength

= 558 nm

(need to convert in m)

$$558\,nm \times \frac{10^{-9}\,m}{1\,nm} = 5.58 \times 10^{-7}\,m$$

$$\nu = \frac{3.00 \times 10^{8}\,m/s}{5.58 \times 10^{-7}\,m}$$

$$= 5.38 \times 10^{14}\,s^{-1}$$

$$= 5.38 \times 10^{14}\,Hz$$

The electromagnetic spectrum (range)

- **Gives the classification of the electromagnetic radiations, it is a list of light arranged in order of <u>increasing wavelength</u>**

- **In a vacuum, light & other EMR can be identified quantitatively by either wavelength or frequency.**

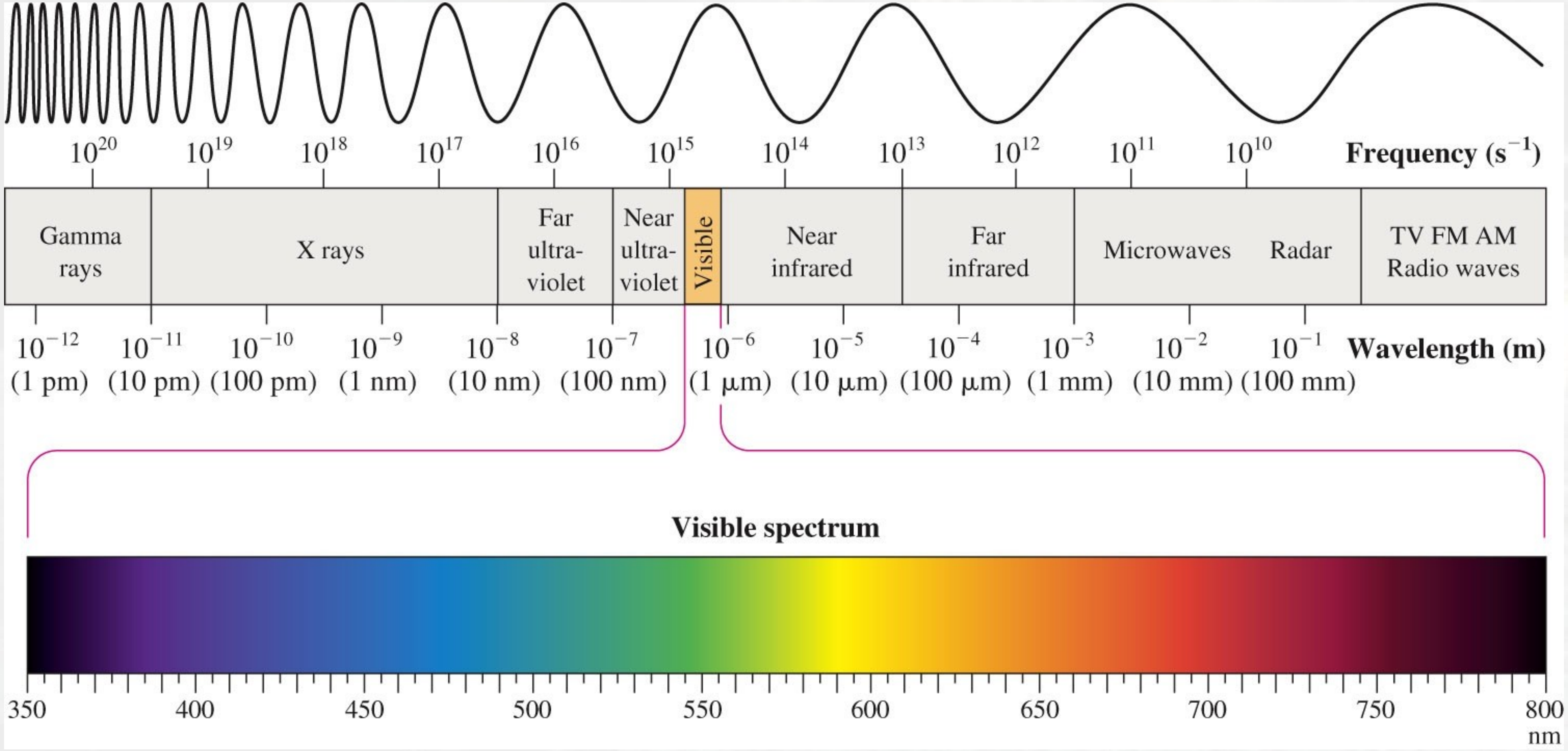
The electromagnetic spectrum (range)

- **Depending on their characteristics (wavelength , frequency & wave number)….**

  … EMR are of many types & constitute what is called as an electromagnetic spectrum.

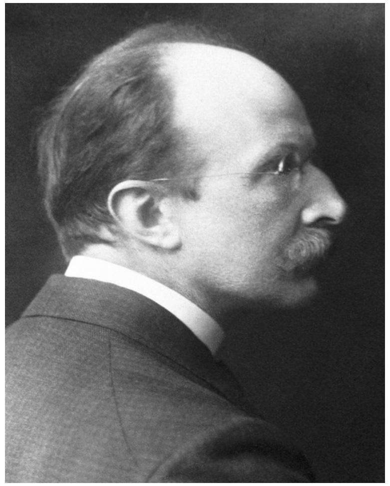
- **The part of the spectrum that we can see is called visible spectrum & is a very small part of the**

The range of frequencies & wavelengths of electromagnetic radiation is called the **electromagnetic spectrum.**



The Nature of Matter
Max Planck

- A German physicist, best known as the ***originator of the quantum theory of energy*** for which he was awarded the Nobel Prize in 1918.
- Contributed significantly to the understanding of atomic & subatomic processes.
- Proposed that energy is radiated in very minute & *discrete quantized amounts or packets rather than in a continuous unbroken wave.*
    - postulated that energy can be gained or lost only in *whole-number multiples* of the quantity ***nhv***, where *h* is a constant called **Planck's constant**



Max Planck
(1858–1947)

Planck’s Constant

- Transfer of energy is quantized, and can only occur in discrete units, called ***quanta***.

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

ΔE = change in energy, in J

h = Planck’s constant, 6.626×10^{-34} J s

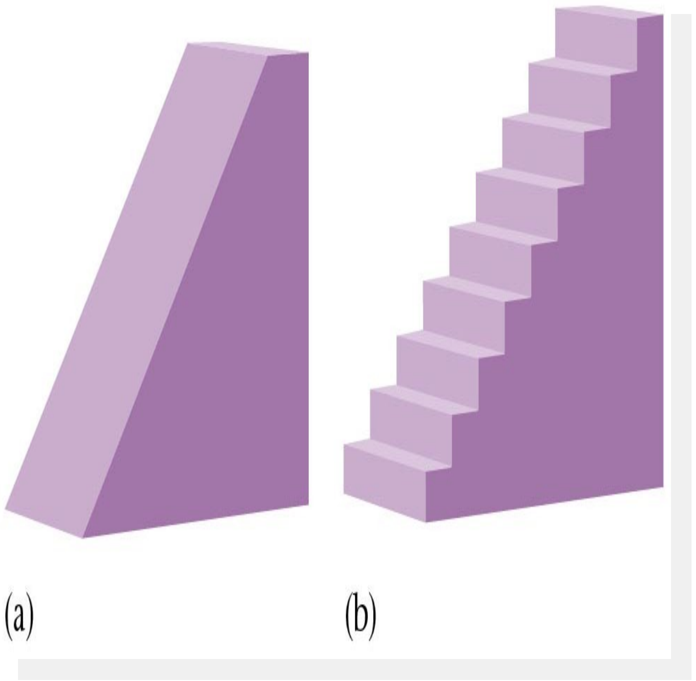
ν = frequency, in s^{-1}

λ = wavelength, in m

- Electromagnetic radiation is a stream of “particles”called ***photons.***

Planck and Quatized Energy

- Found that energy is quantized.
- Matter can only absorb or emit certain quantities of energy.
- Like stairs (b) as opposed to a ramp(b).
- Energy can be gained or lost only in whole number multiples of ***hv*** .
- A system can transfer energy only in whole quanta (or packets
- Energy seems to have particulate properties too.



EMR-The Particulate Nature

- The energy of the quantum can also be related to the wavelength or wave number as:

$$E = h\frac{c}{\lambda} \text{ or } E = hc\bar{v}$$

- Hence, energy of photon can be readily calculated from these equations if we know the frequency, wavelength or wave number.

EXAMPLE!

The Blue color in fireworks is often achieved by heating copper (I) chloride (CuCl) to about 1200^{o}C. Then the compound emits blue light having a wavelength of 450 nm. What is the increment of energy (the quantum) that is emitted at 4.50 x 10^{2} nm by CuCl?

The quantum of energy can be calculated from the equation

$\Delta E = h\nu$

The frequency ν for this case can be calculated as follows:

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^{8} m/s}{4.50 \times 10 m} = 6.66 \times 10^{14} s^{-1}$$

So,

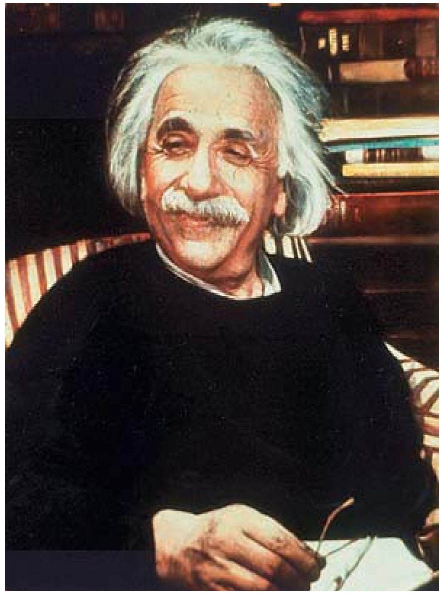
$\Delta E = h\nu = (6.626 \times 10^{-34} J.s)(6.66 \times 10^{14}\ s^{-1})$

$= 4.41 \times 10^{-19} J$

A sample of CuCl emitting light at 450 nm can only lose energy in increments of 4.41 x 10^{-19}J, the size of the quantum in this case.

The Photoelectric effect

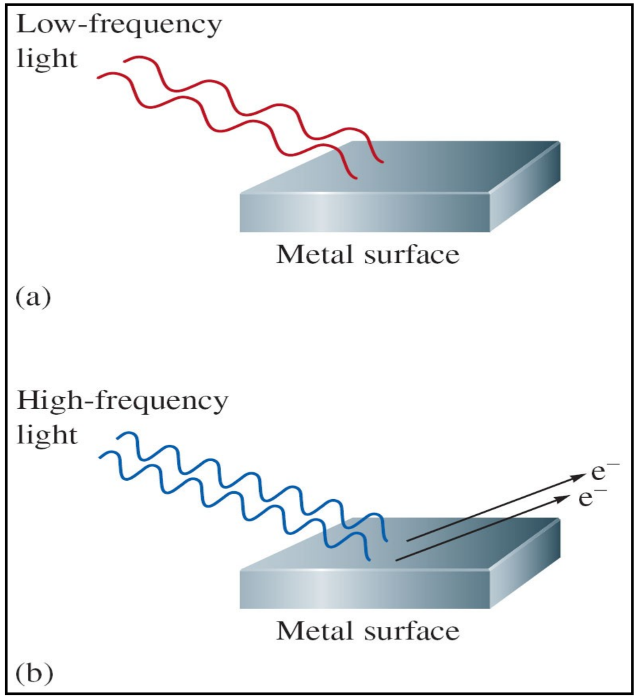
- In 1887, Heinrich Hertz discovered that certain metals emit electrons when light is incident on them.
- This was the first instance of light interacting with matter, so it was very mysterious.
- In 1905 Albert Einstein published a paper which provided the explanation for the effect - light is made up of small particles.
- The **photoelectric effect** is the result of collisions between photons & electrons that knock the electrons out of the metal



Albert Einstein (1879–1955)

The Photoelectric effect

- Surface electrons are bound to metals with a small amount of energy.
- Some of the incident photons enter the surface, collide with atoms of the metal and are totally absorbed.
- They give their Energy to an electron, which, if the absorbed Energy was great enough, the electron break free from the atom.
- Electrons can only leave the surface of the metal if the frequency is above a certain minimum value called the threshold frequency
- Electron emitted are known as **photoelectrons**

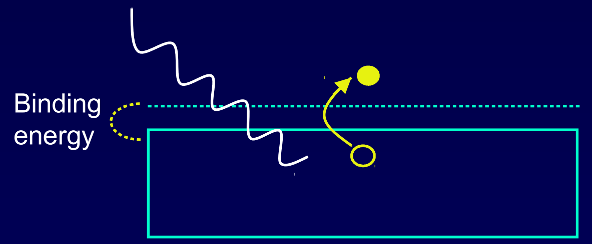


Photoelectric Effect (1)

The energy that bound the electroons to a the metal is called the work function, Φ.

If you shine light on a clean metal surface, electrons can emerge ☾ the light gives the electrons enough energy ($> \Phi$) to escape.

Measure the flow of electrons with an ammeter.



Φ is the minimum energy needed to liberate an electron from the metal.

Φ is defined to be positive.

The Photoelectric effect

Photoelectric effect showed that photons transfer all of their energy or none at all

→ Light is made of individual particles (photons)

Electrons are emitted from a metal's surface when struck by light

K.E. of electron = $h\nu - h\nu_0$ $\qquad K.E = \frac{1}{2} m_e v^2 = h\nu - h\nu_0$

Energy of the photon ($h\nu$)

Energy required to remove the electron from the metal's surface ($h\nu_0$)

If the energy of the photon is less than the threshold $h\nu_0$, electrons are not emitted, no matter how many photons we send. E_0 $(\nu < \nu_0)$

Minimum energy required to remove an electron = $E_0 = h\nu_0$

Energy and Mass

- According to Einstein theory of relativity-Energy has mass; Einstein equation,

  $E = mc^2$

  where, E = energy, m = mass c = speed of light

- After rearrangement of the equation,

$$m = \frac{E}{c^2}$$

Now we can calculate the mass associated with a given quantity of energy, ***Energy has mass***

Wave-Particle Duality

- Einstein suggested that electromagnetic radiation can be viewed as a stream of “particles” called ***photons***. The energy of each photon is given by,

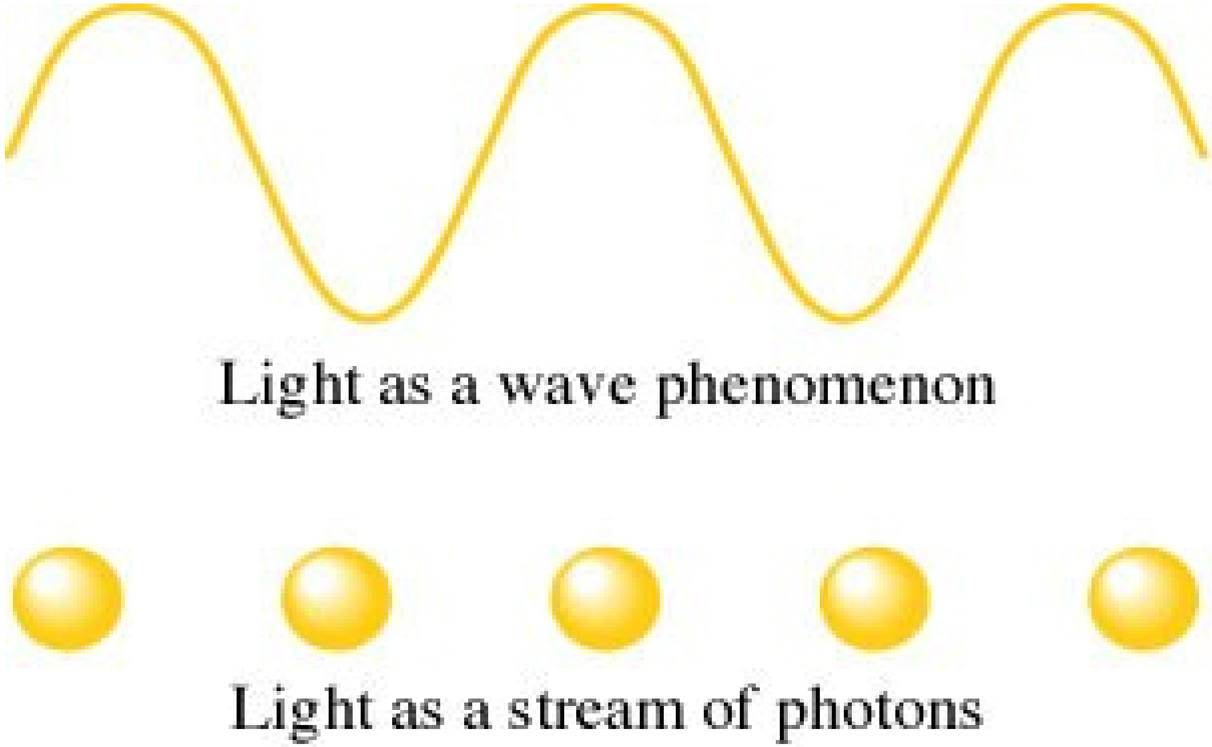
$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

$$m_{photon} = \frac{E}{c^2} = \frac{hc/\lambda}{c^2} = \frac{h}{\lambda c}$$

- It was then Einstein realized that light could not be explained completely as waves but had to have particle properties. This is called the ***dual nature of light***.

Wave-Particle Duality

Dual nature of light:
Electromagnetic radiation (& all matter) exhibits wave properties & particulate properties.



Electromagnetic Radiation

Photoelectric Effect

Summary of Results:

- Electron energy depends on frequency, not intensity.
- Electrons are not ejected for frequencies below f_0.
- Electrons have a probability to be emitted immediately.

Conclusions:

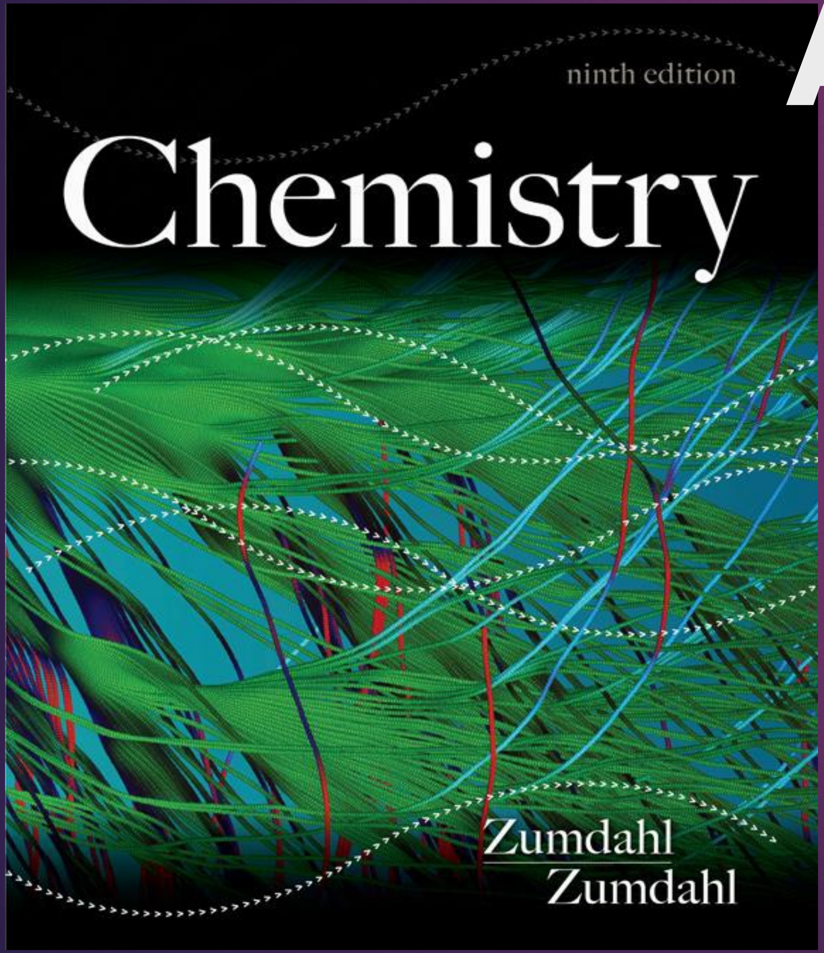
- Light arrives in “packets” of energy (photons).
- $E_{photon} = hf$ ← We will see that this is valid for all objects. It is the fundamental QM connection between an object’s wave and particle properties.
- Increasing the power increases # photons, not the photon energy. Each photon ejects (at most) one electron from the metal.

Recall: For EM waves, frequency and wavelength are related by: $f = c/\lambda$.
Therefore: $E_{photon} = hc/\lambda$

Beware: This is only valid for EM waves, as evidenced by the fact that the speed is c.

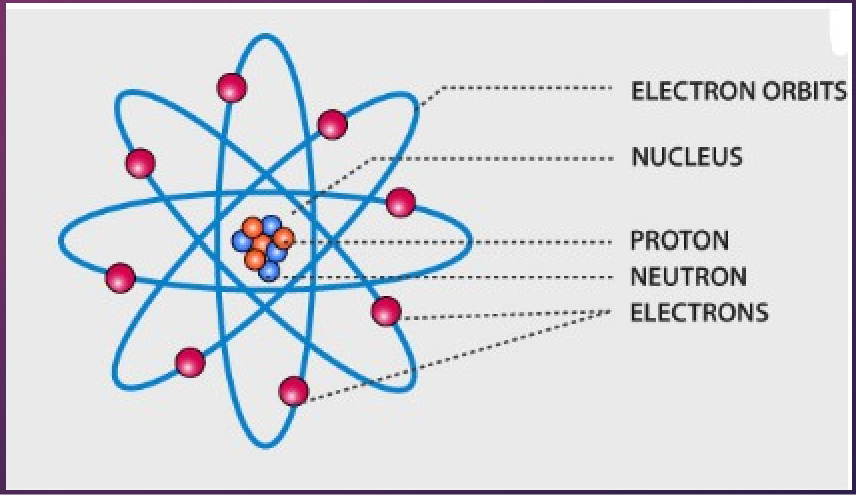
Summary of the work of Planck & Einstein as follows:

- **Energy is quantized. It can occur only in discrete units called quanta.**
- **EMR, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well. This phenomenon is sometimes referred to as the *dual nature of light.***
- **So, light could under some conditions behave like a particle and other conditions behave as a wave.**



Atomic Structure

continues

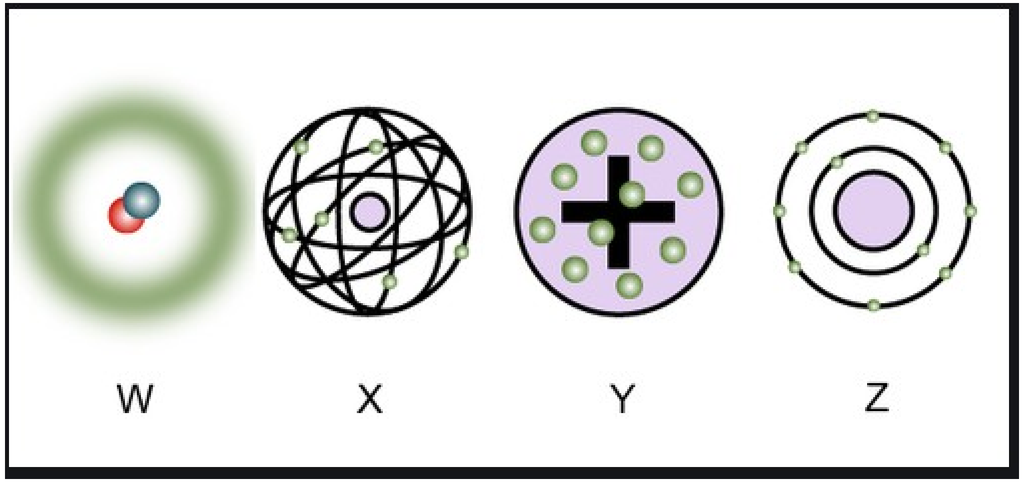


Earlier models of an atom

- Once it was established that the atom is not indivisible, the scientists made attempts to *understand the structure of the atom.*

- A # of models were proposed for the internal structure of the atom.

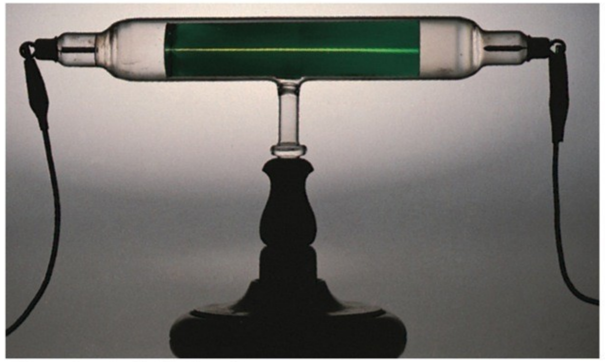
- *The first attempt to describe the structure of atom in terms of a model was made by J.J Thomson.*



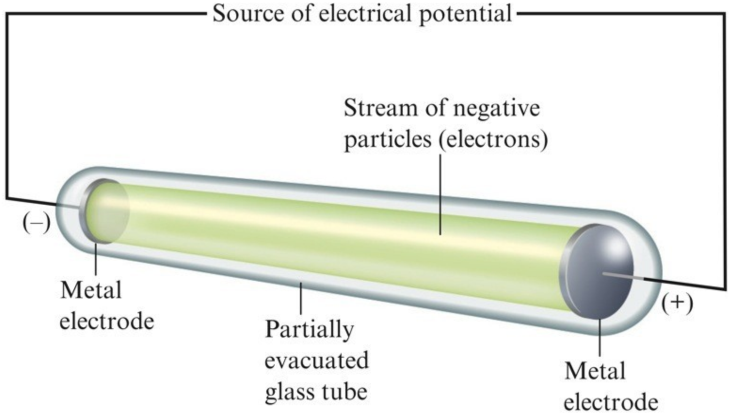
Early Experiments to Characterise the Atom
J. J. Thomson (1898—1903) Atomic Model

- Postulated the existence of negatively charged particles, that we now call electrons, using **cathode-ray tubes**.
- Determined the charge-to-mass ratio of an electron.
- The atom must also contain positive particles that balance exactly the negati charge carried by electrons….**rendering the atom neutral!**

Cathode-Ray Tube



Richard Megna/Fundamental Photographs © Cengage Learning



Joseph John Thomson won the Nobel Prize in 1906 for the discovery of the electron.

Thomson atomic model

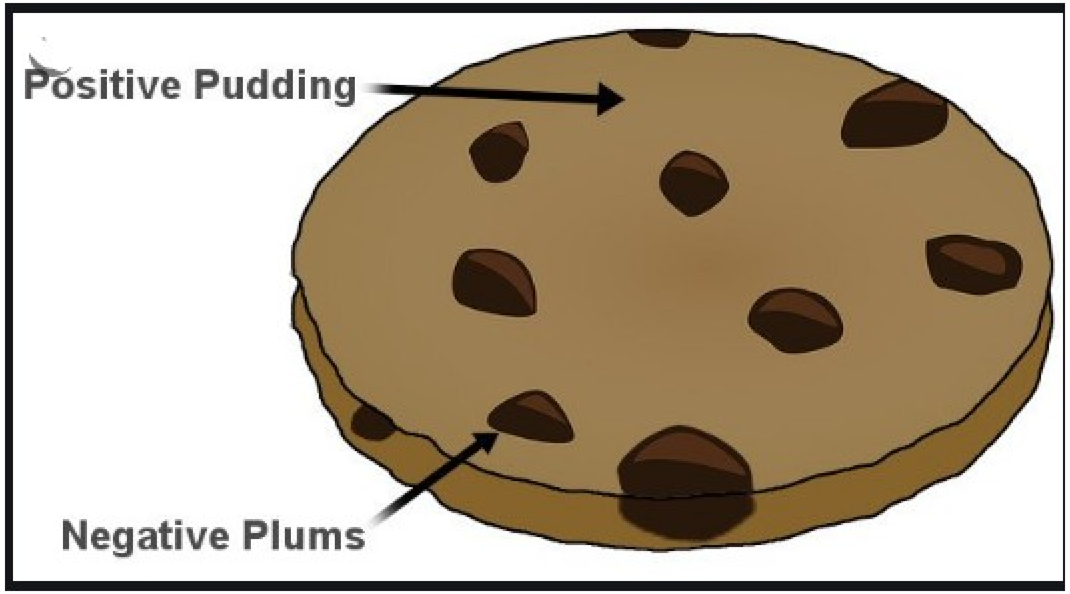
- He discovered the e in *1897*, proposed the ***Plum Pudding Model of the Atom*** *in 1904.*

- *The model was proposed* **before the discovery of the atomic nucleus** in order to include the electron in the atomic model.

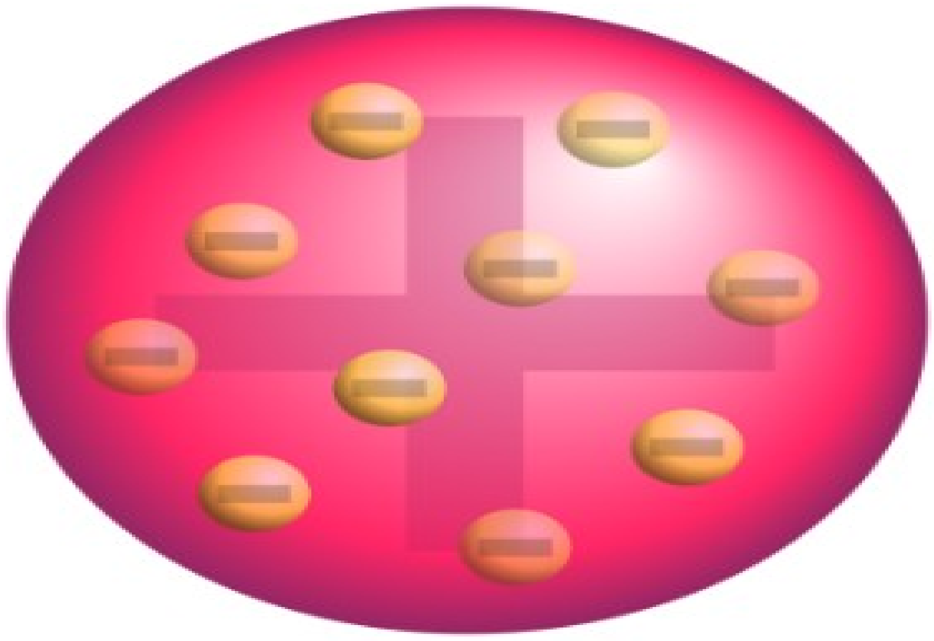
- Proposed that atoms can be considered as a large positively charged body with a # of small negatively charged electrons scattered throughout it.

The Plum Pudding Model

- **it envisaged the atom as a sphere of positive charge, with electrons dotted throughout like plums in a pudding.**



Plum pudding model of the atom



Plum pudding model of the atom: A schematic presentation of the plum pudding model of the atom; in Thomson's mathematical model the "corpuscles" (in modern language, electrons) were arranged non-randomly, in rotating rings.

Thomson atomic model

- Though several alternative models were advanced in the 1900s…
- Thomson held that atoms are uniform spheres of postively charged matter in which electrons are embedded.
- Abandoned (1911) on both theoretical & experimental grounds in favour of the

Robert Millikan (1909)

- Performed experiments involving charged oil drops.
- Determined the magnitude of the charge on a single electron.
- Calculated the mass of the electron

  (9.11×10^{-31} kg).

Henri Becquerel (1896)

- Discovered radioactivity by observing the spontaneous emission of radiation by uranium.
- Three types of radioactive emission exist:
  - Gamma rays (ϒ) – high energy light
  - Beta particles (β) – a high speed electron
  - Alpha particles (α) – a particle with a 2+ charge

Rutherford atomic model

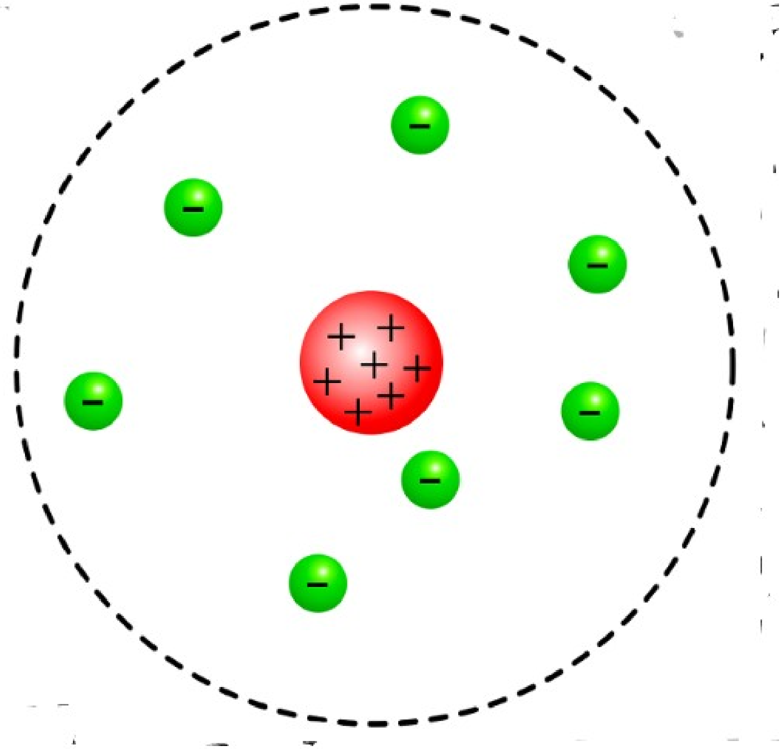
- AKA *nuclear atom* or *planetary model of the atom.*

- is description of the structure of atoms proposed (1911) by the New Zealand-born physicist Ernest Rutherford.

- model described the atom as a tiny, dense, +vely charged core called a nucleus.

Rutherford atomic model

- The model shows an atom as an **empty space** where electrons orbit a positively charged fixed nucleus in a predictable & set paths.

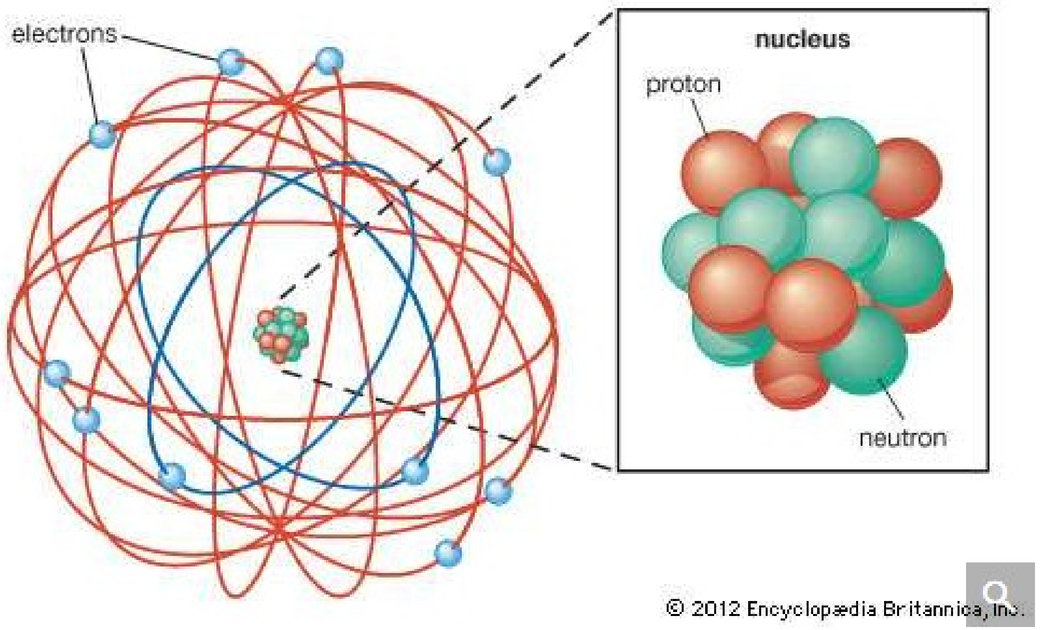


- He researched extensively on radioactivity..
  - & won the Nobel Prize for his discoveries in 1908.

- It was then that he started developing the model of the atom.

Rutherford atomic model

- **Mass of an atom is concentrated in the nucleus.**
- **Around the nucleus are light negative constituents, called electrons,.**
- **Electrons circulate at some distance, much like planets revolving around the Sun.**

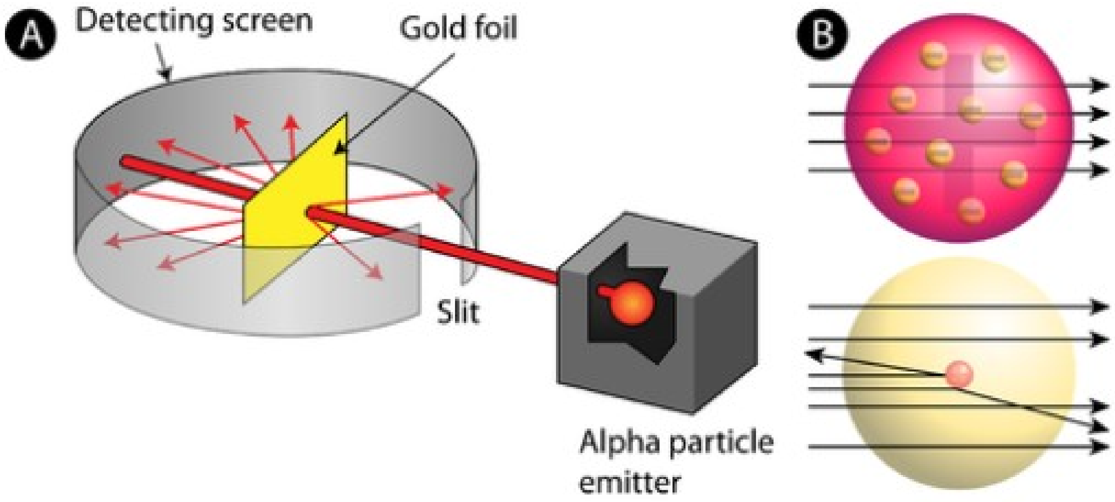


Rutherford’s Experiment

- Performed an experiment called ‘*Gold Foil Experiment’ or ‘α- ray scattering experiment*’ to test the structure of an atom as proposed by Thomson.
- These results led Rutherford to conclude that:

- ✓ The atom contained some dense & positively charged region located at the center of the atom that he called as *nucleus.*

Rutherford atomic model



(A) A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles.

(B) According to the plum pudding model (top) all of the alpha particles should have passed through the gold foil with little or no deflection.

Rutherford found that a small percentage of alpha particles were deflected at large angles, which could be explained by an atom with a very small, dense, positively-charged nucleus at its center (bottom).

Rutherford's Atomic Model

- Rutherford proposed that an atom has a positively charged core (nucleus) surrounded by the negative electrons.

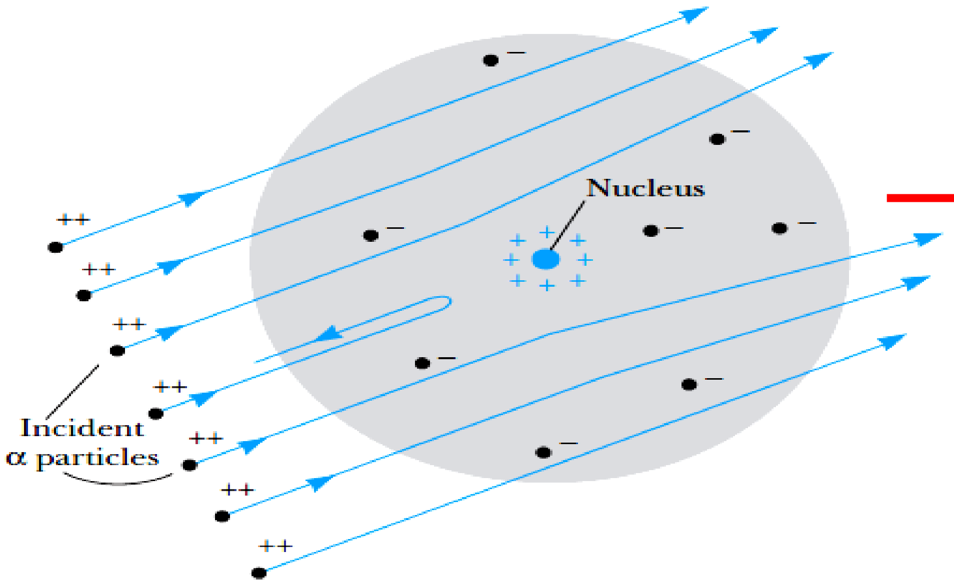
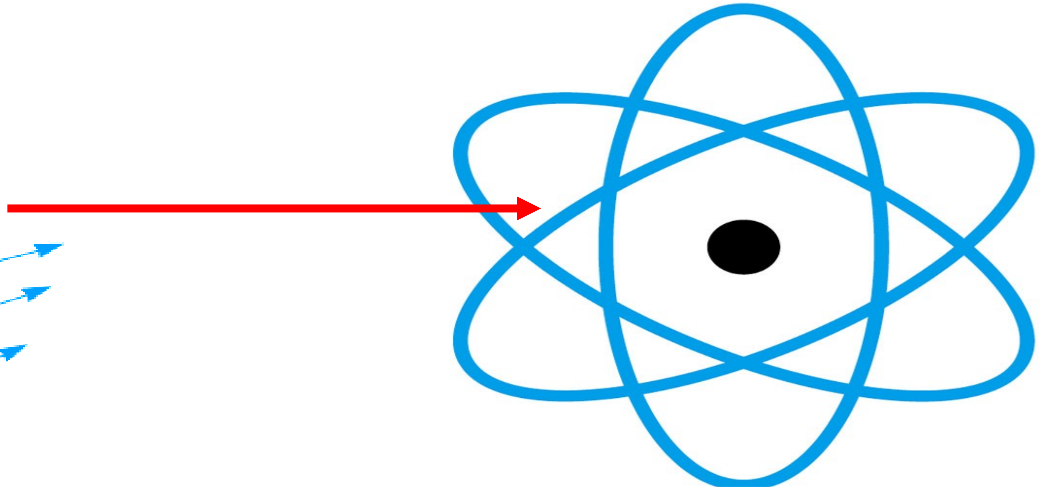


Figure 4.11 Scattering of α particles by a dense, positively charged nucleus.



Something 3-D where there is a particle nucleus and particle electrons in certain orbits, not correct

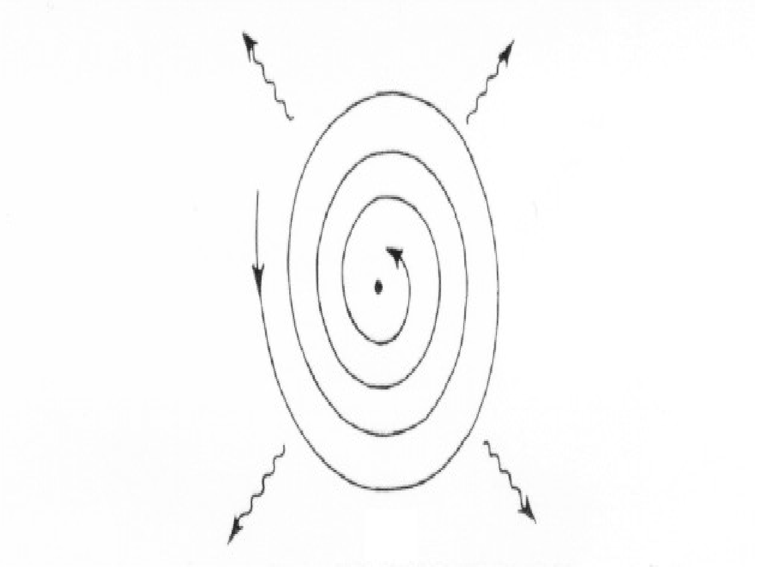
Rutherford's conclusion

- All the positive charge of the atom & most of its mass was contained in the nucleus.
- Nucleus occupies a very small volume relative to the volume of the atom.
- The rest of the atom must be empty space which contains the much smaller & -vely charged e *undergoing continuous random acceleration*.

Rutherford's Experiment

Main problem with this theory:

- According to the Maxwell's theory of electromagnetic radiation, a charged particle undergoing acceleration would continuously emit radiation and lose energy.
- Since the electron in the atom is also a charged particle & is under acceleration, it is expected to continuously lose energy.
- As a consequence, the e moving around the nucleus would approach the nucleus by a spiral path & the atom would collapse.



According to classical physics, an electron in orbit around an atomic nucleus should emit electronmagnetic radiation (photons) continuously, because it is continually accelerating in a curved path. The resulting loss of energy implies that the electron should spiral into the nucleus in a very short time (i.e. atoms can not exist).

Rutherford’s Experiment

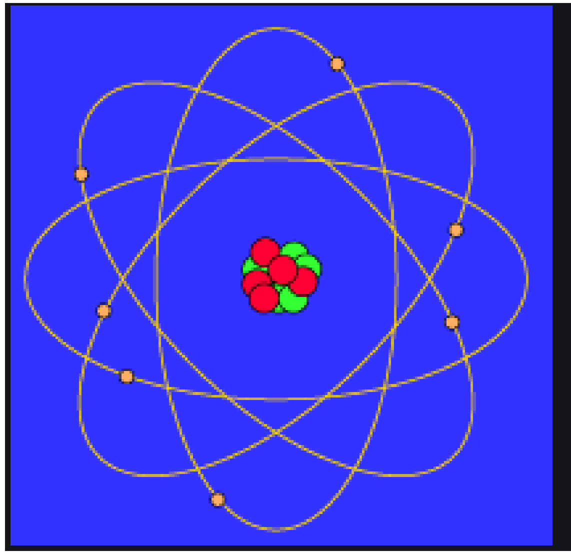
- Since the atom doesn't’ collapse, the Rutherford’s model *failed to explain the stability of the atom.*
- Rutherford’s model proved to be an important step towards a full understanding of the atom.
- However, it did not completely address the nature of the electrons & the way in which they occupied the vast space around the nucleus
- The next attempt to suggest a model for atom was made by Neils Bohr- **a student of Rutherford.!!**

Bohr's model of an atom

- **Bohr model**, description of the structure of atoms, especially that of hydrogen, proposed (1913).

- In this model *e* moves around the nucleus in **circular paths-**..

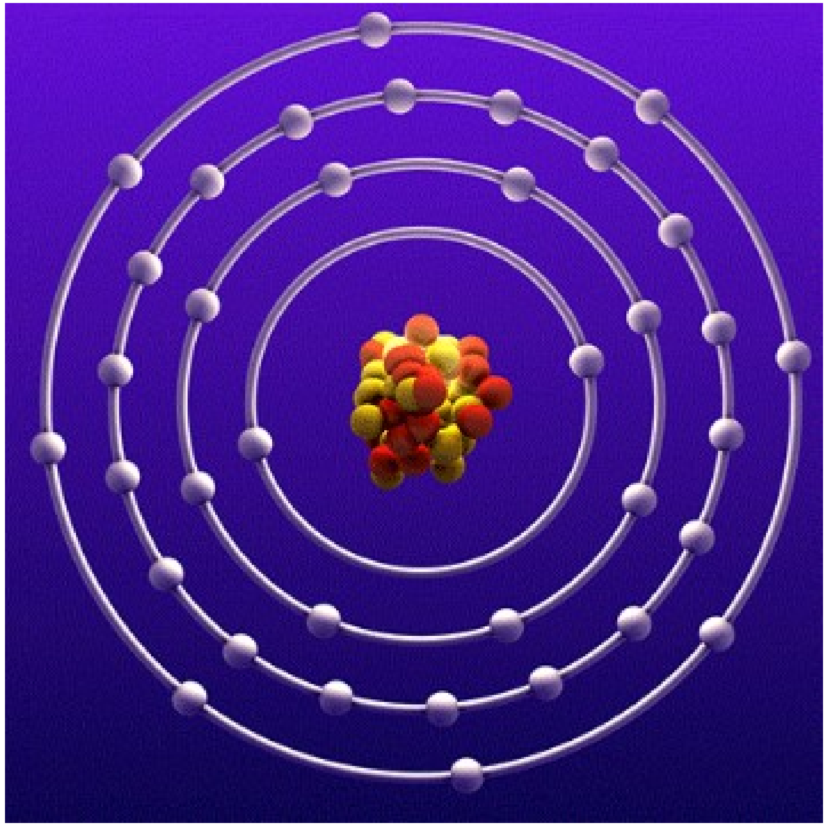
- **Model similar in structure to the Solar System but with attraction provided by electrostatic forces rather than gravity.**



Bohr’s model of an atom

- He **modified** the Rutherford model by requiring that the electrons move in *orbits of fixed size & energy i.e they are quantized.*

- When something is quantized, it means that only specific values are allowed.



Bohr model

- **He explained why the e isn't pulled into the nucleus (stability of an atom) & why H atom only** *emits certain wavelength of light.*

- Niels Bohr used Planck's theories to develop a *new* & *more accurate model of the atom.*

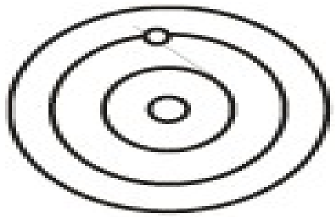
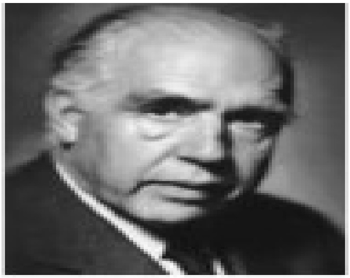


Fig. 3.10: *Bohr's model*



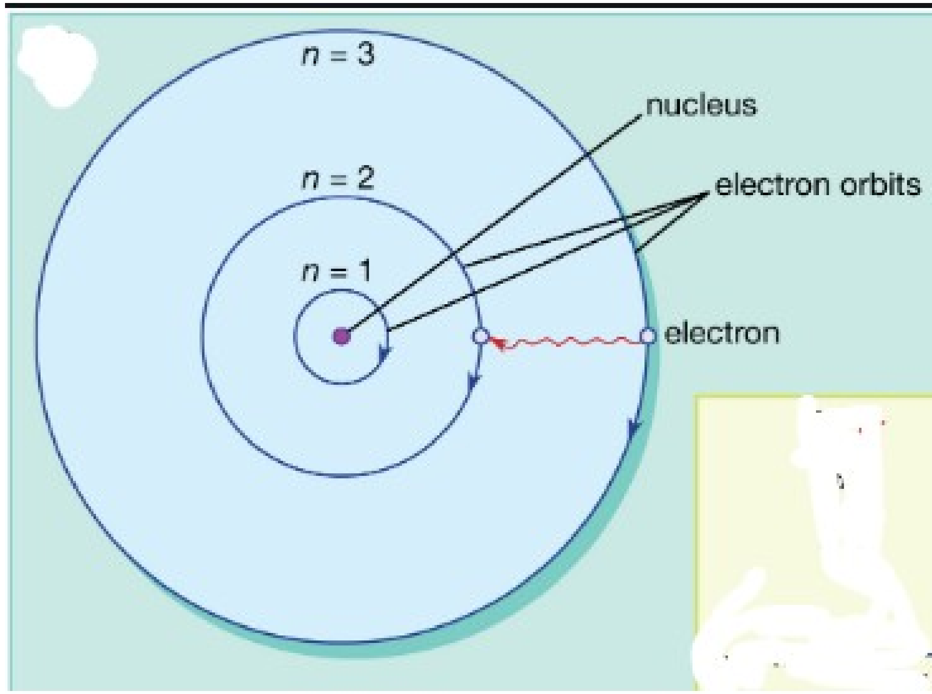
Bohr won the Nobel Prize in Physics in 1922 for his work.

Bohr model

- The Bohr model is a relatively primitive model of the H atom, compared to the *valence shell atom*.
- However, because of its simplicity, &its correct results for selected systems,..
- … the Bohr model still commonly taught to introduce students to quantum mechanics or energy level diagrams before moving on to the more accurate, but more complex, valence shell atom!!

Bohr model

- In order to explain the **stability of an atom**, Neils Bohr gave a new arrangement of electrons in the atom.
- According to him, e could revolve around the nucleus in only '*certain orbits*' (*energy levels*).
- each orbit has a different radius.!!

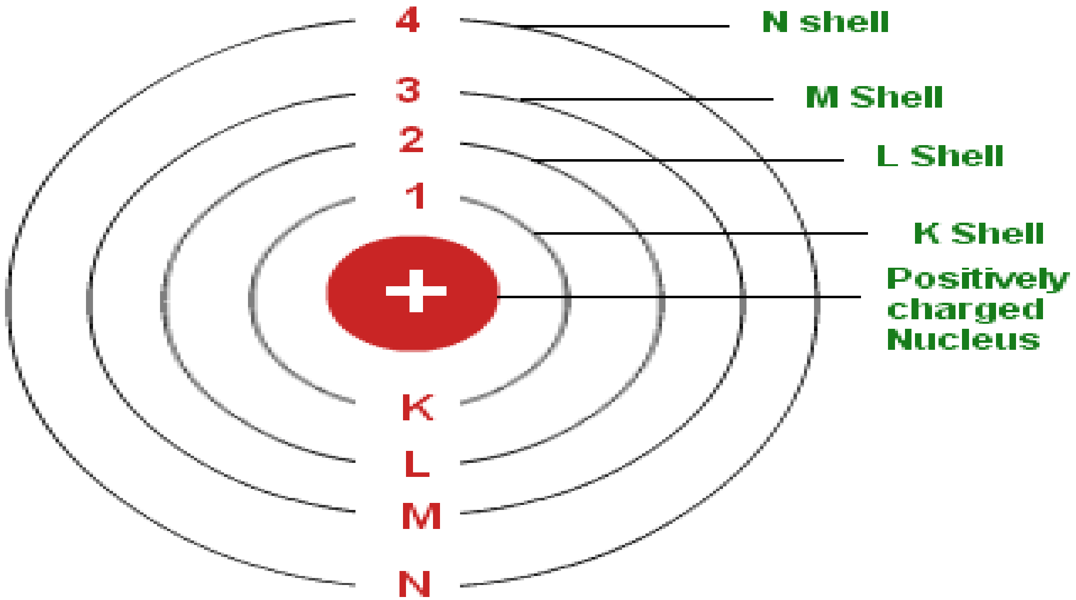


Bohr model

- The *fixed circular* paths are called *energy levels or shells* or orbits or stationary orbits.

- The energy levels are represented in 2 ways: either by the numbers 1, 2, 3, 4, 5 & 6 or by letters K, L, M, N, O & P.

Bohr model



Arrangement of energy levels around the nucleus

- *can show how many e can be present in each electron shell or orbit.!!*

Bohr model

- The energy levels are counted from center outwards.
- Each energy level is associated with a *fixed amount of energy.*
- The shell nearest to the nucleus has minimum energy & the shell farthest from the nucleus has maximum energy.

The Bohr model

- *Niels Bohr was coupling the Rutherford postulation & the Max Planck quantum theory,..*
- … proposed that the atom consists of a +vely charged nucleus of protons & neutrons..
- …. surrounded by -vely charged e traveling in discrete orbits at a fixed distance from the nucleus.
- An e has a discrete or specific quantity of energy (E) which is called as quantum.

Postulates of the Bohr atomic model

- Bohr's atomic model is built upon a set of postulates, which are as follows (Salient features of Bohr's atomic model):

1. The electrons move in definite circular paths around the nucleus.

- ✓ called these circular paths as orbits & postulated that as long as the e is in a given orbit its energy does not change (or energy remains fixed).
- ✓ These orbits were therefore referred to as stationary orbits or stationary states or non radiating orbits.

Postulates of the Bohr atomic model

- ✓ Electrons revolve around the nucleus in stable orbits without emission of radiant energy.
- ✓ Each orbit has a definite E & is called E shell or E level.
- ✓ Each orbit has a certain energy associated with it i.e., only certain values of energy are possible.
- ✓ Based on this, the energy of an e is said to be **quantized.**

Postulates of the Bohr atomic model

2. The electron can change its orbit by ***absorbing or releasing energy***.

- ✓ An e at a lower (initial) state of energy, E_i can go to a (final) higher state of energy, E_f by absorbing a single photon of energy given by:

$$E = h\nu = E_f - E_i$$

$$\Delta E = E_{final\ state} - E_{initial\ state}$$

Postulates of the Bohr atomic model

- Similarly, when an e changes its orbit from a higher initial state of energy E_i to a lower final state of energy E_f, a single photon of energy hν is released.
- This is called *Bohr's frequency condition*

Fig. 3.11 : *Absorption and emission of photon causes the electron to change its energy level.*

Postulates of the Bohr atomic model

- The E of an e changes only when it moves from one orbit to another. !!

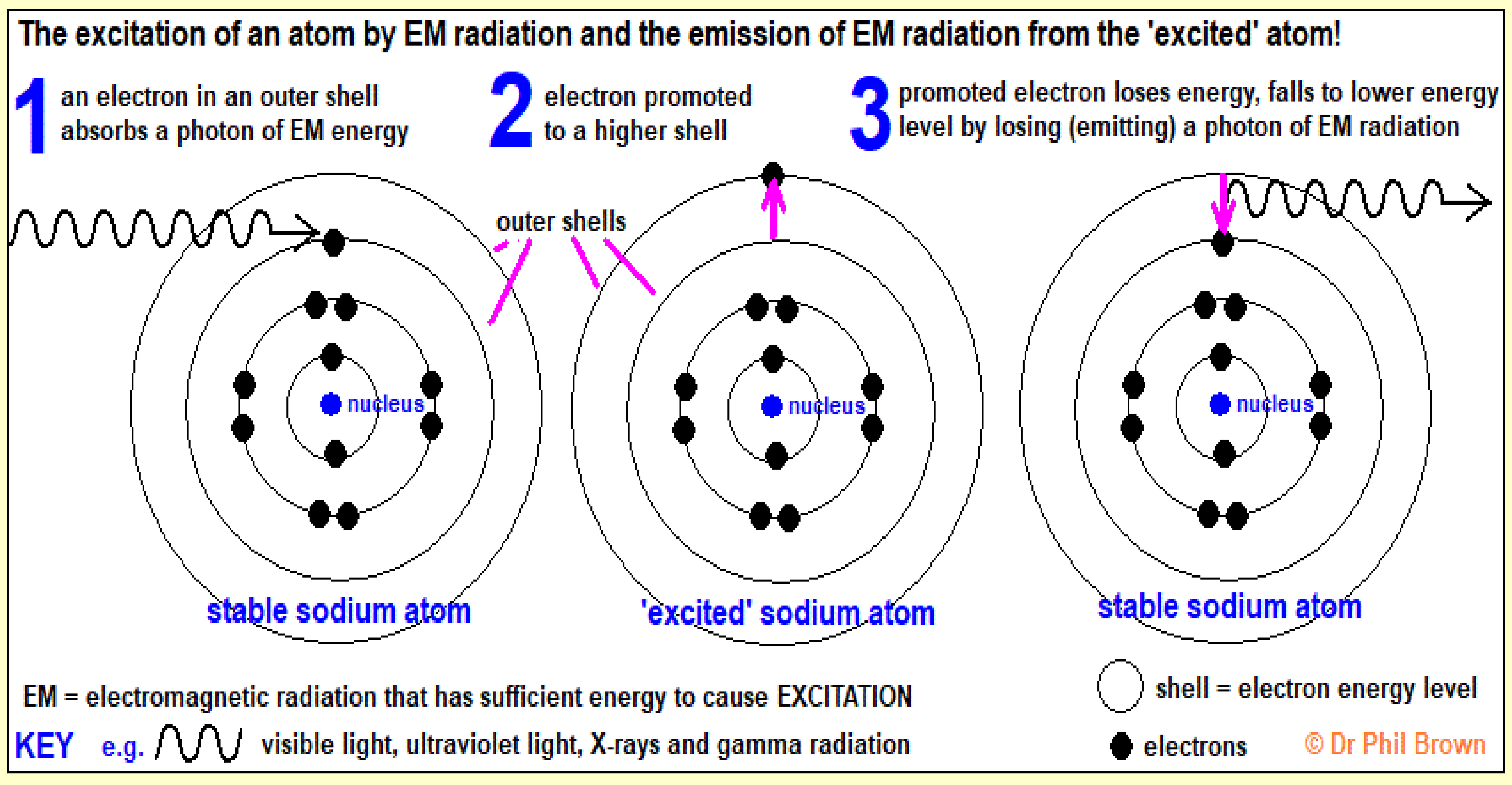
- An electronic transition from an inner orbit to outer orbit involves *absorption of energy*.

- Similarly, when an e jumps from an outer orbit to inner orbit it releases energy, which is equal to the difference between the two energy levels.

Postulates of the Bohr atomic model

- **Ground State**: The lowest possible energy state for an atom…No e has moved to a higher energy level.

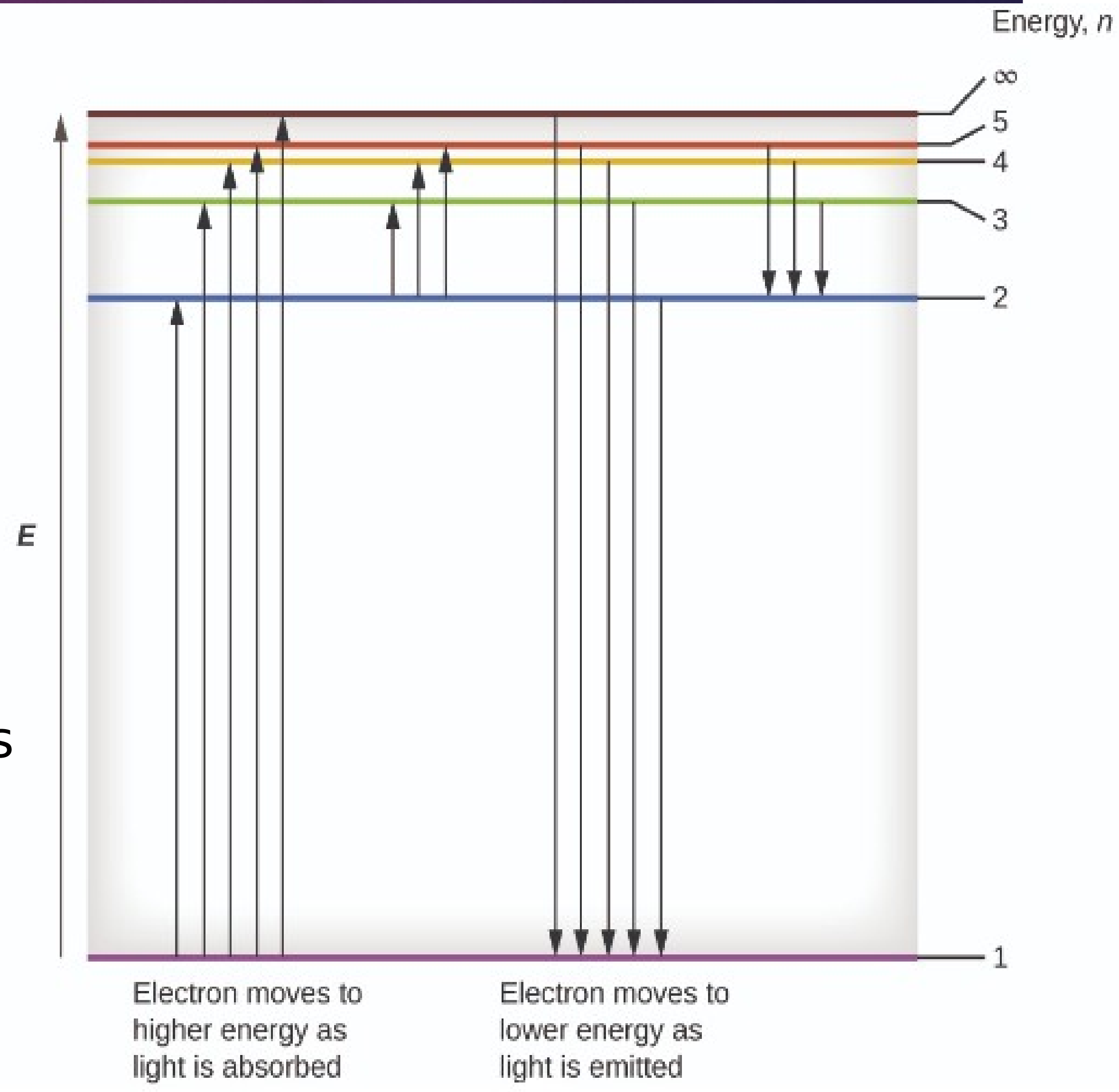
- When in a higher level it is in an **Excited state…can only occur if atom is exposed to Energy.!!**



Electronic Transitions in the Bohr Model for the Hydrogen Atom

- **An Energy-Level Diagram for Electronic Transiti**

  - The horizontal lines show the **relative E** of orbits in the Bohr model of the H atom.
  - The vertical arrows depict the E of photons absorbed (left) or emitted (right) as electrons move between these orbits.



Postulates of the Bohr atomic model

3. The different energy levels are denoted by integers such as n=1 or n=2 or n=3 & so on.

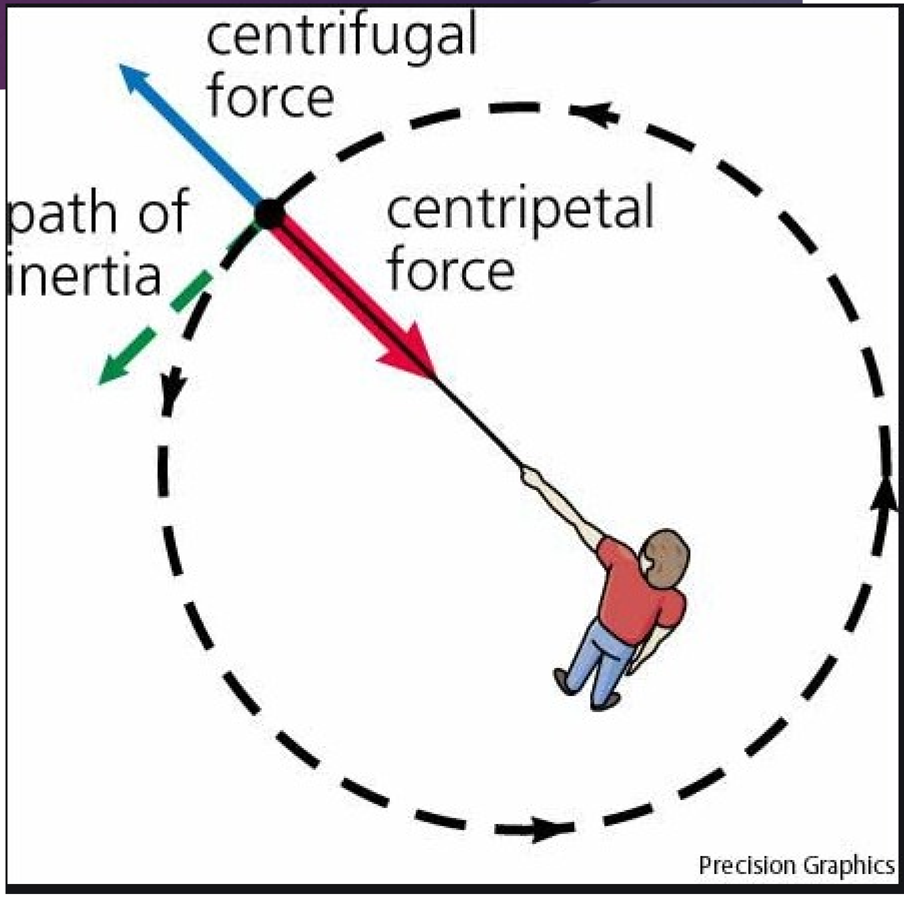
- These are called as **quantum numbers.**

- The range of quantum number may vary and begin from the lowest energy level (nucleus side n=1) to highest energy level.

Bohr atomic model

- **Stability of an atom:**

- Explained based on **centripetal force & centrifugal force,** action-reaction force pair associated with circular motion

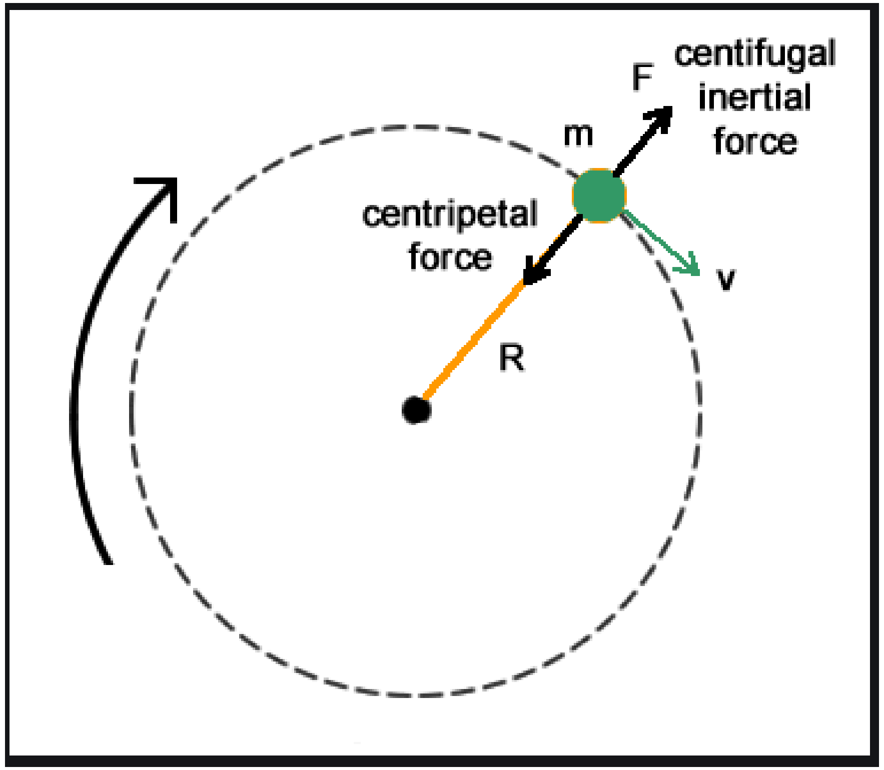


Bohr atomic model

- The attraction force between e & nucleus is balanced by centrifugal force of electron & the electrostatic forces between the nucleus & +ve nucleus!

- Centrifugal force is due to motion of electron and tend to take electron away from nucleus.

- **Centripetal force is the** electrostatic forces between the nucleus & +ve nucleus!



Bohr atomic model

- Bohr came up with an equation that describes the energy of an electron in the H atom:

$$E = -2.178 \times 10^{-18}\,\mathrm{J}\left(\frac{Z^2}{n^2}\right)$$

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

- n is an integer (the larger the value of n, the larger is the orbit radius) & Z is the nuclear charge
- n = principal quantum number = orbit number

Bohr atomic model

- The energies of the Bohr orbits are inversely proportional to the square of the quantum number n.
- As n increases the value of the energy increases (becomes lesser negative or more positive).
- It means that as we go farther from the nucleus the energy of the orbit goes on increasing.

Bohr atomic model

- *The -ve sign indicates that the E of an e bound to the nucleus is lower than that of an e at infinite distance given by:*

$$E = -2.178 \times 10^{-18}\,\text{J}\left(\frac{Z^2}{\infty}\right) = 0$$

- Note that for n=1 the e has a more negative energy than it does for n>1, ...
- .....which means that the e is more tightly bound in the smallest allowed orbit.

Bohr atomic model

- The change in energy ΔE when the electron falls from a lower level to a higher one or vice versa is

$$\Delta E = \text{energy of final state} - \text{energy of initial state}$$

- Electrons could jump from one orbit to another only by *emitting or absorbing energy in fixed quanta*.
- eg, if an e jumps one orbit closer to the nucleus, it must emit energy equal to the difference of the energies of the two orbits.

Bohr atomic model

- Conversely, when the electron jumps to a larger orbit, it must absorb a quantum of light equal in energy to the difference in orbits.

- If there is a -ve sign for the change in energy indicates that the atom has lost energy and is now in a more stable state.

Bohr atomic model

- The wavelength of the emitted photon can be calculated from the equation

$$\Delta E = h\left(\frac{c}{\lambda}\right) \quad \text{or} \quad \lambda = \frac{hc}{\Delta E}$$

- where ΔE represents the change in energy of the atom, which equals the energy of the emitted photon.

Example:

- 1. Calculate the energy required to excite the hydrogen atom from level n = 1 to level n = 2. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.

Solution

Solution

$$E_1 = -2.18\,x10^{-18}\,J\left(\frac{1^2}{1^2}\right) = -2.18\,x10^{-18}\,J$$

$$E_2 = -2.18\,x10^{-18}\,J\left(\frac{1^2}{2^2}\right) = -5.445\,x10^{-19}\,J$$

$$E_2 - E_1 = (-5.445\,x10^{-19}\,J) - (-2.18\,x10^{-18}\,J) = 1.6\,x10^{-18}\,J$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626\,x10^{-34}\,J\,x\,2.9979\,x10^{8}\,m\,s^{-1}}{1.633\,x10^{-18}\,J} = 1.216\,x10^{-7}\,m$$

Determination of wavelength associated with e transition

- 2nd method
- Since energy associated with a particular orbit (energy level) is known i.e

$$E = -\frac{b}{n^2}$$

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = -\left(\frac{b}{n_2^2}\right) - \left(-\frac{b}{n_1^2}\right)$$

$$\Delta E = b\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Bohr model

Estimation of wavelength associated with electron transition

The earlier equation can be re-written

$$\Delta E = b\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Delta E = \frac{hc}{\lambda} = hc\left(\frac{1}{\lambda}\right)$$

$$\frac{1}{\lambda} = \frac{b}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

1 where $n_2 > n_1$

- b/hc has a value of 109, 730 cm^{-1} differs only by 0.05 % from experimentally determined value of R_H

Bohr Theories

- The eq derived from Bohr's theory matches the Rydberg equation obtained from atomic spectrum of hydrogen
- The Rydberg equation can be used to calculate all the wavelengths of the spectral lines of hydrogen

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

- where R_H is the Rydberg constant = 109,678 cm^{-1}

Bohr model

- We can draw the following points so far:
- Energy of an electron in any particular orbit can be calculated.
- The energy of the e depends on the orbit it occupies.
- The smaller the radius of the orbit, the lower the energy of the electron in the orbit stable is the atom.
- Allowed values of n are whole numbers n = 1, 2, 3,4 …

Bohr model

- According to Bohr model, the e does not fall into the nucleus because it cannot occupy an orbit with a radius smaller than radius of the first orbit or energy lower than the energy of the first orbit.
- When the e is in the lowest orbital, the H atom is said to b in its *ground state* & when in a higher level it is in an *excited stated*.

Drawbacks of Bohr's theory

- **Bohr's theory - great accomplishment but was flawed.**

- Biggest contribution in his model was to **introduce quantum principles** to classical physics, but his model had a few limitations/drawbacks.

1. The model could make accurate predictions for the smaller sized atoms like Hydrogen, but it failed to make predictions for larger atoms.

- As more evidence is gathered about the e, Bohr's idea of an electron in an "orbit" is discredited

Drawbacks of Bohr's theory

2. According to Bohr, the radiation results when an electron jumps from one energy orbit to another energy orbit, but how this radiation occurs is not explained by Bohr.

3. Mixture of Sciences…The Bohr model was a **mixture of quantum & classical physics.**

- This is an issue because it was thought that quantum physics was **completely irrelevant** and different to classical physics.

Drawbacks of Bohr’s theory

4. Bohr assumes that an e in an atom is located at a definite distance from the nucleus & is revolving round it with definite velocity.

- i.e. it is associated with a fixed value of momentum.
- This is against the Heisenberg's Uncertainty Principle according to which it is *impossible to determine simultaneously with certainty the position & the momentum of a particle.*

EXAMPLE!

Calculate the energy required to excite the hydrogen electron from level n = 1 to level n = 2. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.

Using Equation,

$$E = -2.178 \times 10^{-18} J (z^2/n^2)$$

with Z = 1 we have

$E_1 = -2.178 \times 10^{-18} J(1^2/1^2) = -2.178 \times 10^{-18} J$

$E_2 = -2.178 \times 10^{-18} J(1^2/2^2) = -5.445 \times 10^{-19} J$

$\Delta E = E_2 - E_1 = (-5.445 \times 10^{-19} J) - (-2.178 \times 10^{-18} J)$

$= 1.633 \times 10^{-18} J$

The positive value for ΔE indicates that the system has gained energy. The wavelength of light that must be absorbed to produce this change is

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\ \text{J.s})(2.9979 \times 10^{8}\ \text{m/s})}{1.633 \times 10^{-18}\ \text{J}}$$

$$= 1.216 \times 10^{-7}\ \text{m}$$

EXAMPLE!

Calculate the energy required to remove the electron from a hydrogen atom in its ground state.

- **Solution**: Removing the electron from a hydrogen atom in its ground state corresponds to taking the electron from $n_{initial}$ = 1 to n_{final} = $\propto$. Thus,

$$\Delta E = -2.178 \times 10^{-18}\ J \left[\frac{1}{n^2_{final}} - \frac{1}{n^2_{initial}} \right]$$

$$= -2.178 \times 10^{-18}\ J \left[\frac{1}{\propto} - \frac{1}{1^2} \right]$$

The energy required to remove the electron from a hydrogen atom in its ground state is 2.178 x 10^{-18} J.

EXAMPLE!

What color of light is emitted when an excited electron in the hydrogen atom falls from:

a) n = 5 to n = 2
b) n = 4 to n = 2
c) n = 3 to n = 2

blue, λ = 434 nm

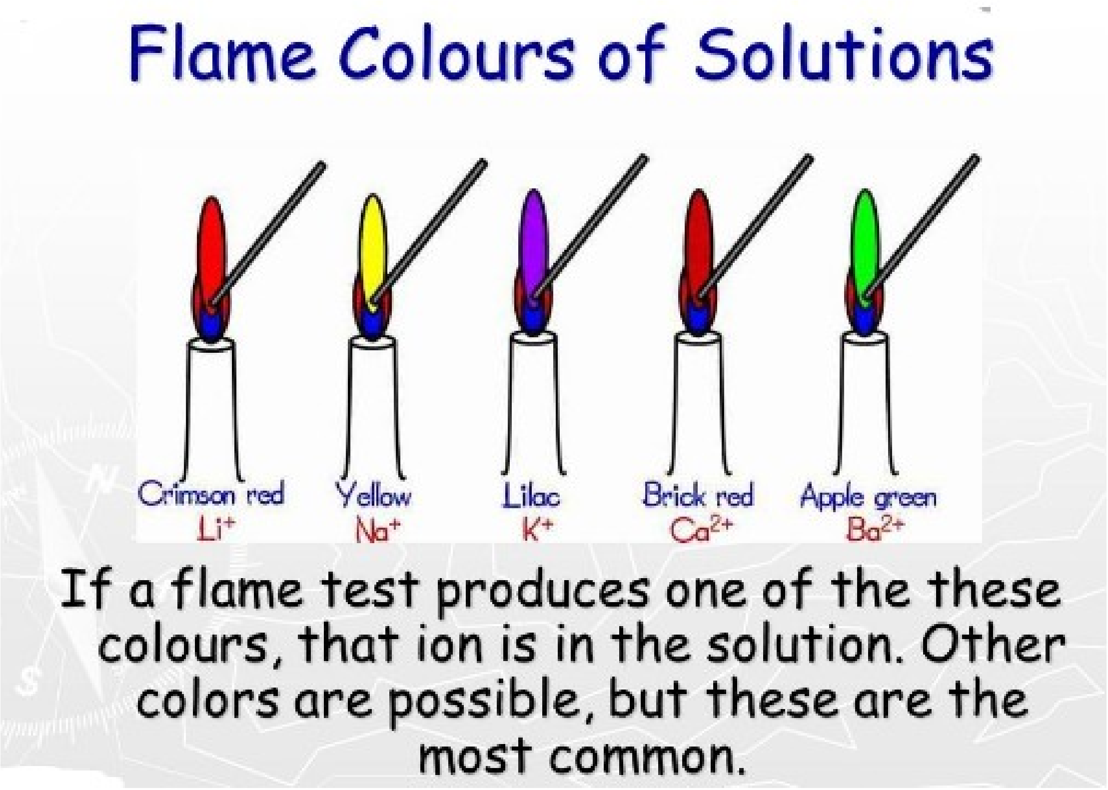
green, λ = 486 nm

orange/red, λ = 657 nm

Which transition results in the longest wavelength of light?

Atomic Spectra & the Bohr Model

- Let's first consider the following:
- You are aware of the flame tests for identifying cations in **qualitative analysis.**
- Na impart a bright yellow colour to the flame, Cu gives a green flame.
- If we pass such a light through a **prism** it gets **separated into a set of lines.**
- This is called as a **line spectrum.**



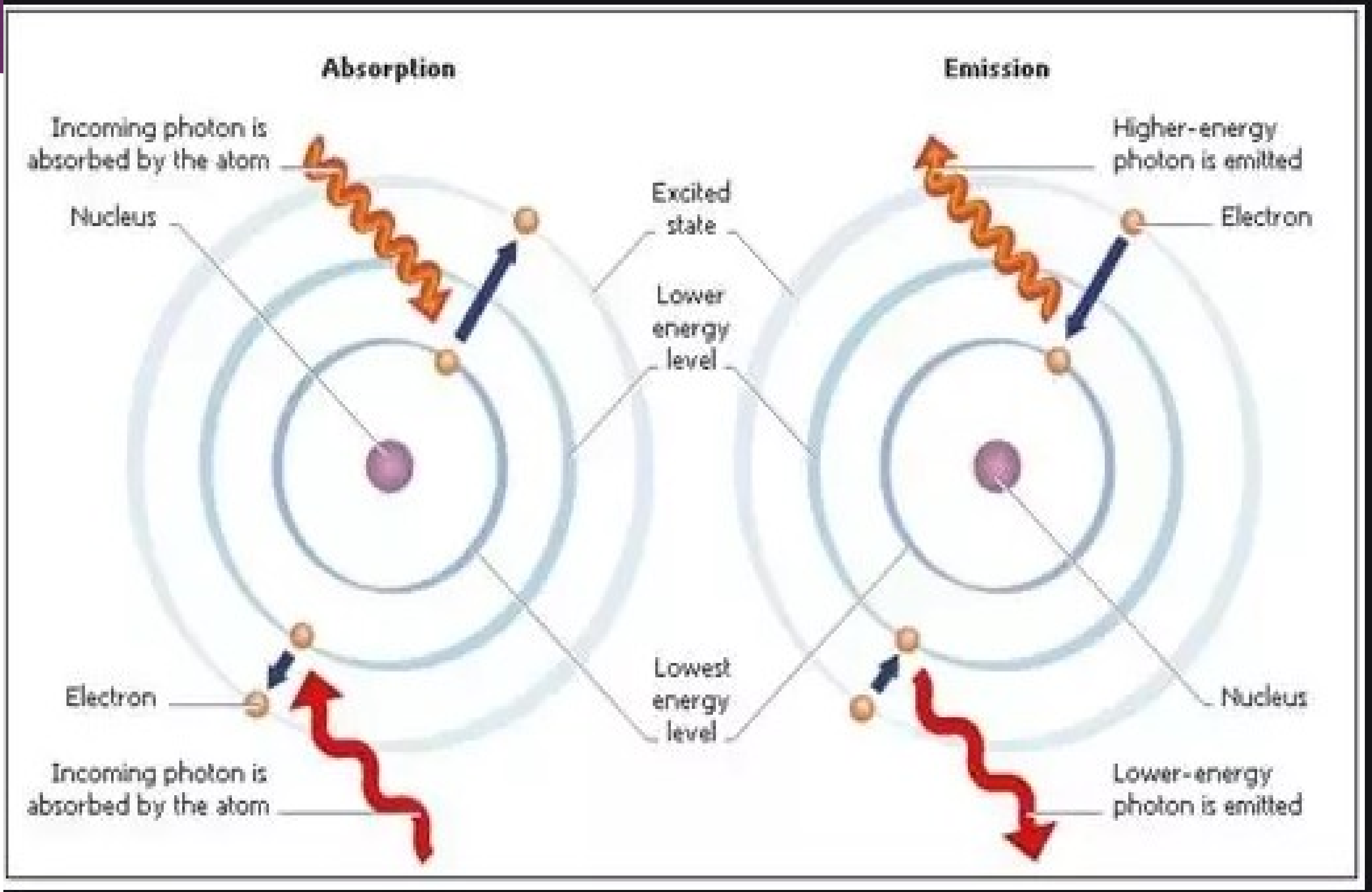
Atomic Spectra & the Bohr Model

- **Each Element Has Its Own Spectrum!!!**
- By passing an electric current or an electric spark through certain types of matter, it's possible to make that matter glow.
- Ne lights are one common example of this phenomenon.
- When an electric current travels through Ne gas, the Ne glows bright orange.
- Electricity (energy) causes *every* element

Atomic Spectra & the Bohr Model

- Another important experiment was the study of the emission of light by **excited H atoms.**

- Greatly helped in the study of atomic structure.

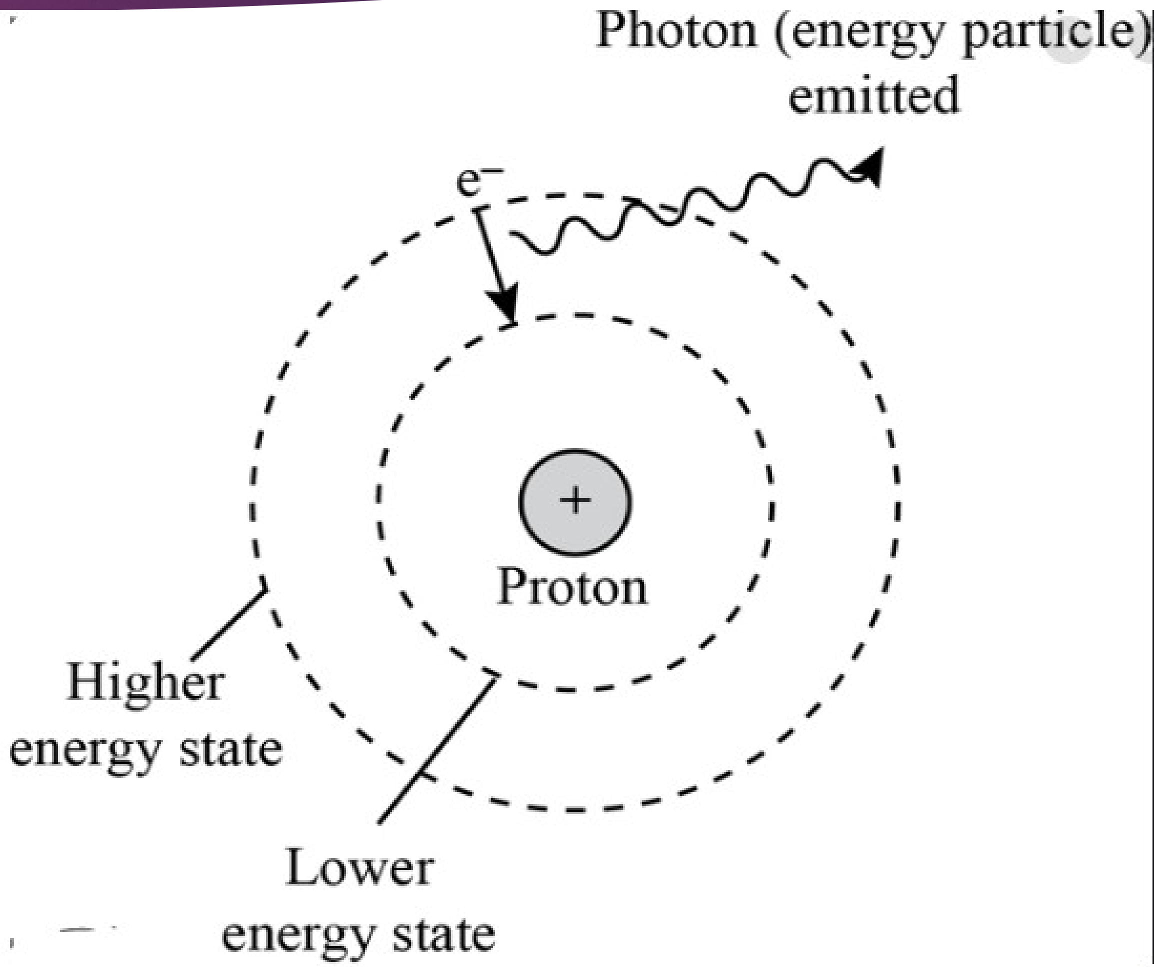


Atomic Spectra & the Bohr Model

- An atom emits a photon when it "jumps" from a higher state (state with higher energy) to lower.

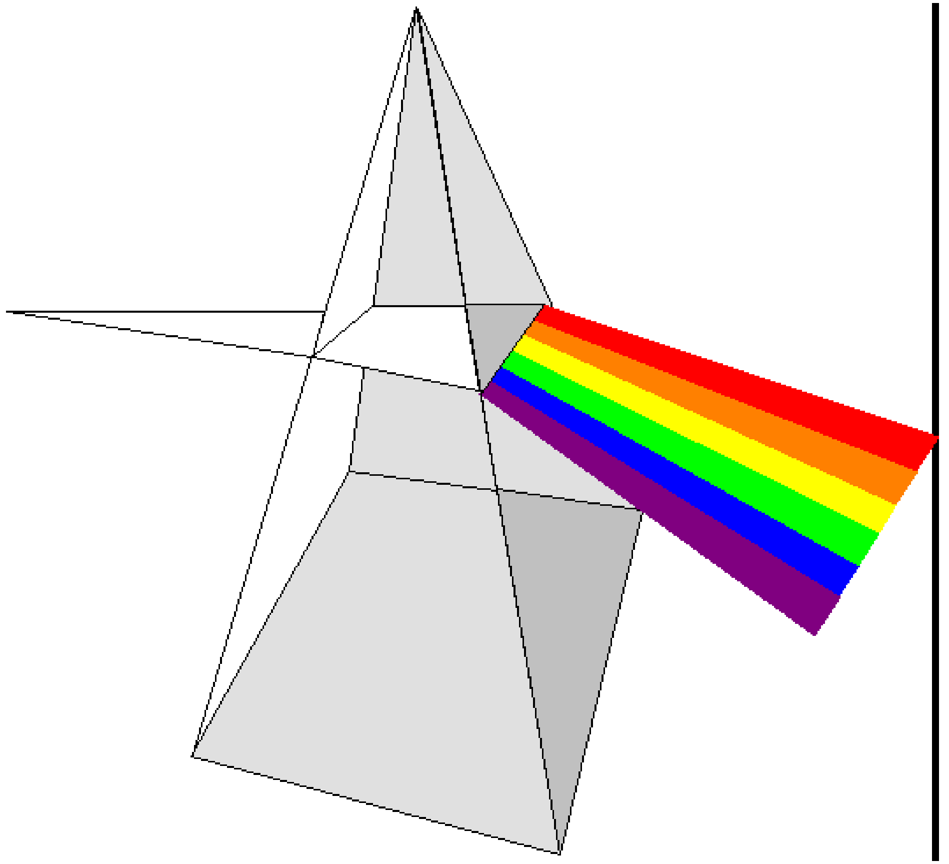
- As the energy of a state is discrete, so are the energies associated with these jumps (or transitions).

- Specific wavelength are emitted.!



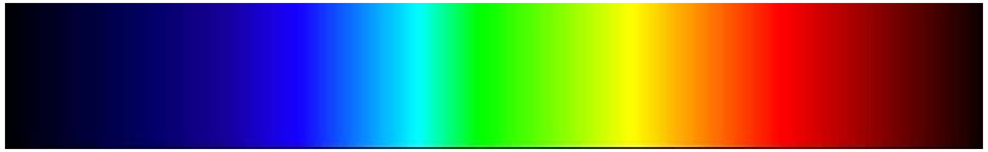
continuous spectrum

- To understand the significance of the H emission spectrum, we must first describe the **continuous spectrum….**
- This results when white light is passed through a **prism.**
- When we pass a beam of sunlight through a) we get a range of colours.
- The first **continuous spectrum** starts with a deep indigo blue & ends with red.



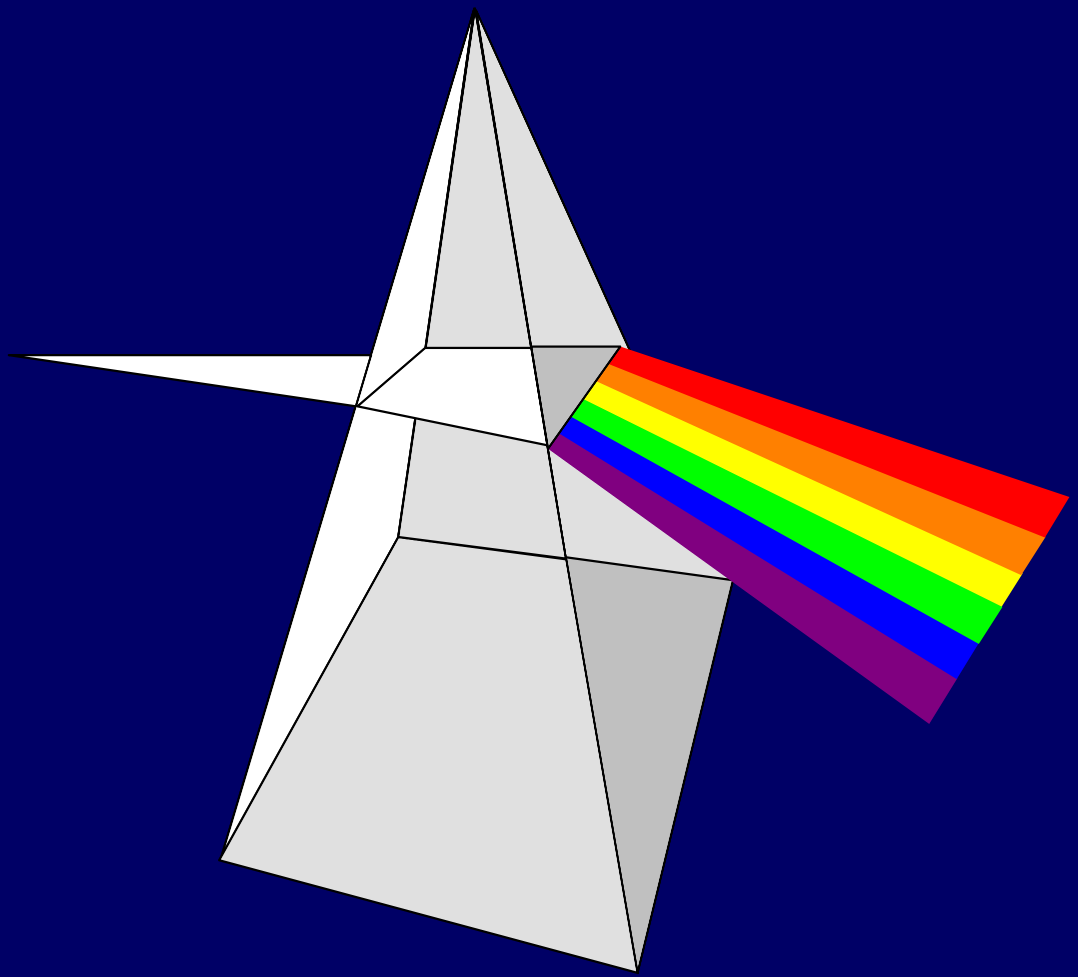
Continuous spectrum

- Notice how the colors in this spectrum change smoothly all the way from indigo to red.
- There are no gaps, or missing colors.
- Colors in the spectrum change smoothly without any gaps or holes, which makes the spectrum continuous.



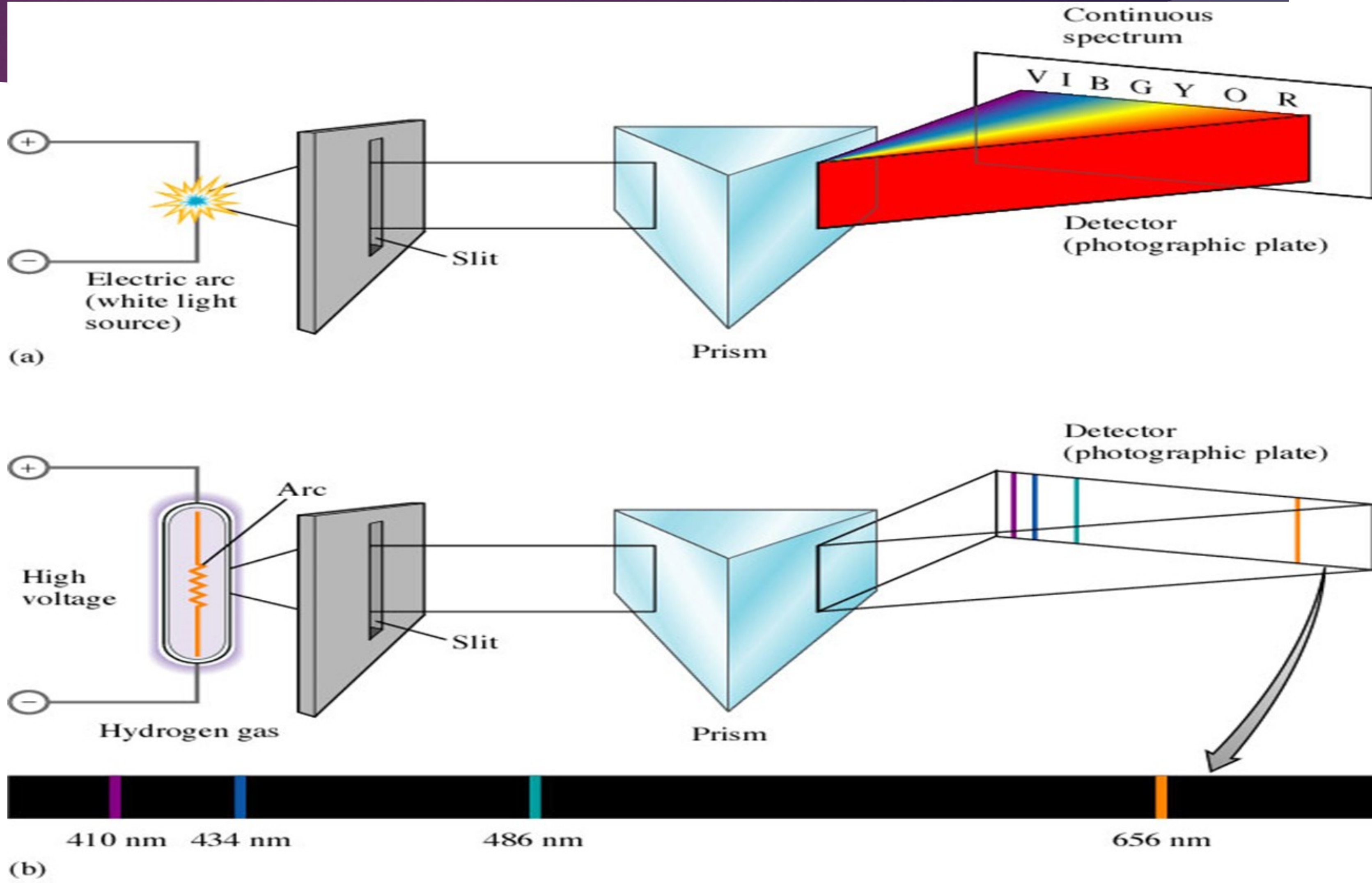
Prism

- White light is made up of all the colors of the visible spectrum.
- Passing it through a prism separates it.

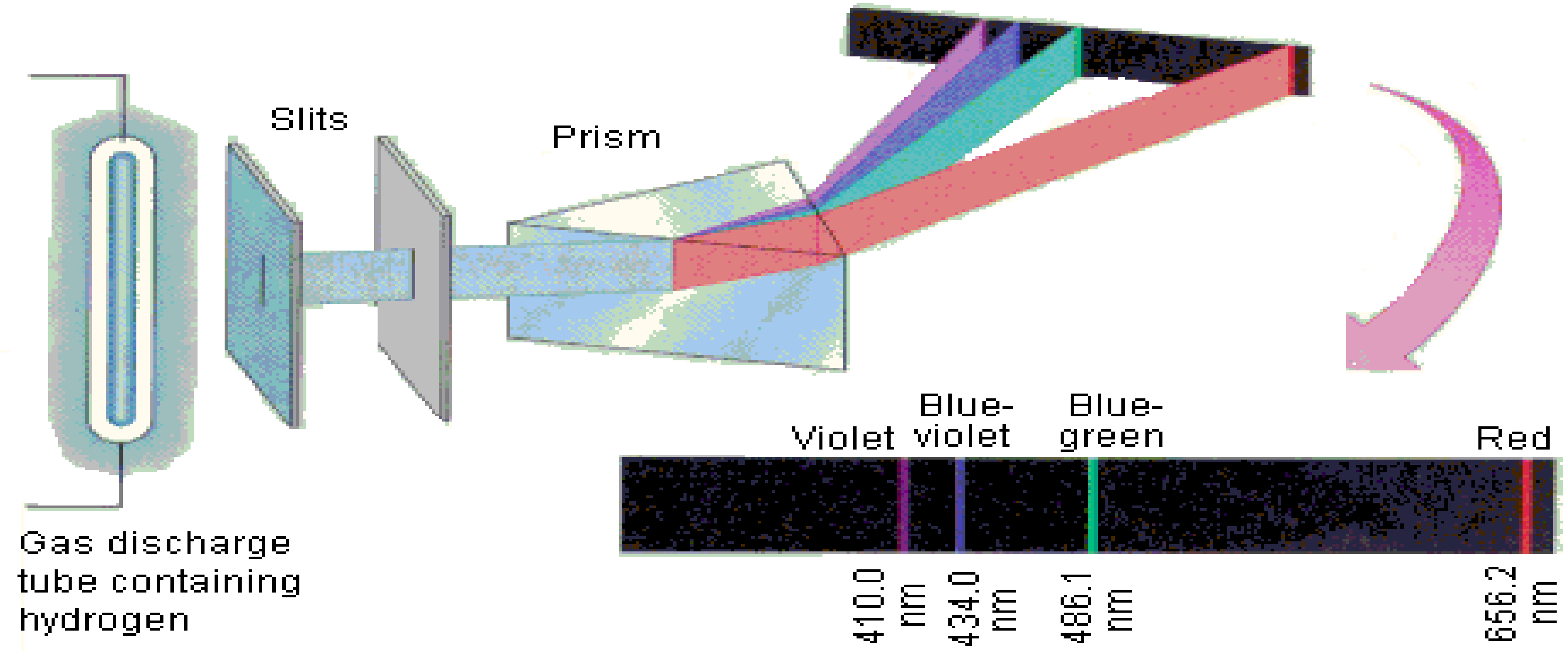


Atomic spectra of hydrogen

- When an **electric current** is passed through a glass tube that contains hydrogen gas at low pressure the tube gives off blue light.
- When this light is passed through a prism, 4 narrow bands of bright light are observed against a black background.



Atomic spectra of hydrogen



➤**This is called a line emission spectrum of H atom**

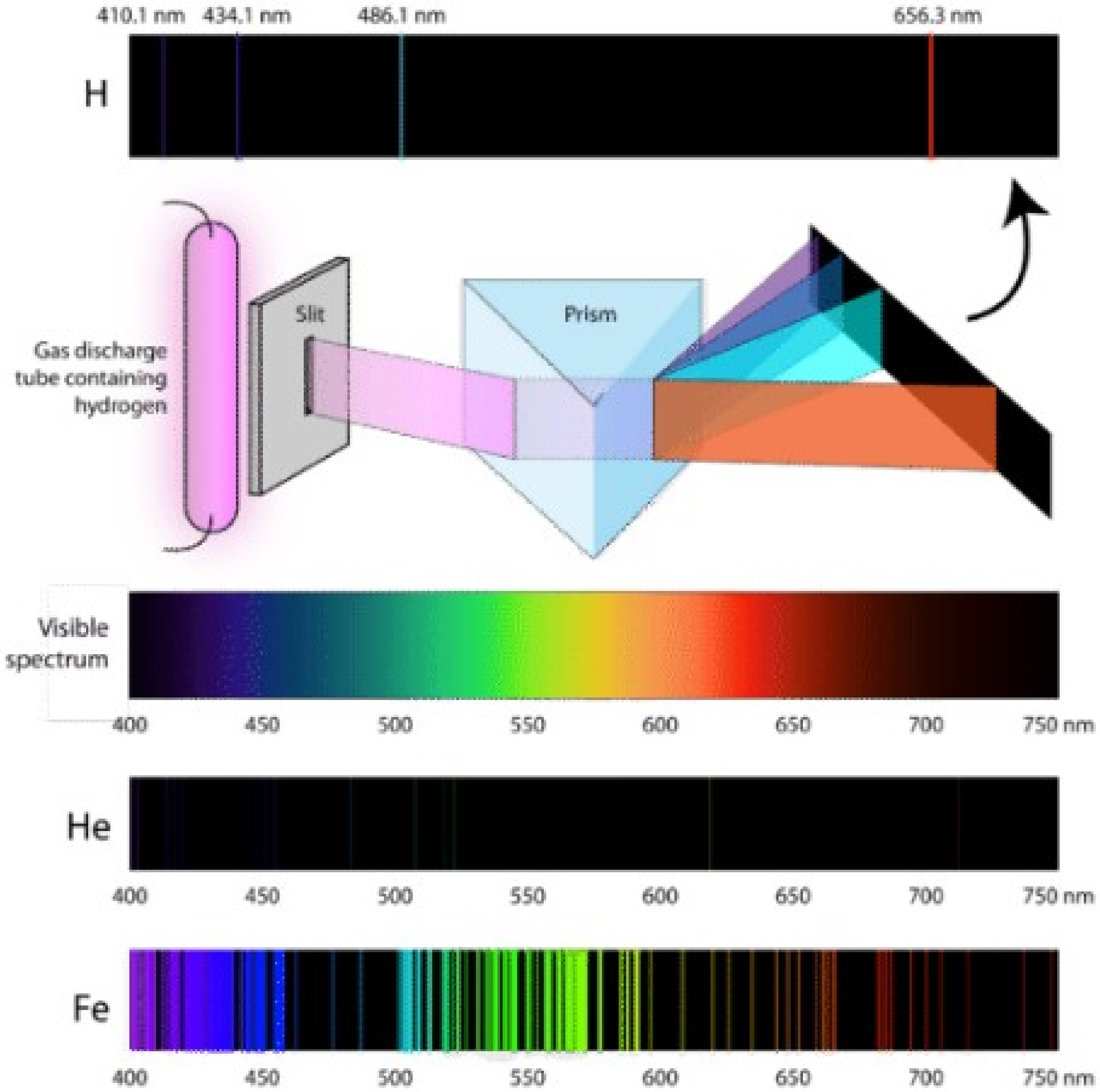
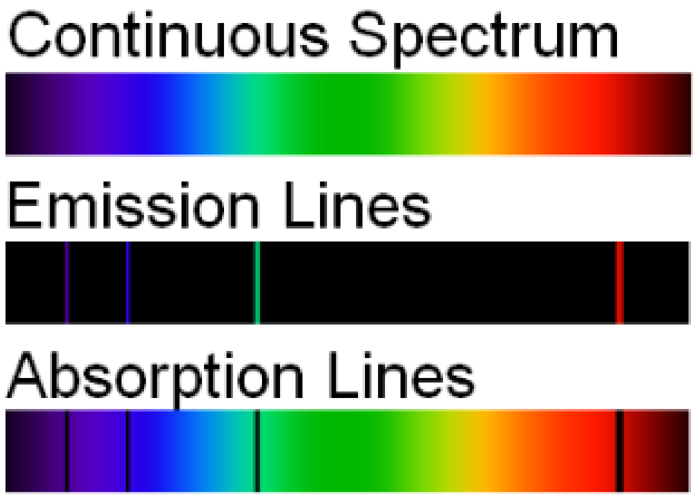
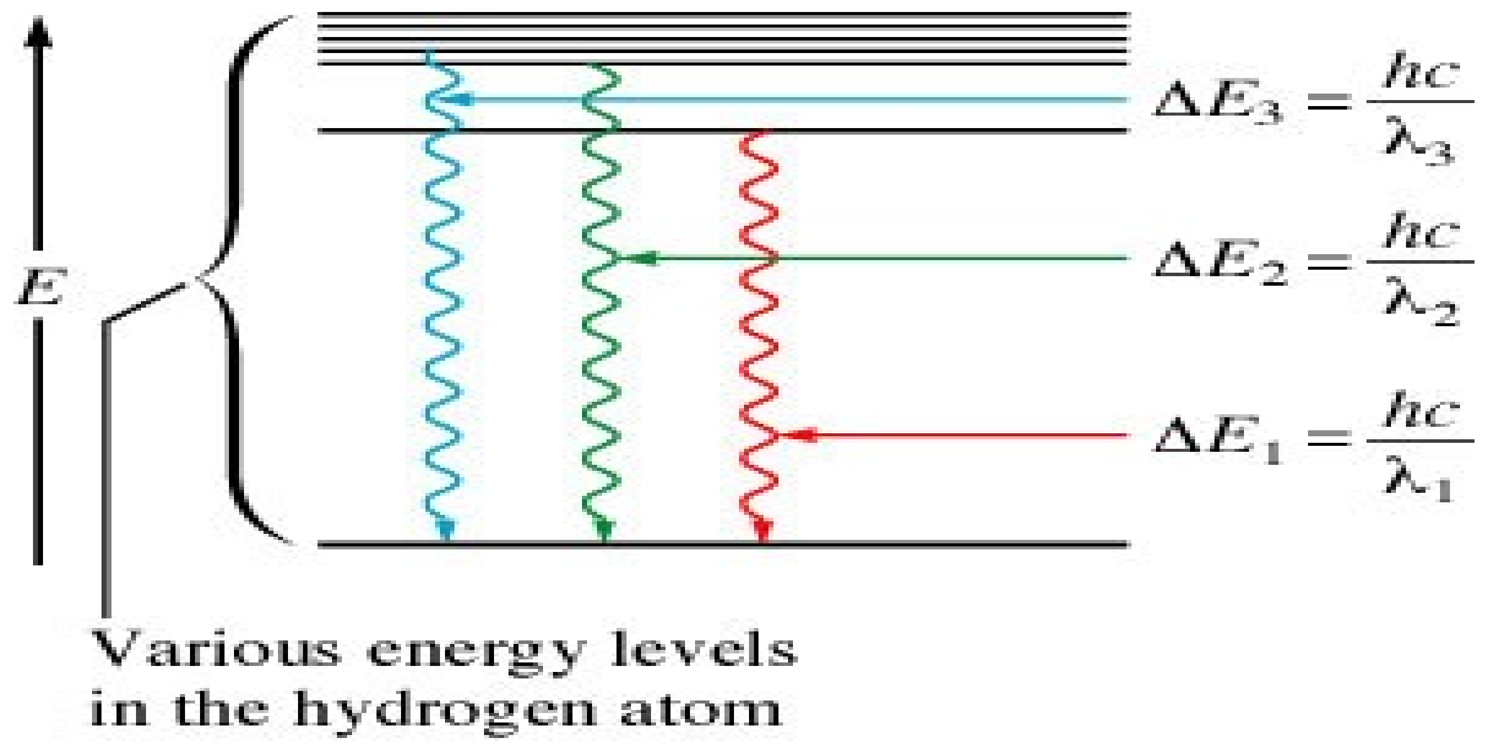


Figure 5.13: Several examples of continuous spectra in the visible range.



Significance

- Only certain energies are allowed for the electron in the hydrogen atom.
- Energy of the electron in the hydrogen atom is quantized.
- A Change between Two Discrete Energy Levels



Hydrogen (Line) spectra

- These narrow bands have the characteristic wavelengths and colors shown below.

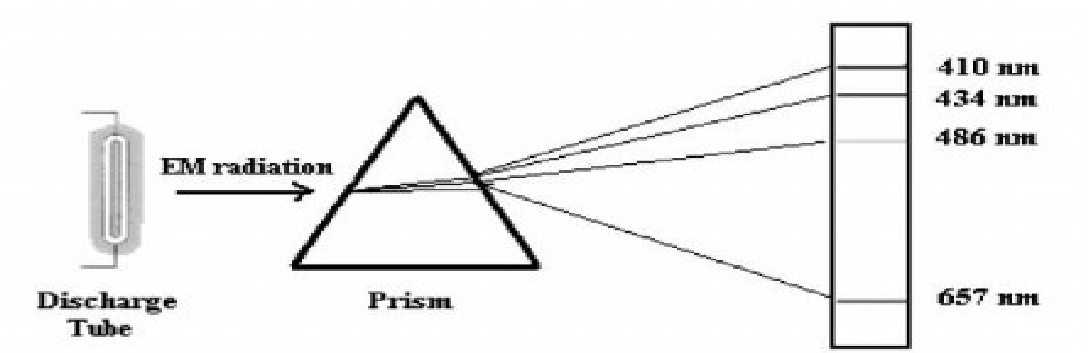


Fig. 3.9: *A schematic diagram showing line spectrum of hydrogen in the visible range*

Johann Balmer
(1825-1898)

Hydrogen (Line) spectra

- These observed spectral lines are due to the electron making transitions between two energy levels in the atom
  - ✓ If the energy of the electron is increasing, this is from absorption of the light energy.
  - ✓ If the light is being emitted, this is from the energy of the electron decreasing.

- The emission spectrum of atomic hydrogen has been divided into a number of spectral series, with wavelengths given by the **Rydberg formula.**

Hydrogen (line)spectra

- These spectral emission lines (studied by different scientists) could be expressed in the form of a general formula as:

$$\bar{v} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} ; R_H = 109677 \text{ cm}^{-1}$$

  - *Where n_1 & n_2 are positive integers ($n_1 < n_2$) (known as the principle quantum number) lamda is wavelength of light emitted and R_H is called Rydberg's constant.*

- This Formula is known as the ***Rydberg equation***.
- The classification of the series by the Rydberg formula was important in the development of **quantum mechanics**

Hydrogen (Line) spectra

- The specific wavelengths of light that are either absorbed or emitted from a sample of H atoms, are associated with electronic transitions.
- This means that there are discrete energy levels that the electron is moving between.

Table 3.2 : Summary of the emission lines observed in hydrogen spectrum

Series	n_1	n_2	Region of spectrum
Lyman	1	2,3,4…..	Ultraviolet
Balmer	2	3,4,5…..	Visible
Paschen	3	4,5,6…..	Infrared
Bracket	4	5,6,7…..	Infrared
Pfund	5	6,7,8…..	Infrared

CONCEPT CHECK!

- ✓ Why is it significant that the color emitted from the hydrogen emission spectrum is not **white**?

- ✓ How does the emission spectrum support the idea of quantized energy levels?

EXAMPLE!

Calculate the wavelength of the Balmer line with an electronic transition corresponding to $n_2 = 3$

Solution: According to Balmer series $\bar{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$

where $R_H = 109{,}677 \text{ cm}^{-1}$

$$\text{For } n_2 = 3 \text{ ; } \bar{\nu} = 109{,}677 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 109{,}677 \left(\frac{5}{36} \right)$$

$$\text{Since, } \quad \lambda = \frac{1}{\nu} ; \lambda = \frac{36}{109{,}677 \times 5}$$

$$= 6.56 \text{ x } 10^{-5} \text{ cm}$$

$$= 656 \text{ nm}$$

Atomic Structure

continues

Albert Einstein & the Photoelectric effect

- **Became famous for the theory of relativity, which laid the basis for the *release of atomic energy.***
- **used Planck's quantum theory to describe the particle properties of light.**
- **Demonstrated that emr, has characteristics of both a *wave &, consistent with Planck's theory, a particle.***

Mosaic

Albert Einstein and the Photoelectric effect

- **These particles were later called photons**

- ***He confirmed that the energy of a photon of electromagnetic radiation is directly proportional to the radiation's frequency,***

$$E = h\upsilon$$

h is a proportionality constant known as Planck's constant (6.63×10^{-34} J s).

Albert Einstein and the Photoelectric effect

Equation can also be written

$$E = h\nu = \frac{hc}{\lambda}$$

- **Left hand side deals with properties of energy (as a particle) & right hand side deals with <u>wave properties</u>**
- **Einstein arrived at this conclusion through his analysis of the <u>*photoelectric effect*</u>**

Mosaic

Albert Einstein and the Photoelectric effect

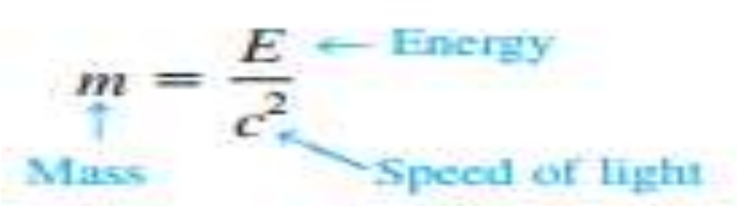
He established law of mass- energy equivalence; through his famous formula:

$$E=mc^2$$

where c is speed of light, m is mass

Main significance of this equation is that energy has mass.

Eq can be rearranged:



- **Can be used to calculate the mass associated with a given quantity of energy <u>hence apparent mass of a photon can be calculated.</u>**

Albert Einstein and the Photoelectric effect

- For emr of wavelength , the energy of each photon is given by the expression

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

Then the apparent mass of a photon of light with wavelength λ is given by

$$m = \frac{E}{c^2} = \frac{hc/\lambda}{c^2} = \frac{h}{\lambda c}$$

The Photoelectric effect

- **In 1887, Heinrich Hertz discovered that certain metals emit electrons when light is incident on them.**

- **This was the first instance of light interacting with matter, so it was very mysterious.**

- **In 1905 Albert Einstein published a paper which provided the explanation for the effect - light is made up of small particles.**

Mosaic

THE PHOTOELECTRIC EFFECT

- **refers to the phenomenon in which electrons are emitted from the surface of a metal when light strikes.**

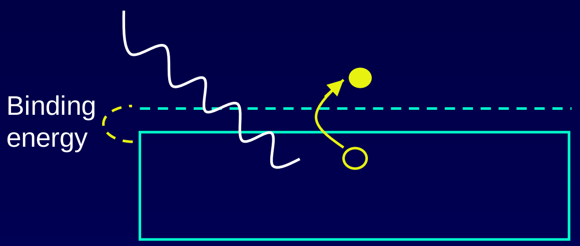
- **Electron can only leave metal surface if frequency is above a certain minimum value called the threshold frequency.**

Electron emitted are known as photoelectrons

Mosaic

Photoelectric Effect (1)

Electrons in a metal are bound by an energy Φ, called the work function.



If you shine light on a clean metal surface, electrons can emerge → the light gives the electrons enough energy (> Φ) to escape.

Φ is the minimum energy needed to liberate an electron from the metal.

Φ is defined to be positive.

Measure the flow of electrons with an ammeter.

Photoelectric Effect

$$\text{Minimum energy required to remove an electron} = E_0 = h\nu_0$$

- **Photoelectric effect is only seen if the photon E <u>exceeds the binding energy of the electron in the metal.</u>**

- **So light with a frequency less than the threshold frequency produces no electrons i.e**

$$E_0 \ (\nu < \nu_0)$$

Mosaic

Photoelectric Effect

- **The conservation of energy requires that, kinetic energy of the ejected electrons obey the eq:**

$$K.E = \frac{1}{2} m_e v^2 = h\nu - h\nu_o$$

(Energy of incident photon – threshold energy)

V=velocity of e

Summary of the work of Planck & Einstein

- **Energy is quantized.**
  - **occur only in <u>discrete units</u> called quanta.**

- **EMR, doesn't only exhibit only wave properties, but can also behave as a particle matter.**

  - **This phenomenon is sometimes referred to as the *dual nature of light.***

  - **So, light could under some conditions behave like a particle and other conditions behave as a wave.**

In 1923, **Louis de Broglie,** a French physicist, reasoned that **particles (matter)** might also have wave properties.

- **argued that:**

  if light can show wave as well as particle nature, why should particles of matter (e.g., electron) not possess wave like characteristics?

Louis de Broglie

- **Discovered that electrons had a dual nature-similar to both particles & waves. Particle/wave duality.**

- **Hence wavelength can be calculated!**

- **<u>Supported Einstein.</u>**

The wavelength of a particle of mass, *m* (kg), & velocity, *v* (m/s), is given by the de Broglie relation:

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

$$h = 6.626 \times 10^{-34}\ \text{J} \bullet \text{s}$$

Louis de Broglie

mv (p) is momentum of the particle.

- **The de Broglie wavelength of a body is inversely proportional to its momentum.**
- **magnitude of h is very small, wavelength of objects of our everyday world would be too small to be observed.**
- **The inverse relationship is why we don't notice any wavelike behavior for the macroscopic objects we encounter in everyday life**

Louis de Broglie

Example 3.4 : Calculate the de Broglie wavelength associated with a cricket ball weighing 380 g thrown at a speed of 140 km per hour.

Solution: Mass of the cricket ball = 380 g = 380×10^{-3} kg = 0.38 kg

Speed or Velocity = 140 km/hr = $(140 \times 1000)/3600$

$= 38.89 \text{ m s}^{-1}$

The wavelength associated with the cricket ball will be

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,\text{JS}}{(0.380kg)\,(38.89\text{m s}^{-1})}$$

$= 4.48 \times 10^{-35}$ m $(\text{J} = \text{kg m}^2\,\text{s}^{-2})$

de-Broglie (1892-1987)
de-Broglie proposed the theory of wave-particle dualism as a part of his PhD thesis in 1924. He got the physics Nobel prize in 1929

Where is the electron located?

- **Erwin Schrödinger theorized that the behavior of electrons within atoms could be explained by treating them mathematically as *matter waves*.**

- **This model, which is the basis of the modern understanding of the atom,..**
- **… is known as the quantum mechanical or wave mechanical model.**

The uncertainty principle

- **An important consequence** of **wave-particle** duality of matter & radiation was discovered by Werner Heisenberg in 1927 & is called the **uncertainty principle.**

- According to this principle ***it is not possible to simultaneously measure both the position & momentum (or velocity) of an electron accurately.***

The uncertainty principle

- In simple words we may state that the more accurately you measure a particle's position,..
- … the less accurately you're able to measure its momentum, & vice versa.

Mathematical expression is

- $$\Delta x \, \Delta p \geq \frac{h}{4\pi}$$

- Where Δx & Δp are the uncertainties in the measurements of position & momentum

Heisenberg Uncertainty Principle

Werner Karl Heisenberg (1901–1976).

- The uncertainty principle implies that we cannot know the exact motion of the electron as it moves around the nucleus.
- **Thus, Heisenberg's principle questioned the validity of Bohr's model.**
-

Important points about the principle

- **Viewed electrons as continuous clouds & introduced "wave mechanics" as a mathematical model of the atom.**

- **Resulted into development of a *Quantum mechanical or Wave Mechanical Model* of the atom.**

- Notable scientists to this theory: **Erwin Schrödinger**, **Louis De Broglie** & **Werner Heisernberg.**

Building on de Broglie's work, in 1926, Erwin Schrödinger devised a theory that could be used to explain the wave properties of electrons in atoms and molecules.

Branch of physics that mathematically describes wave properties of **submicroscopic particles** is called **quantum mechanics or wave mechanics.**

- **By mid-1920s it had become apparent that the Bohr model could not be made to work.**

- **A totally new approach was needed.**

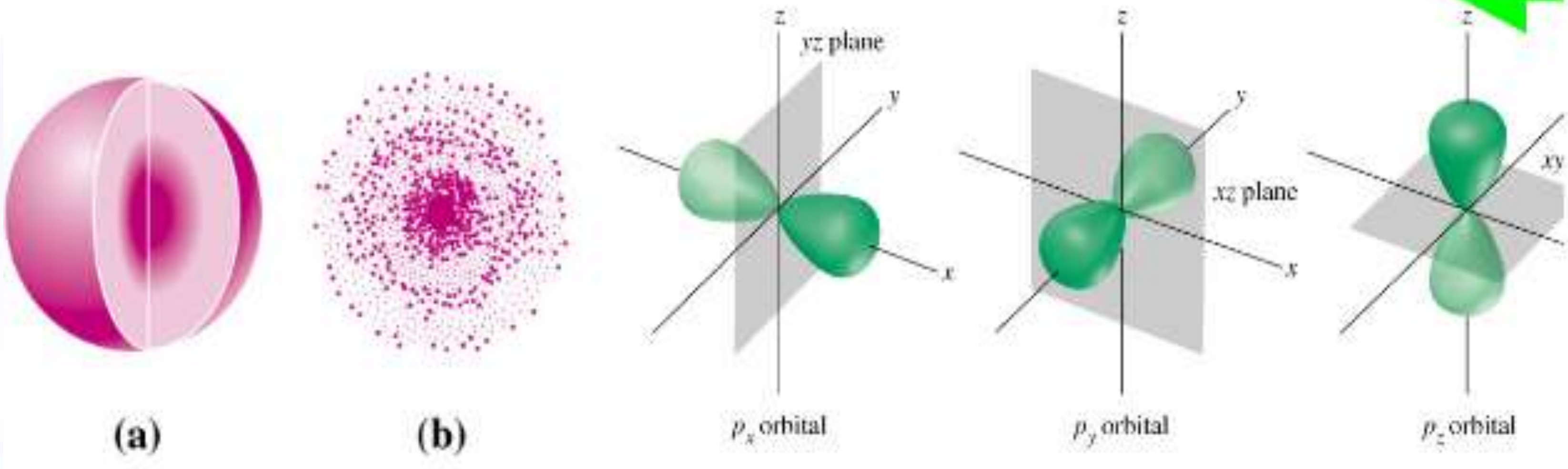
- *An Austrian and French scientist found Bohr's model to be insufficient in* ***locating electrons and came up with a new model.***

Updates to Bohr Model:

-Electrons are NOT in circular orbits around nucleus.

-Electrons are in a 3-D region around the nucleus called **atomic orbitals.**

-The atomic orbital describes the probable location of the electron



- Schrödinger & de Broglie noticed that electrons & light behaved not only as particles, but also as waves.
- Schrödinger began working with a mathematical model to understand the behavior of electrons.
- He came up with the following:

$$[(-h^2/8\pi^2 m)\ {}^2 + E_p] = E\Psi$$

In simpler form:

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

- Where E: is the binding energy of the electron.; ψ: wave function, H: Hamiltonian operator

Quantum Mechanical Model of atom

- **Schrödinger develops equations that detail the <u>probability of finding</u> an electron in a certain space.**

- In the QMM we speak of probability that the electron will be in a certain region of space at a given instant.

Quantum Mechanical Model of atom

- **For the H atom, allowed energies are the same as those predicted by the Bohr model**
- **However, the Bohr model assumes that the e is in a circular orbit.**
- **In the QMM, the electron's location can not be described so simply**

Quantum Mechanical Model of atom

- **Based on the Uncertainty principal, we cannot hope to specify the exact location of an individual electron around the nucleus.**

- **Rather we must be content with a kind of *statistical knowledge***

Wave Mechanical Model of atom

- Idea of “quantized” energy levels still applies, **but defined orbits do not exist.**

- Orbitals characterized by 3 quantum numbers that are related to **size**, **shape** & **orientation** of the orbital.

Orbitals and Quantum Numbers

- These wave functions are known as **orbitals.**
- Each orbital therefore has characteristic energy & shape

Orbitals and Quantum Numbers

- ✓ **The Bohr model introduced a single quantum number, n, to describe an orbit!**

- ✓ **The QMM uses three quantum numbers to describe an orbital**

Orbitals and Quantum Numbers

- ✓ **Principal quantum number, n**
- ✓ **Azimuthal quantum number, l**
- ✓ **Magnetic quantum number, m_l**
- These quantum numbers arise in the process of logically solving the wave equation

Significance of Quantum Numbers

- **An additional quantum number which does not follow from the Schrödinger wave equation but is introduced to account for electron spin.**

- **This is *Magnetic spin quantum number,* m_s**

Principal quantum number, n

- **Describes main energy level (or principal shell) of the electron within the atom.**

- **n indirectly describes energy of an orbital.**

  - **As '*n*' increase, orbital becomes large & electron spends more time further away from the nucleus.**

Principal quantum number, n

- **n can have only positive non zero integral values (i.e., n = 1,2,3,4……) …& designated as follows:**

Principal quantum No.	1	2	3	4
Letter designation	K	L	M	N
Max number of e ($2n^2$) electrons	2	8	18	32

- Each principal shell can accommodate a maximum of $2n^2$ electrons.

Azimuthal quantum number (Orbital Angular Momentum Number) *l*

- Related to the ***geometrical shape*** of the orbital. **Determines the shape of the atomic orbitals**
- **The value of l may be zero or a positive integer less than or equal to n–1 (n is the principal quantum number),**
- **i.e., l =0,1,2,3…… (n–1).**
- **i.e. for *n* = 1, l = 0**
- ***n* = 2, l = 0 to (2 – 1)**
- **= 0, 1**
- ***n* = 3, l = 0, 1, 2**

Azimuthal quantum number

- **e within an atom can be assessed according to the *shell, subshell,* & *orbital* to which they are assigned.**
- **Shells can be subdivided into subshells.**

- **Different values of l correspond to different types of subshells & each subshell contains orbitals of a given shape.**

Azimuthal quantum number

- **The maximum number of subshells is equivalent to the shell number.**
- **eg, when n=1 (first shell), only one subshell is possible & when n=2 (second shell), two subshells are possible.**

- **Each subshell is further divided into orbitals (Region of space in which an electron can be found).**

- **Only 2 electrons are possible per orbital.**

Azimuthal quantum number

- **There are 4 different types of subshells.**
- **These various types of subshells are denoted by the letters *s, p, d, & f***
- **Each subshell has a maximum number of electrons which it can hold: s - 2 electrons, p - 6 electrons, d - 10 electrons, and f - 14 electrons.**

Azimuthal quantum number

- **When n=1, the only subshell possible is the 1s subshell.**

- **When n=2, two subshells are possible the 2s & 2p.**

- **When n=3, three subshells are possible the 3s, 3p, and 3d.**

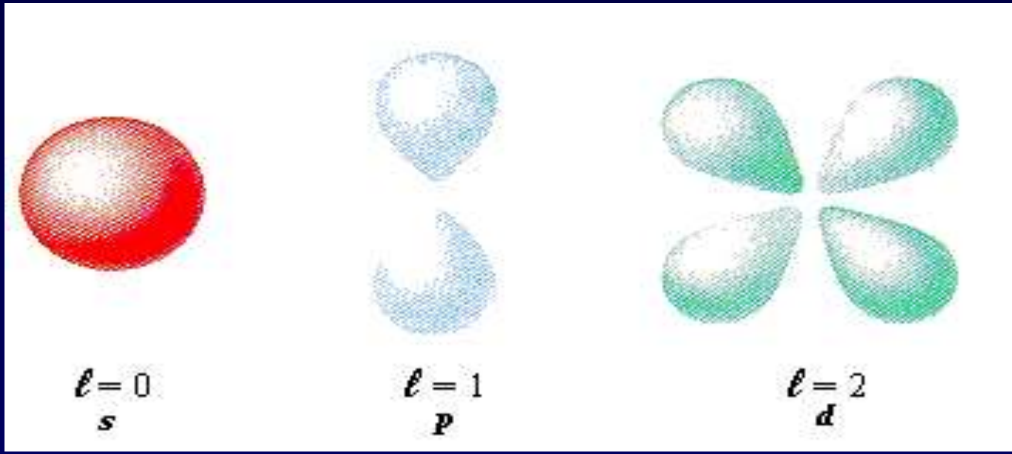
Azimuthal quantum number

- **l = 0 , corresponds to s-subshell & contains the orbital with spherical shape called as s orbital.**
- **l = 1, corresponds to p-subshell & contains the orbitals with a dumb-bell shape called**
- **p-orbitals. There are three p-orbitals in each p-subshell. Own orientation.**
- **The p_x orbital lies along the x axis, the p_y orbital lies along the y axis, and the p_z orbital lies along the z axis.**

Azimuthal quantum number

- **l = 2, corresponds to d-subshell & contains the orbitals with a cloverleaf shape called as d-orbitals.**
- **l = 3, corresponds to f-subshell & contain f orbitals. There are seven f-orbitals in each f-subshell.**

Azimuthal quantum number



- They can even take on more complex shapes as the value of the angular quantum number becomes larger.
  - **The greater the value of l, the greater the energy of the subshell**
- s < p < d < f…

Magnetic Quantum Number (m_l)

- Describes the direction or orientation of the orbital in space.
- It may be a negative or positive integer, including zero. integral value from – l to + l
- eg, for l = 1 ; m_l can have the values as –1,0 and 1.

Magnetic Quantum Number (m_l)

s orbital	p orbitals	d orbitals	f orbitals
l= 0	l = 1	l = 2	l = 3
m_l= 0 one s orbital in an s subshell	m_l = 0, ±1 three p orbitals in a p subshell	m_l= 0, ± 1, ± 2 five d orbitals in a d subshell	m_l = 0, ± 1, ± 2, ± 3 seven f orbitals in an f subshell

Magnetic spin quantum number, m_s

- **Describes the spin of the e i.e., whether it is clockwise or anticlockwise as well as the orientation of the *magnetic field* produced by the spin.**

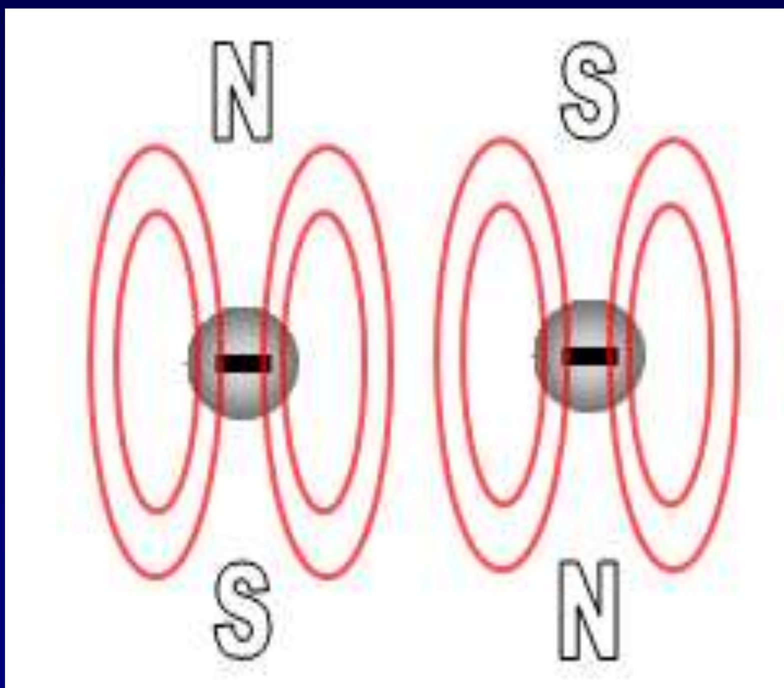
- **Specifies how many electrons can occupy a particular orbital.**

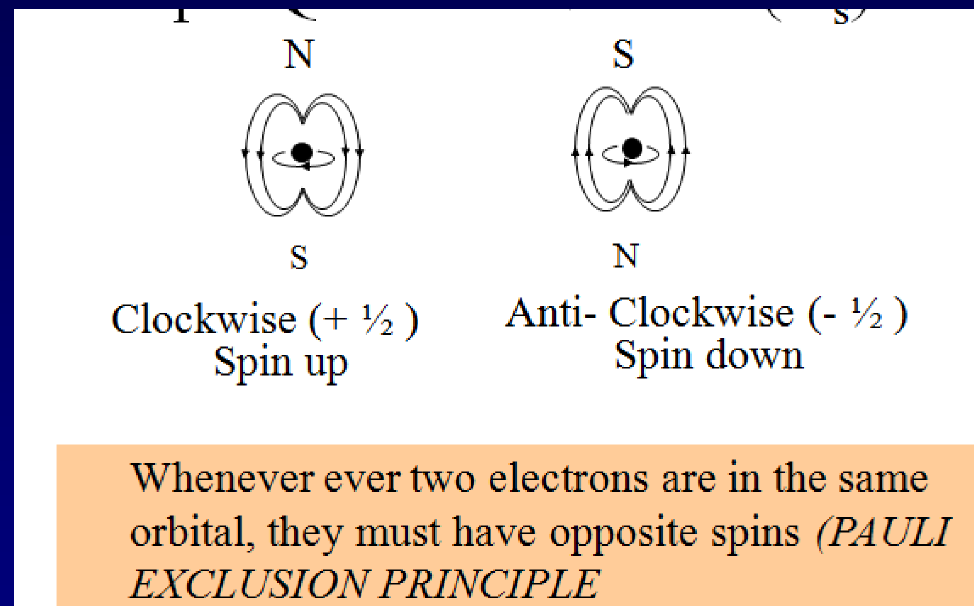
- **The quantum number, m_s does'nt arise while solving SWE.**

Magnetic spin quantum number, m_s

- The electron spin quantum number may have values of + ½ (also denoted by the arrow ↑) or – ½ (also denoted by the arrow ↓)
- For a pair of electrons with opposing spins, **no net magnetic field exists**
- The direction of the net magnetic in an atom depends only on the unpaired electron

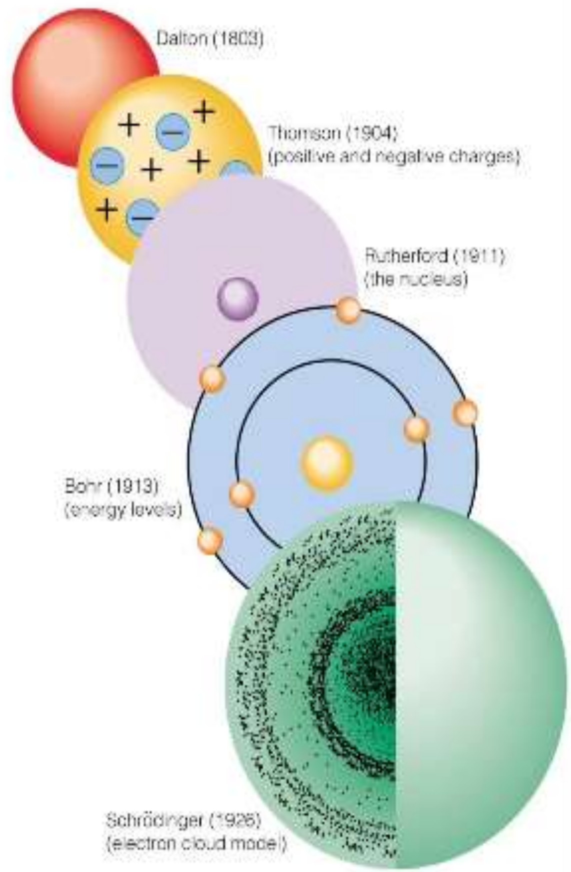
Magnetic spin quantum number, m_s





Evolution of the Atomic Model

- Shown to the right is a progression of our "picture" of an atom
  - ➢ Dalton – Solid Sphere
  - ➢ Thomson – "Plum Pudding"
  - ➢ Rutherford – Nucleus
  - ➢ Bohr – Planetary/Orbits
  - ➢ Schrödinger – Electron "Clouds"



Electronic Configuration of Elements

- The distribution of electrons **among the orbitals** of an atom/ions is called the electron configuration.
- The electron configuration of an atom/ions is the designation of how electrons are distributed among the various orbitals in the principal and subshells
- Chemical and physical properties can be correlated to the electronic configuration.

Electronic Configuration of Elements

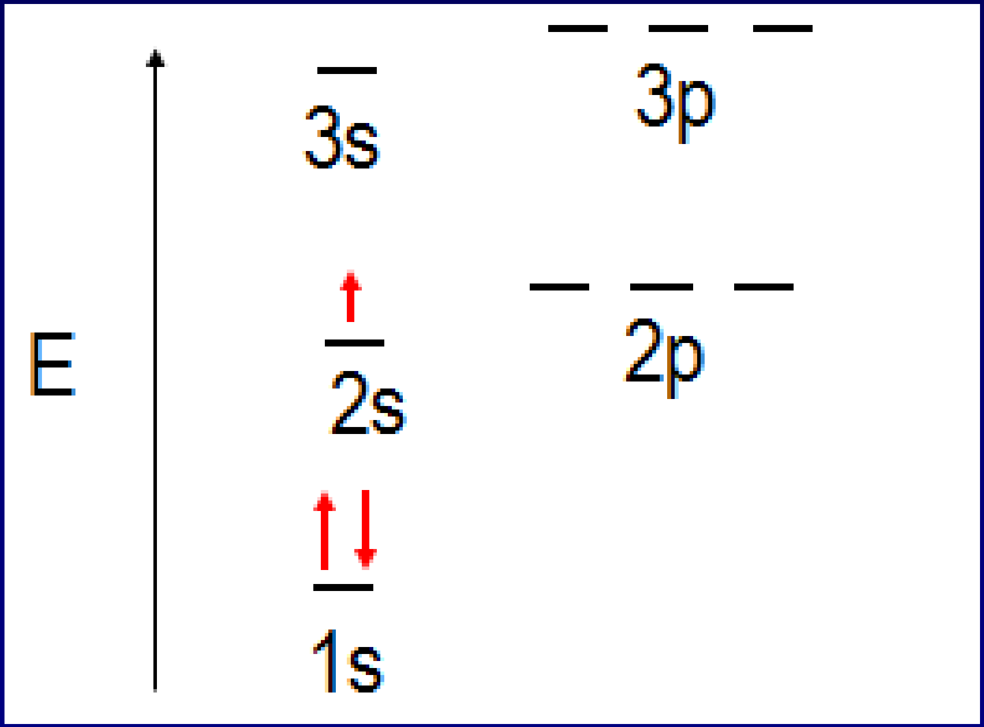
- They are organized in shells, subshells and orbitals.
- Many atoms are multi-electron
- The electrons occupying the inner orbits are known as **core electrons**, those outside are **valance electrons.**
- Electronic Configuration is governed by three basic rules or principles

Electronic Configuration of Elements

- Aufbau (or building up) Principle
- When placing electrons into orbitals in the construction of polyelectronic atoms, we use the <u>Aufbau Principle</u>
- This principle concerned with the E of the atom & states that the electrons should occupy the orbitals in such a way that the E of atom is minimum.
- In other words the electrons in an atom are filled in the increasing order of their energies.
- Orbitals with lowest energy are filled first.

Electronic Configuration of Elements

- Electrons add one by one to atomic orbitals to“build up” from lower to higher energy states.



Electronic Configuration of Elements

- **Now, how does one know the increasing order of the orbital energies?**
- You have learnt above that the principal quantum number determines the energy of the orbitals.
- Higher the value of n higher the energy.
- This is true only for hydrogen atom.

Electronic Configuration of Elements

- For other atoms, we need to consider both n and l.
- This means that different sub-shells in a given shell have different energies.
- The order of orbital energies can be determined by the following (n + l) rules.

Electronic Configuration of Elements

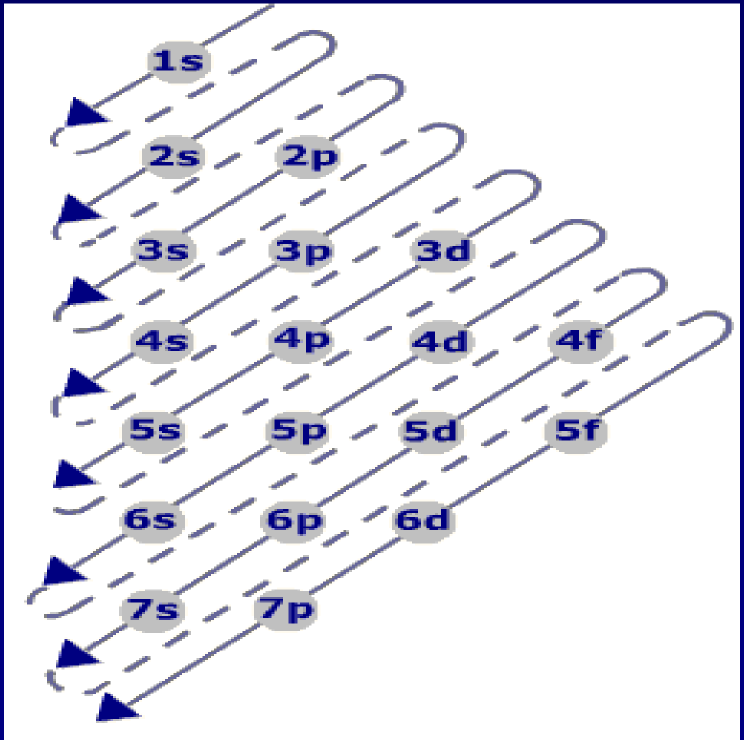
- Rule 1: An orbital with a lower value for (n + l) has lower energy. For example, the 4s orbital (n + l = 4+0=4) will fill before a 3d orbital (n + l =3 + 2 =5).

- Rule 2: If the value of (n + l) is same for two orbitals then the orbital with lower value of n will be filled first.

For example, the 3d orbital (n + l = 3+2=5) will fill before a 4p orbital (n + l =4 + 1 =5).

Electronic Configuration of Elements

- Following these rules the increasing order of the orbital energies comes out to be
- 1s < 2s< 2p< 3s< 3p< 4s< 3d< 4p< 5s < 4d< 5p< 6s



Electronic Configuration of Elements

- **Pauli's Exclusion Principle**
- This principle concerns the spin of electrons present in an orbital.
- Pauli's principle: No two electrons can have all the four quantum numbers to be same.
- This limits the number of electrons in a given orbital to two ($m_s = \pm ½$),

Electronic Configuration of Elements

- **As you know that an orbital is characterized by 3 quantum numbers so the electrons occupying a given orbital would have same values of these 3 quantum numbers.**
- **These electrons are distinguished in terms of their spin quantum number, m_s. & that 2 electrons in the same orbital <u>must have opposite spins</u>.**
- **Since the spin quantum number can have only two values so only two electrons can occupy a given orbital.**
- **In fact this fourth quantum number was introduced through Pauli's principle only.**

Atoms can be magentic?

- **Because an e spins, it creates a magnetic field, which can be oriented in one of two directions.**
- **Because unpaired electrons can orient in either direction, they exhibit magnetic moments that can align with a magnet.**
- For 2 electrons in the same orbital, the spins must be opposite to each other; the spins are said to be paired.
- These substances are not attracted to magnets and are said to be **diamagnetic.**

Atoms can be magentic?

- **Atoms with all diamagnetic electrons are called diamagnetic atoms.**
- **Atoms that contain unpaired electrons are weakly attracted to magnets and are said to be paramagnetic.**
- **Diamagnetic atoms** have only paired electrons, whereas **paramagnetic** atoms, which can be made magnetic, have at least one unpaired electron.

Electronic Configuration of Elements

- **Hund's Rule**
- **Concerned with the distribution of electrons in a set of orbitals of the same energy, i.e. constituents of a subshell.**
- **According to this rule if a number of orbitals of the same subshell are available then the electrons are distributed in such a way that each orbital is first singly occupied with same spin.**
- **For example, the six electrons in carbon distribute as:**

$$1s^2\ 2s^2\ 2p^1_x\ 2p^1_y 2p^0_z \quad \text{and not as} \quad 1s^2\ 2s^2\ 2p^2_x\ 2p^0_y 2p^0_z$$

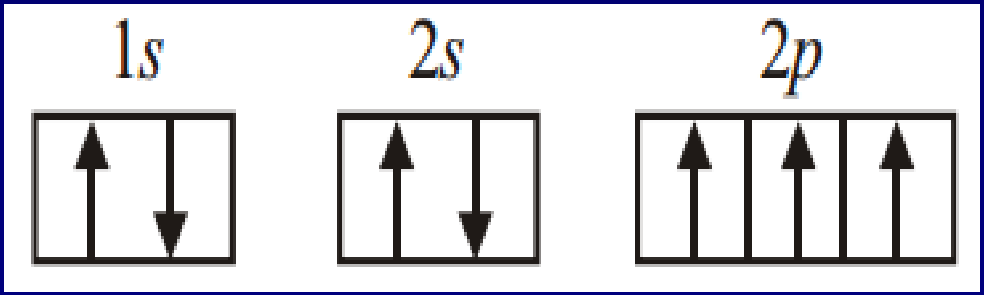
Electronic Configuration of Elements

- **Hund's Rule**

- The rules discussed above can be used to write the electronic configuration of different elements.
- There are **two common ways** of representing the electronic configurations. These are:
- **a) Orbital notation method**: spdf notation (condensed): C $1s^2 2s^2 2p^2$ or spdf notation (expanded): C $1s^2 2s^2 2p_x^1 P_y^1$

Electronic Configuration of Elements

- **b) Orbital diagram method: In this method the filled orbitals are represented by circles or boxes & are written in the order of increasing energies.**
- **The respective electrons are indicated as arrows whose direction represents their spin.**
- **For example, the electronic configuration of nitrogen in the orbital diagram notation can be written as:**

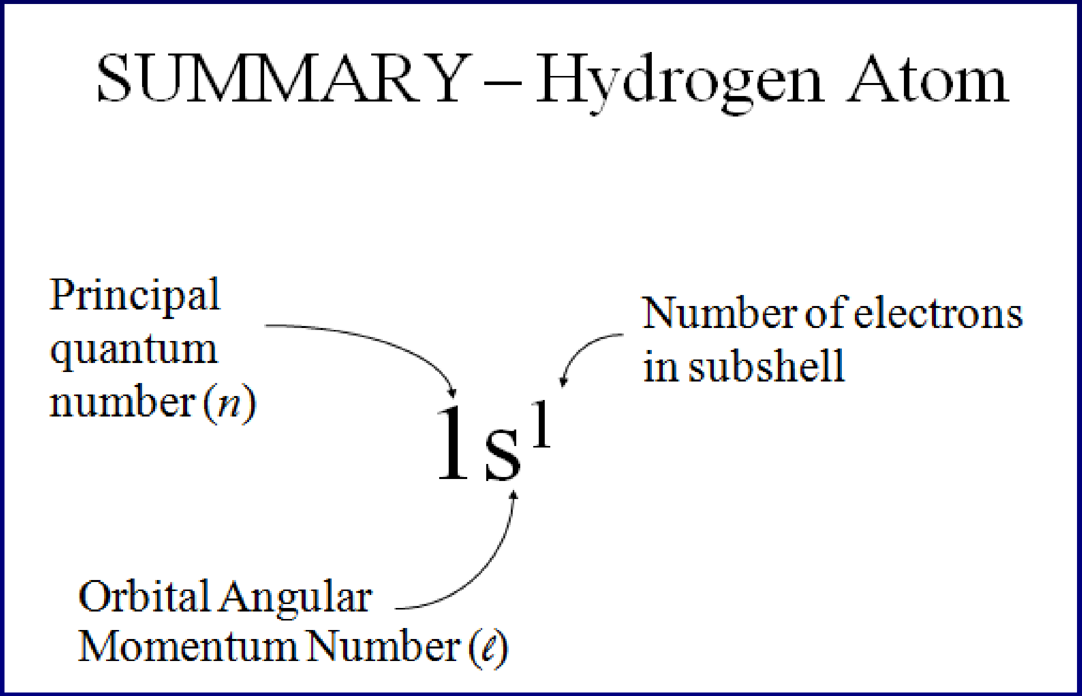


Electronic Configuration of Elements

- Electronic configurations can also be written in a **short** hand form.
- In this method the last completed orbital shell is represented in terms of a noble gas.
- For example, the electronic configuration of lithium and sodium can be written as
    - **Li [He]$2s^1$**
    - **Na [Ne]$3s^1$**

Electronic Configuration of Elements

- The electrons in the noble gas configuration are termed as **core electrons** while the ones in the outer shell are called **valence electrons.**



Unusual configurations

Predicting electron configurations works most of the time but not always.

Typical example: Cu and Cr

	Expected	**Actual**
Cr	**[Ar] $3d^4 4s^2$**	**[Ar] $3d^5 4s^1$**
Cu	**[Ar] $3d^9 4s^2$**	**[Ar] $3d^{10} 4s^1$**

In both cases an electron is ‘borrowed’ from the 4s into 3d

Half-filled and filled configurations have special stability that makes ‘borrowing’ energetically favourable.

Valence Electrons

- The electrons in the outermost principal quantum level of an atom.
- $1s^2 2s^2 2p^6$ (valence electrons = 8)
- The elements in the same group on the periodic table have the same valence electron configuration.
- Valence electrons – most important electrons to chemist as they take part in chemical reactions.
- Directly involved in bonding

End of Topic

Periodic Trends

Periodic Trends

We will rationalize these observed trends:

- Ionization Energy
- Electron Affininty
- Atomic Radius
- Electronegativity

Why do we see trends?

- Trends across a period (left to right) can be explained by increasing effective nuclear charge
- Trends going down in a group can be explained by increasing distance from the nucleus

Effective nuclear charge: Z_{eff}

Effective nuclear charge, Z_{eff}: the net positive charge attracting an electron in an atom.

An approximation to this net charge is

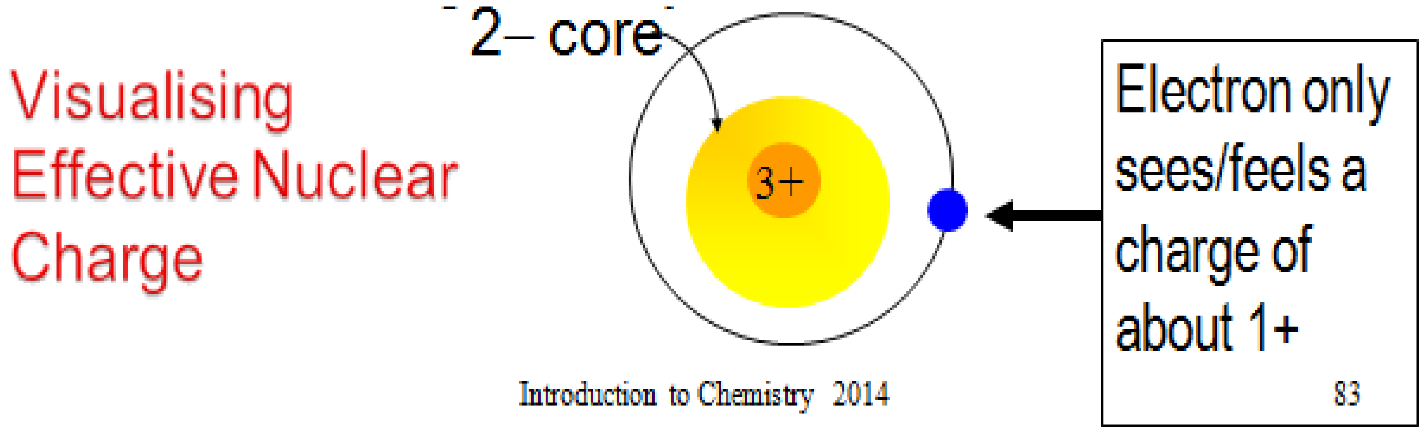
Z_{eff}(effective nuclear charge) = Z(actual nuclear charge) - Z_{core}(core electrons)

The core electrons are in subshell between the electron in question and the nucleus. The core electrons are said to “shield” the outer electrons from the full force of the nucleus

Example – Effective Nuclear Charge

Lithium: $1s^2 2s^1$

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



PERIODIC TRENDS IN ATOMIC PROPERTIES

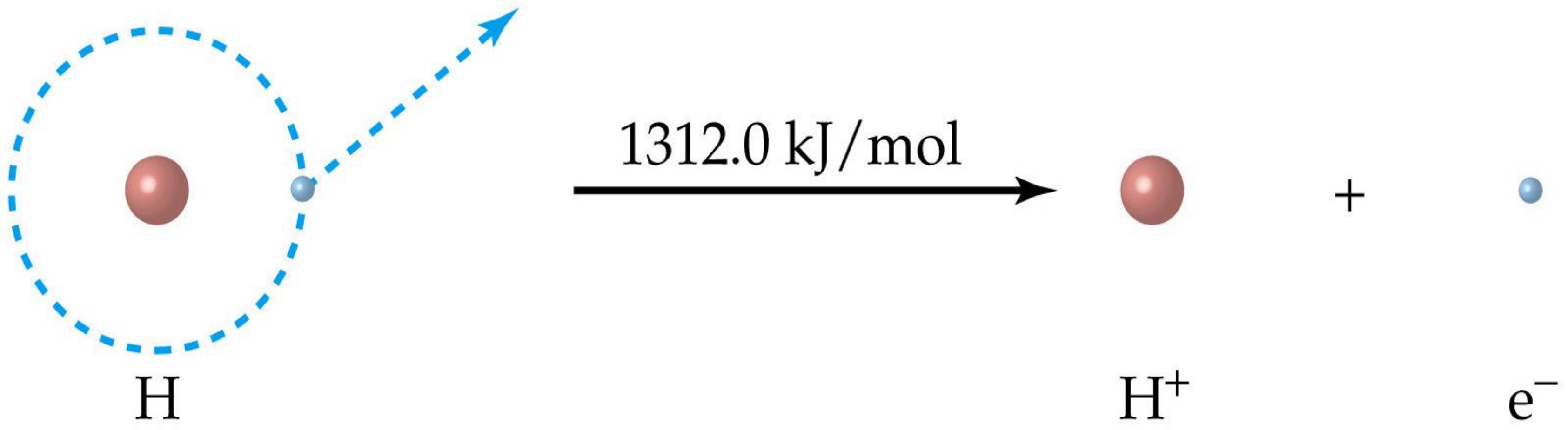
- using the PT can show you how atoms might act
- understand these basic rules and you'll go far...
- **Electrons are attracted to the protons in the nucleus of an atom.**
  - ✓ the closer they are the more they are attracted
  - ✓ the more protons, the more attraction
- **Electrons are repelled by each other**
  - ✓ important because if there are outside electrons, they are prevented from being attracted by the inside electrons
  - ✓ This is called **shielding**

Ionization Energy

The quantity of energy required to remove an electron from the gaseous atom or ion.

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

where, the atom or ion is assumed to be in its ground state.



Ionization Energy

- Knocking an e- off will cost a lot of energy
- Greater the IE, the more difficult to remove the electron
- The amount of Energy needed to knock off the most loosely held e- is called **first ionization energy**
- Knocking another one off that new cation is called **second ionization energy.**

$Mg \rightarrow Mg^{+} + e^{-}$	$I_1 = 735$ kJ/mol(1st IE)	
$Mg^{+} \rightarrow Mg^{2+} + e^{-}$	$I_2 = 1445$ kJ/mol	(2nd IE)
$Mg^{2+} \rightarrow Mg^{3+} + e^{-}$	$I_3 = 7730$ kJ/mol	*(3rd IE)

*Core electrons are bound much more tightly than valence electrons.

IE trend observed

In general, as we go across a period from left to right, the first ionization energy increases.

Why?

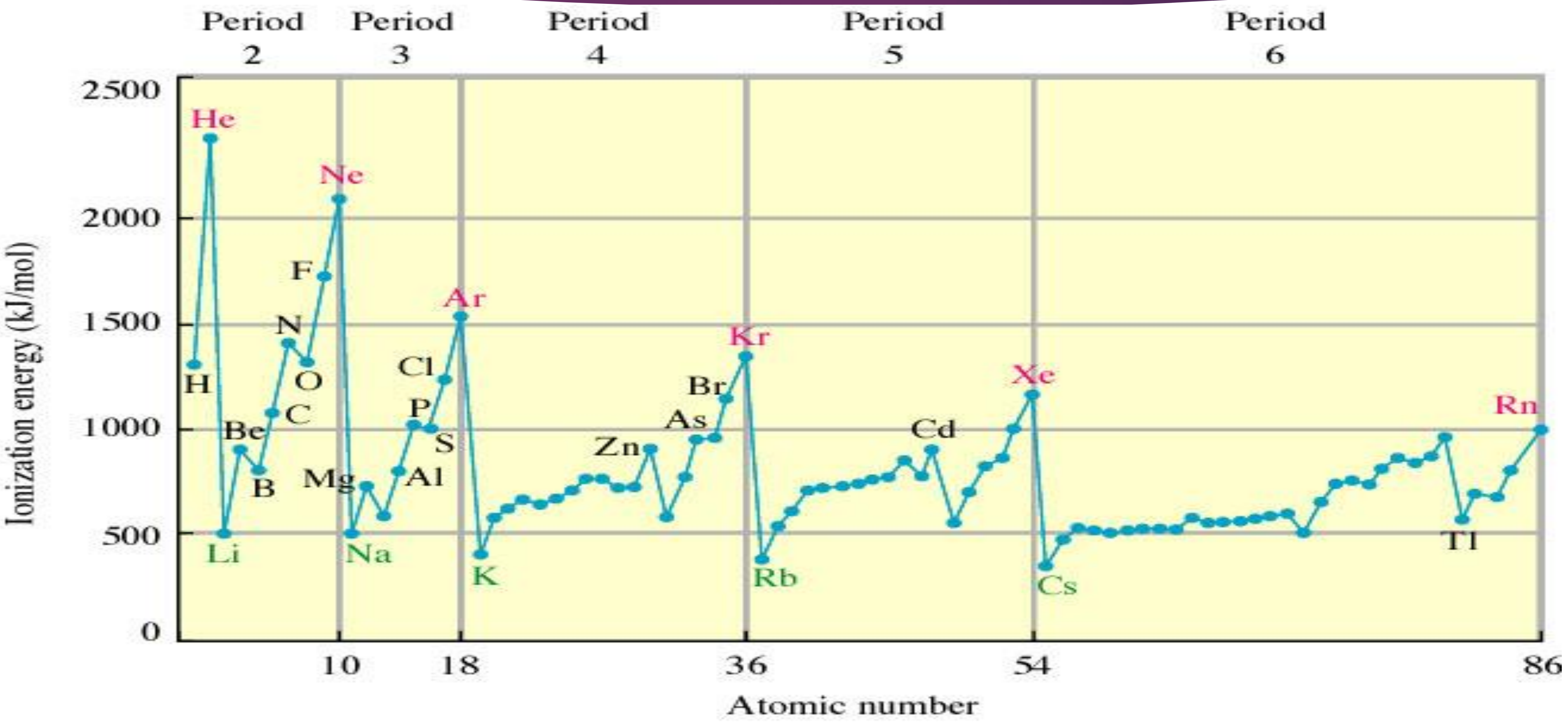
- Electrons added in the same principal quantum level do not completely shield the increasing nuclear charge caused by the added protons.
- Electrons in the same principal quantum level are generally more strongly bound from left to right on the periodic table.

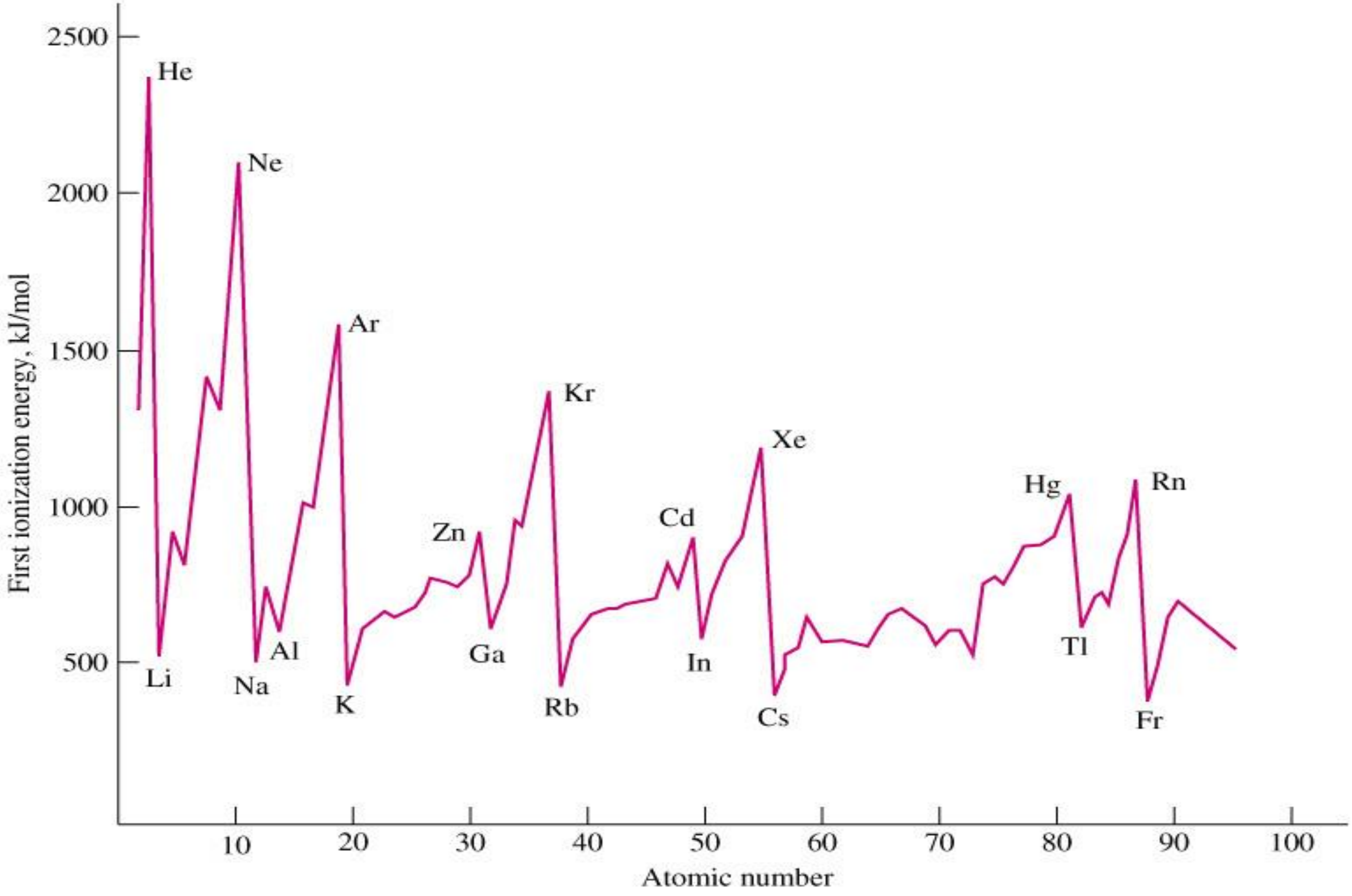
In general, as we go down a group from top to bottom, the first ionization energy decreases.

Why?

- The electrons being removed are, on average, farther from the nucleus.

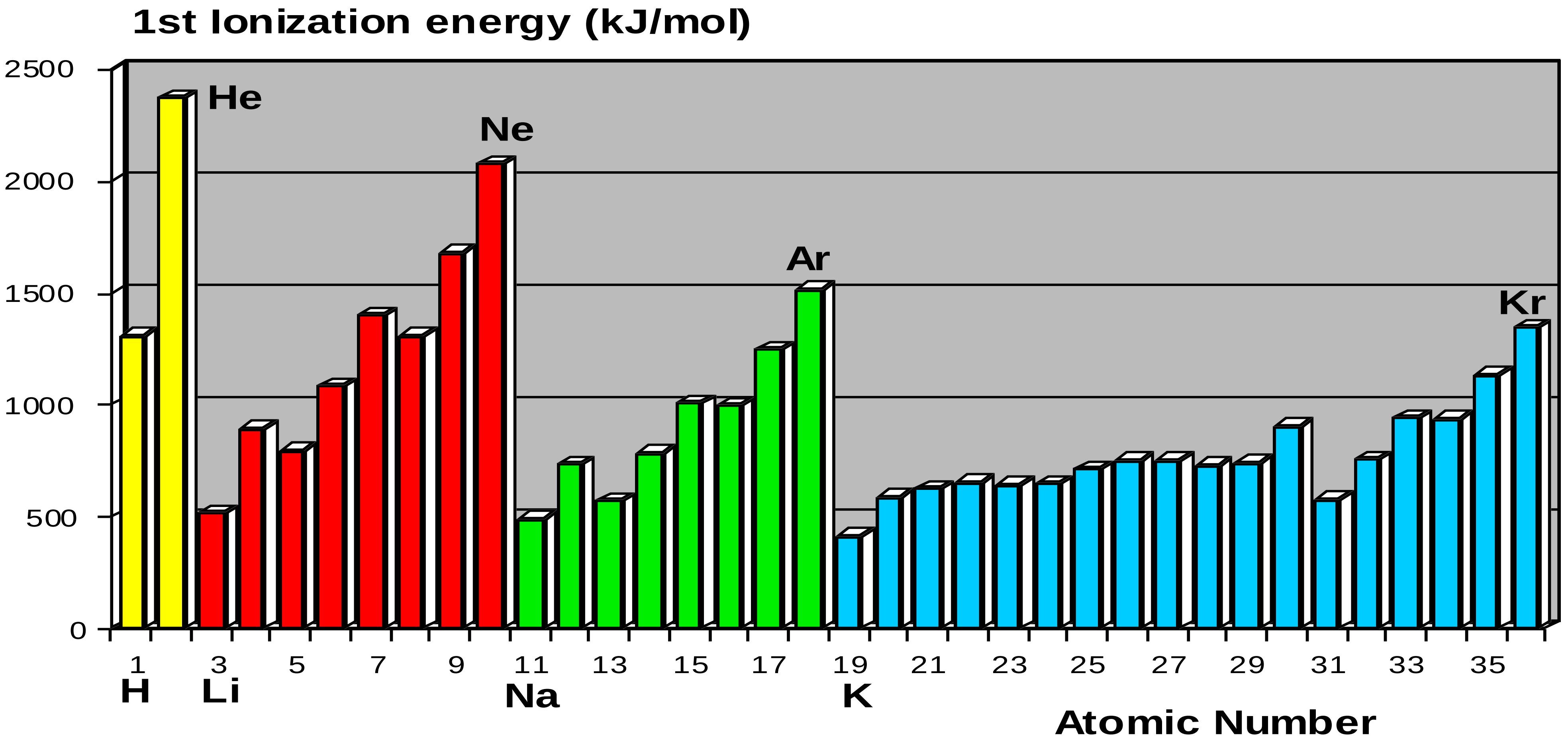
The Values of First Ionization Energy for The Elements in the First Six Periods





First ionization energy, kJ/mol
Atomic number
2500
2000
1500
1000
500
10
20
30
40
50
60
70
80
90
100
He
Ne
Ar
Kr
Xe
Hg
Rn
Zn
Cd
Li
Na
Al
K
Ga
Rb
In
Cs
Tl
Fr

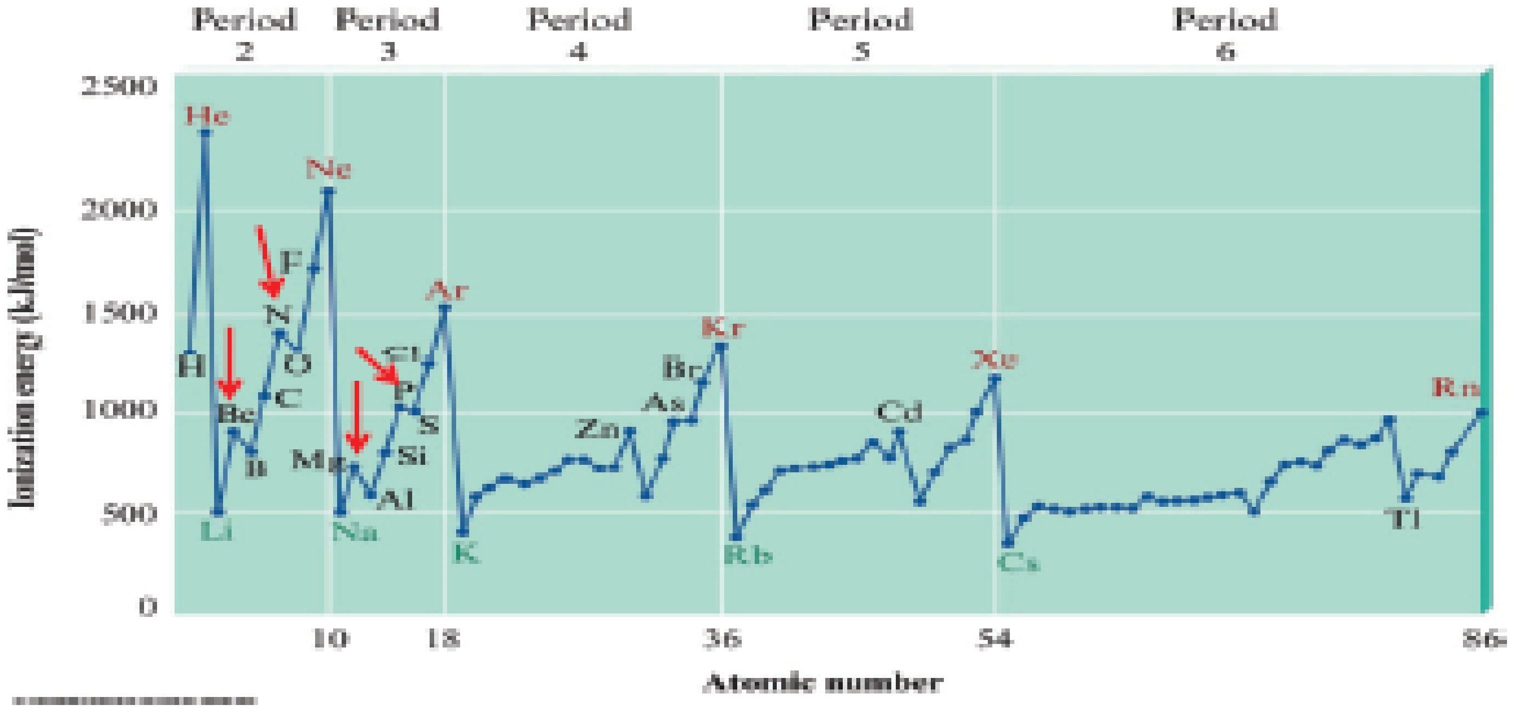
Trends in Ionization Energy



Trends in Ionization Energies for the Representative Elements

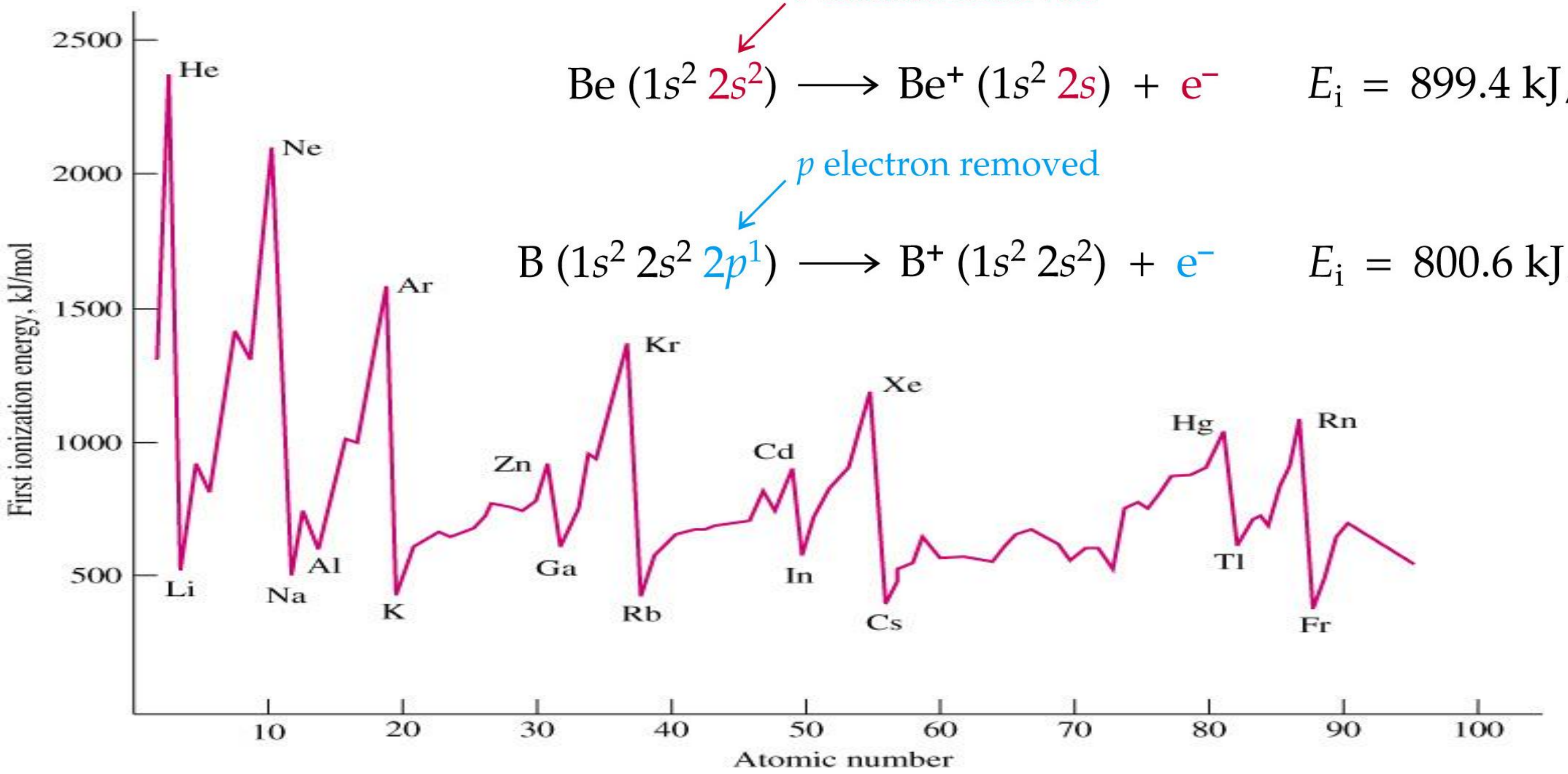
	1A	2A	3A	4A	5A	6A	7A	8A
1	H 1311							He 2377
2	Li 520	Be 899	B 800	C 1086	N 1402	O 1314	F 1681	Ne 2088
3	Na 495	Mg 735	Al 580	Si 780	P 1060	S 1005	Cl 1255	Ar 1527
4	K 419	Ca 590	Ga 579	Ge 761	As 947	Se 941	Br 1143	Kr 1356
5	Rb 409	Sr 549	In 558	Sn 708	Sb 834	Te 869	I 1009	Xe 1176
6	Cs 382	Ba 503	Tl 589	Pb 715	Bi 703	Po 813	At (926)	Rn 1042

First Ionization Energies for the Elements in the First Six Periods



- Ionization energy increases across a period from left to right
  With each increase in Z, electrons go into the same shell
  -- Not very effective in shielding the increased nuclear charge
- Ionization energy falls with increasing period number (going down the table)
  Each period starts filling a new shell that's farther from the nucleus
- Atoms with **filled or half-filled subshells** appear to have anomalously high ionization energies (**more stable than the atoms on their left or right**)

why there are valleys along the way?



s electron removed

$$\text{Be}\ (1s^2\ 2s^2) \longrightarrow \text{Be}^+\ (1s^2\ 2s) + e^- \qquad E_i = 899.4\ \text{kJ/mol}$$

p electron removed

$$\text{B}\ (1s^2\ 2s^2\ 2p^1) \longrightarrow \text{B}^+\ (1s^2\ 2s^2) + e^- \qquad E_i = 800.6\ \text{kJ/mol}$$

Why the mini valley between O and N?

N charges more because it is half-filled; O gets to be half-filled so charges less

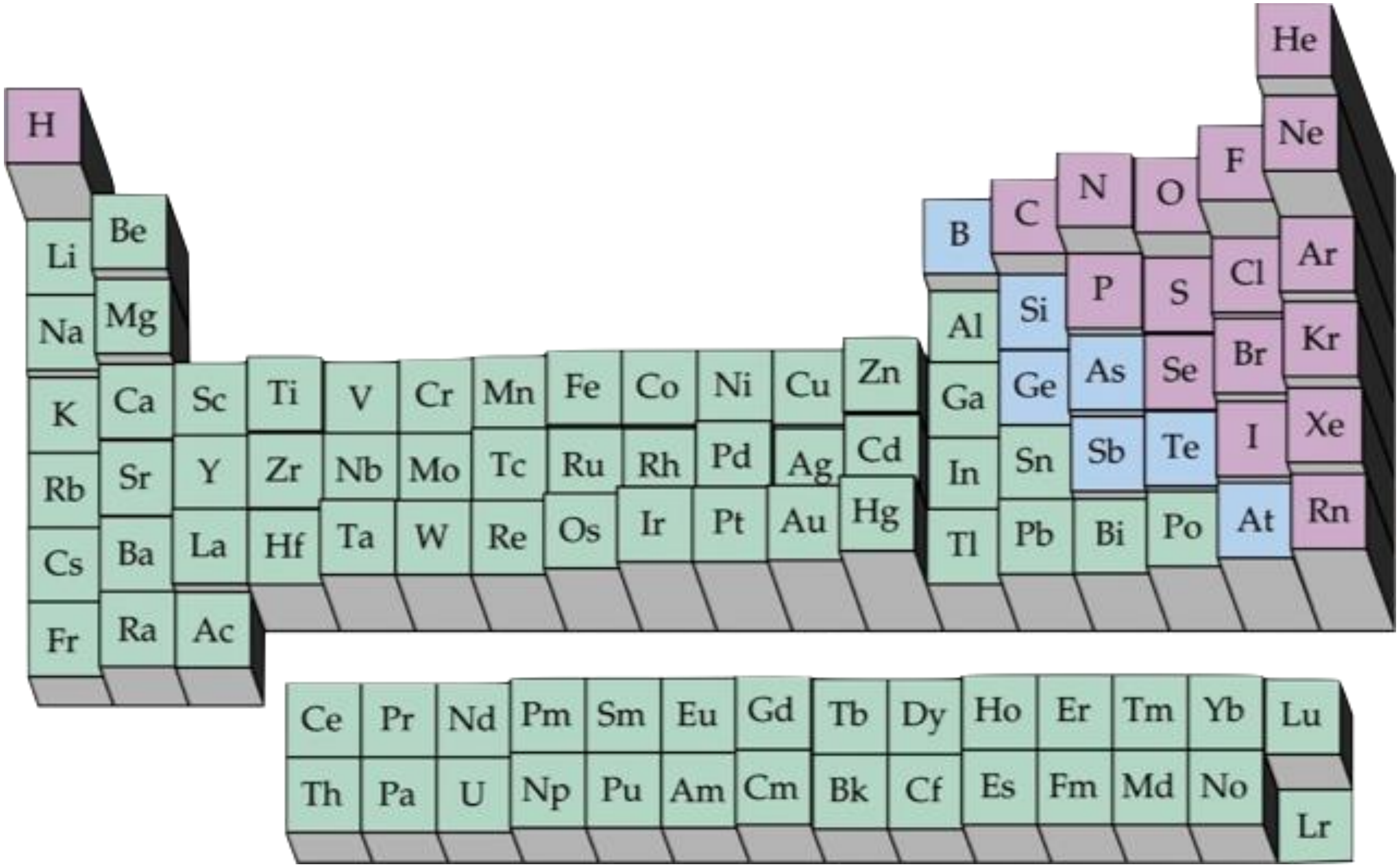
O is lower than N

- **N: [He]$2s^2$ $2p^3$**
- **O: [He]$2s^2$ $2p^4$**

- Hund's rule: 3 e- in the 2p orbitals of a nitrogen atom all have the same spin, but e- are paired in one of the 2p orbitals of oxygen
  - Electrons try to stay as far apart as possible to minimize repulsion
- Force of repulsion between these electrons is minimized to some extent by pairing electrons
  - Slightly easier to remove an electron

why the decrease from He to Ne?...

- this shows relative ionization energy
- which side doesn't like losing electrons?



2nd IE is greater than the 1st IE

- Take an electron away and there is less electron-electron repulsion and the remaining electrons will move in tighter
- and trying to take an electron from a cation is difficuilty
- Removing electrons gets tougher until you lose a whole shell, then it can’t happen

Table 7.5 | Successive Ionization Energies (kJ/mol) for the Elements in Period 3

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

*Note the large jump in ionization energy in going from removal of valence electrons to removal of core electrons.

General decrease (down the table) — General increase (across the table)

Why the increase in Ionization Energies?

- Successive ionisation energies become increasingly larger

$Li(g) \rightarrow Li^+(g) + e^-$	$IE_1 = 520$ kJ
$Li^+(g) \rightarrow Li^{2+}(g) + e^-$	$IE_2 = 7297$ kJ
$Li(g) \rightarrow Li^{2+}(g) + 2e^-$	$IE_{total} = 7817$ kJ

$$IE_1 < IE_2 < IE_3 \ldots$$

- **The primary factor is simply charge.**
  - ✓ Note that the first e is removed from a neutral atom. 2nd e removed from a more positive ion.
  - ✓ The increase in positive charge binds the electrons more firmly, and the ionization energy increases
  - ✓ Sharp increase in I when inner-shell electrons are removed

Example!

1. Explain why the graph of ionization energy versus atomic number (across a row) is not linear

   Electron Repulsions

2. What are the Exceptions?

   Some include from Be to B and N to O

3. Which atom would require more energy to remove an electron? Why?

   Na **Cl**

   Cl would require more energy to remove an electron because the electron is more tightly bound due to the increase in effective nuclear charge.

   Li Cs

   Li would require more energy to remove an electron because the outer electron is on average closer to the nucleus (so more tightly bound).

4. Which has the larger second ionization energy? Why?

   Li Be

   Lithium has the larger second ionization energy because then we are trying to remove a "core" electron, which will require a lot more energy than a valence electron (lower shell is closer to the nucleus, and is more tightly bound).

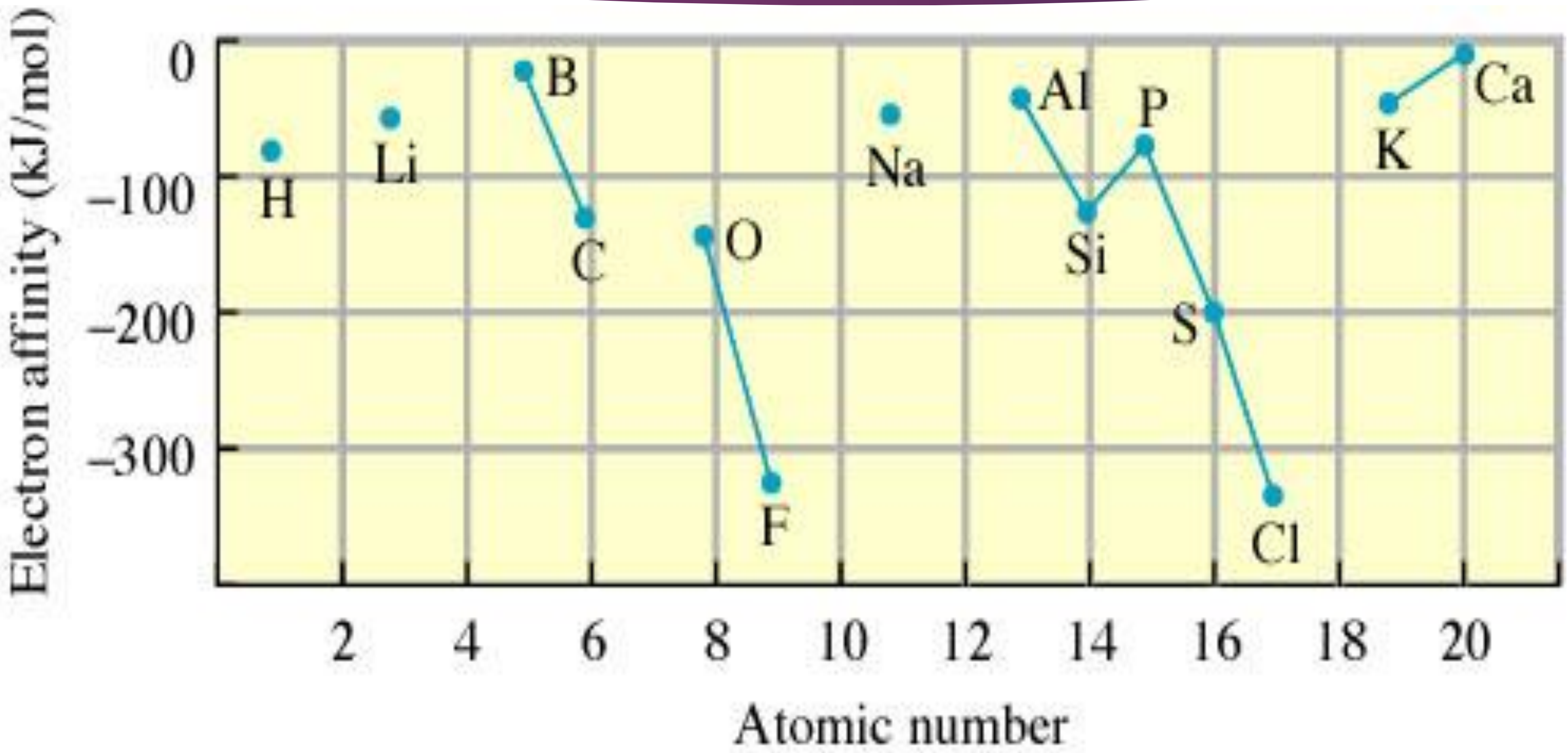
Electron Affinity

- The energy change associated with the addition of an electron to a gaseous atom.

$$X(g) + e^- \rightarrow X^-(g)$$

- These values tend to be exothermic (energy released). Adding an electron to an atom causes it to give off energy. So the value for electron affinity will carry a negative sign.
- throw an electron onto an element
  - ✓ if energy is given off, it is more stable
  - ✓ if energy is needed to keep it there, it is less stable
- details not easy; just pretend it is the love an element has for electrons

The Electronic Affinity Values for Atoms Among the First 20 Elements that Form Stable, Isolated X^- Ions



Electron Affinity

- The more non-metal or higher the electronegativity of an atom the greater (more negative) is the E.A. (A better oxidizing Agent)
- Although electron affinities generally become more negative from left to right across a period, there are several exceptions to this rule in each period/group. Eg in the halogens:
  - ✓ This smaller energy release for F has been attributed to the **small size of the 2p orbitals.**
  - ✓ Because the electrons must be very close together in these orbitals, there are **unusually large electron–electron repulsions**.
  - ✓ In the other halogens with their larger orbitals, the repulsions are not as severe

Table 7.7 ▶ Electron Affinities of the Halogens

Atom	Electron Affinity (kJ/mol)
F	−327.8
Cl	−348.7
Br	−324.5
I	−295.2

Example!

Why is EA so poor for nitrogen?

$N(g) + e^- \longrightarrow N^-(g)$ EA > 0 (unstable)

$1s^22s^22p^3$ $1s^22s^22p^4$

(e^- must go into occupied orbital), loose half filling.

- ✓ The incoming electron would have to occupy a 2 p orbital that already contains one e.
- ✓ The extra repulsion between the electrons in this doubly occupied orbital causes $N^-(g)$ to be unstable.

❖ **Consider Carbon too:**

- ✓ When an e is added to carbon ($1s^22s^22p^2$) to form the $C^-_{(g)}$ ion ($1s^22s^22p^3$), no such extra repulsions occur.

How do these arguments do for O?

- The oxygen atom can add one electron to form the stable O^- (g) ion
- Presumably oxygen's greater nuclear charge compared with that of N is sufficient to overcome the repulsion associated with putting a second electron into an already occupied 2p orbital.

✓ However, it should be noted that a 2nd e, cannot be added to an oxygen atom to form an isolated oxide ion.

✓ This seems strange since we have a stable O^{2-} in various compounds.

✓ The O^{2-} ion is stabilized in ionic compounds by the large attractions that occur among the positive ions & the oxide ions.

$O(g) + e^- \longrightarrow O^-(g)$ EA = -140 kJ/mol

$1s^22s^22p^4$ $1s^22s^22p^5$ Bigger Z^+ overcomes e^- repulsion.

- What about the second EA for O?

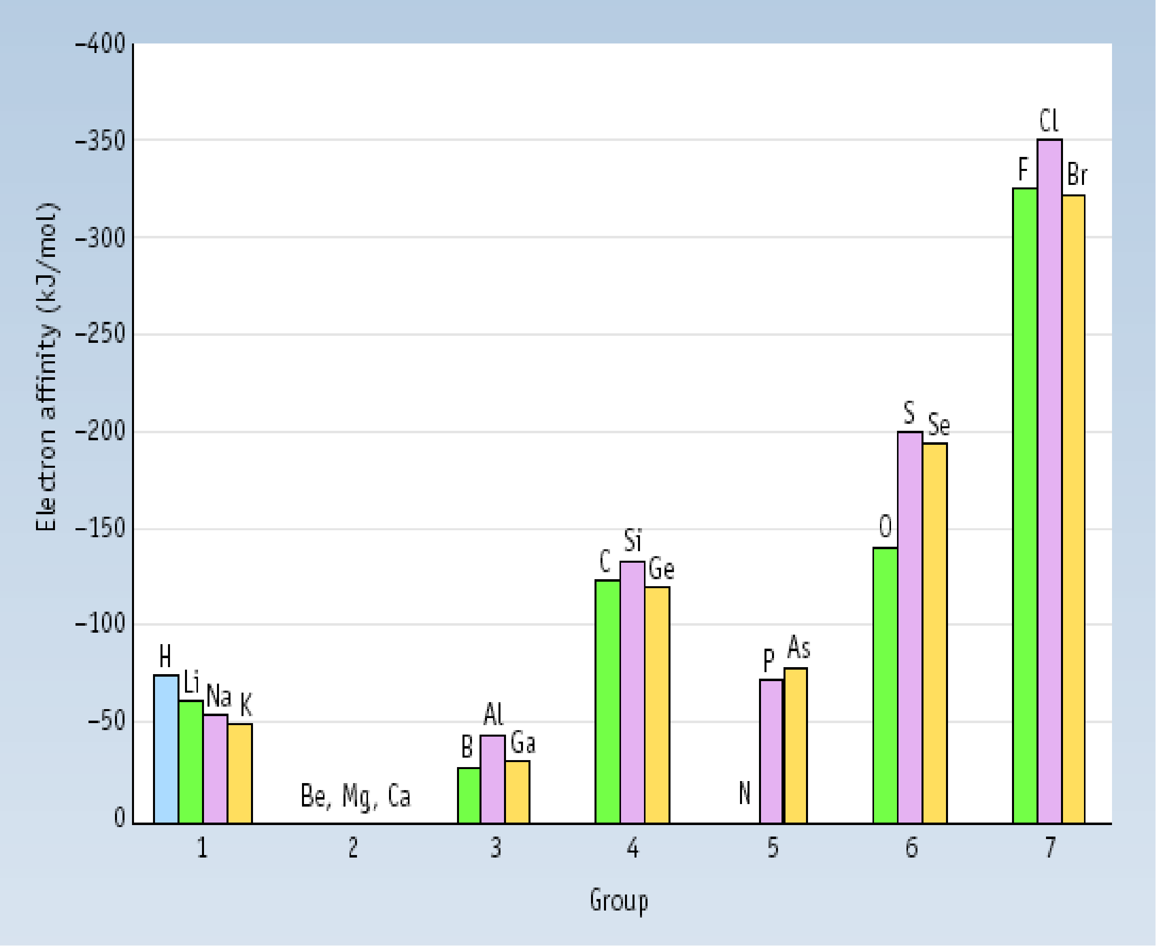
$O^-(g) + e^- \longrightarrow O^{2-}(g)$ EA > 0 (unstable)

$1s^22s^22p^5$ $1s^22s^22p^6$

[Ne] configuration, but electron repulsion is just too great.

Trends in Electron Affinity

- ***Halogens (group 7A, F to At)***
  - ✓ *Most negative EA values, addition of an e^- leads to noble gas configuration, very favorable.*
- ***Group 5A (N to Bi)***
  - ✓ *½ filled shell discourages addition of an electron, EA values less negative than neighbors (groups 4A & 6A).*
- ***Alkaline Earths (group 2A, Be to Ba)***
  - ✓ *Filled s subshell discourages addition of an electron, EA values nearly zero.*
- ***Noble Gases (Group 8A, He to Rn)***
  - ✓ *Completely filled shell strongly discourages addition of an electron, EA values are positive.*
- ***3rd period more negative than 2nd period***
  - ✓ *atoms are larger, more space for the electrons, repulsion between electrons less, more favorable*



In general :

- as we go across a period from left to right, the electron affinities become more negative.

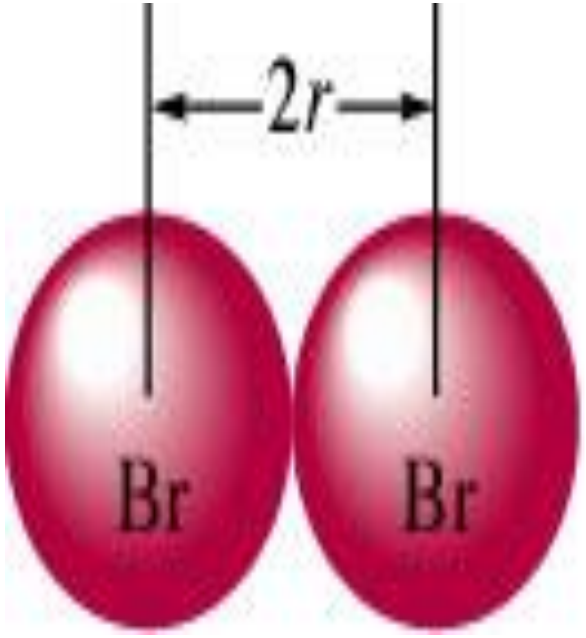
- becomes more positive in going down a group.

1	2	13	14	15	16	17	18
H −72.8							He - -
Li −59.6	Be - -	B −26.7	C −153.9	N −7	O −141.0	F −328.0	Ne - -
Na −52.9	Mg - -	Al −42.5	Si −133.6	P −72	S −200.4	Cl −349.0	Ar - -
K −48.4	Ca - -	Ga −28.9	Ge −119.0	As −78	Se −195.0	Br −324.6	Kr - -
Rb −46.9	Sr - -	In −28.9	Sn −107.3	Sb −103.2	Te −190.2	I −295.2	Xe - -
Cs −45.5	Ba - -	Tl −19.2	Pb −35.1	Bi −91.2	Po −186	At −270	Rn - -

Atomic Radii

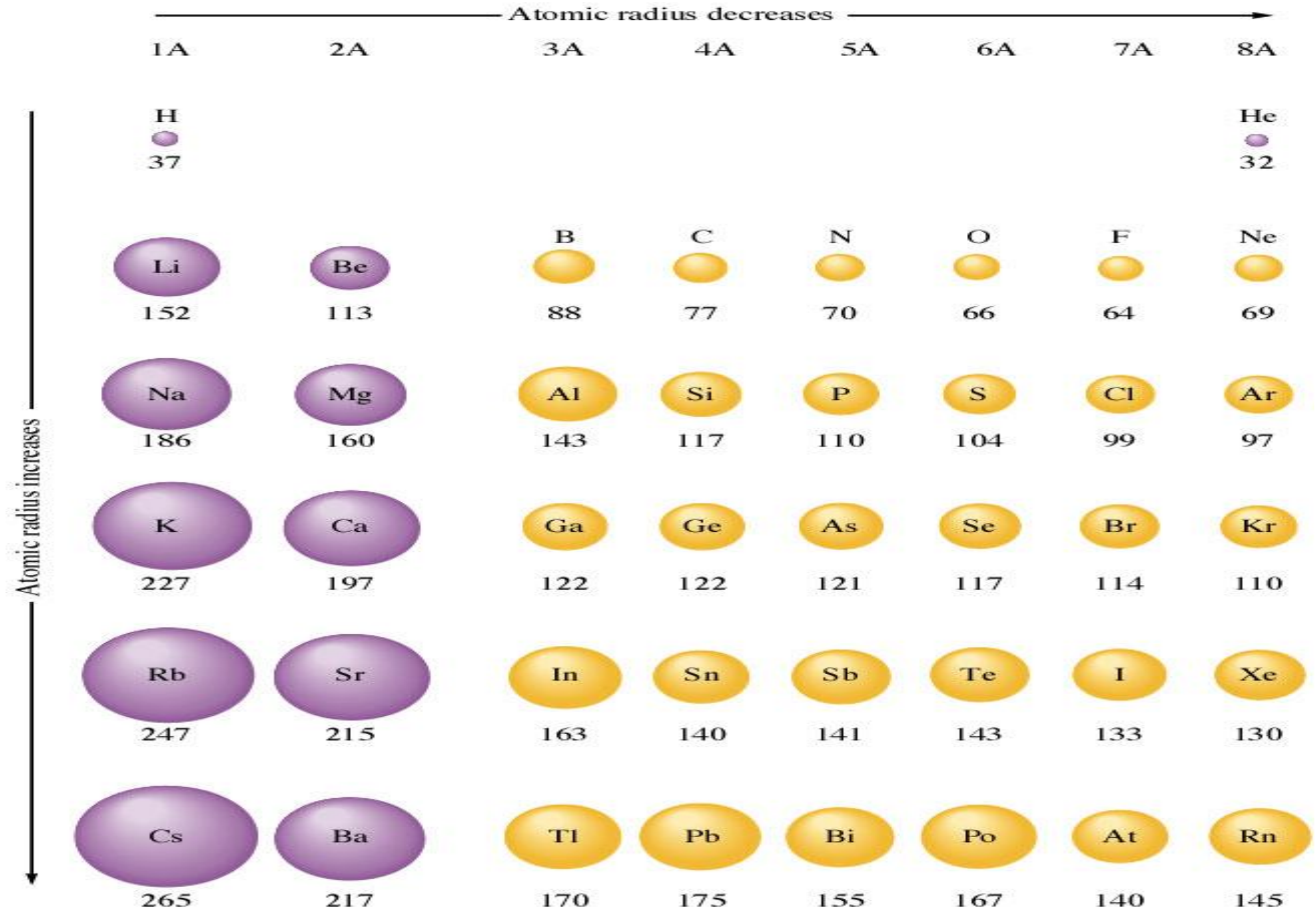
Can be obtained by measuring the distances between atoms in chemical compounds and atomic radius is assumed to be half this distance.

- Decreases going from left to right across a period.
  - This decrease can be explained in terms of the increasing effective nuclear charge in going from left to right.
  - The valence electron are drawn closer to the nucleus, decreasing the size of the atom.
- Increases going down a group,
  - because of the increase in orbital sizes in successive principal quantum levels.

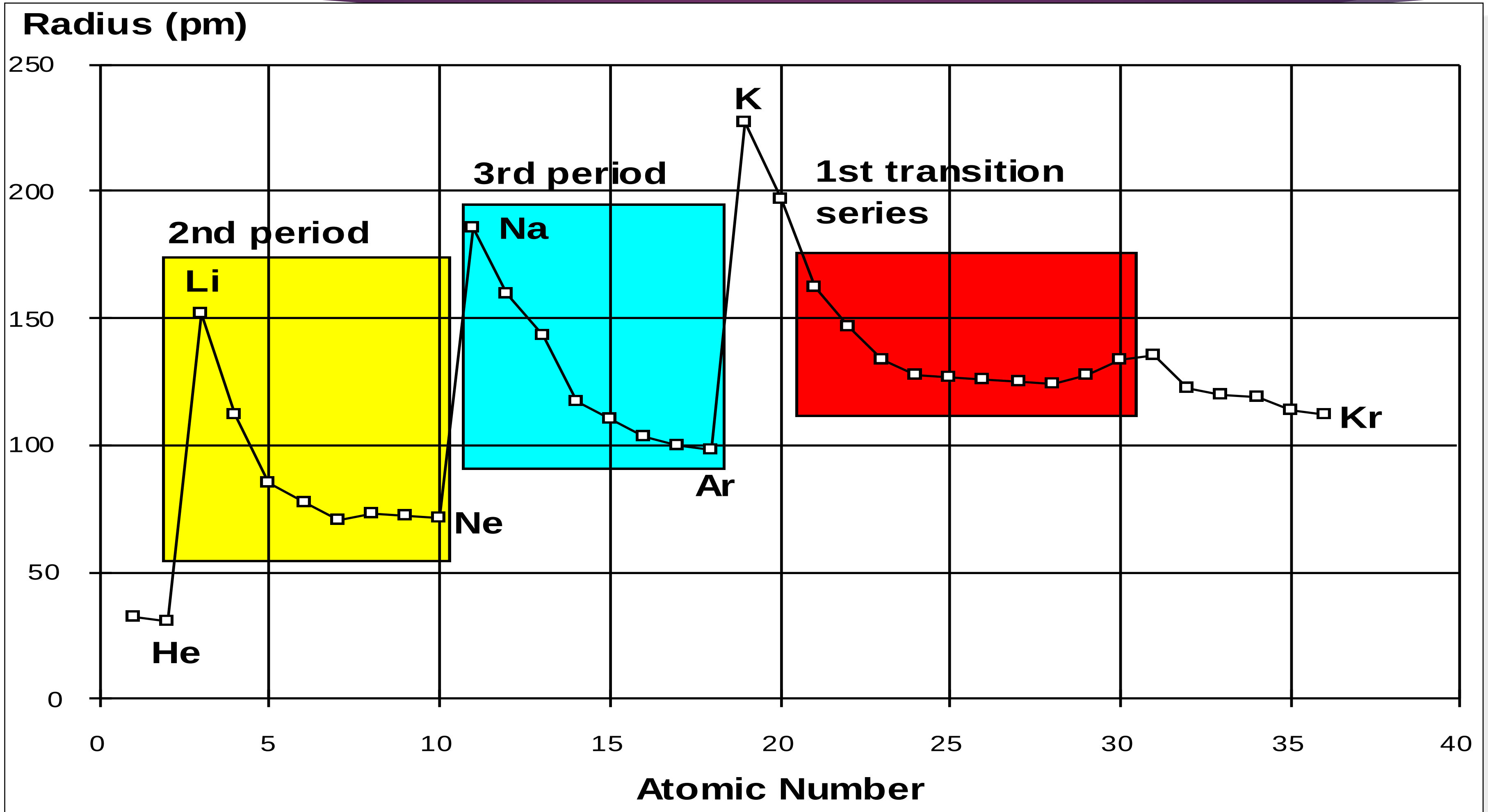


The Radius of an Atom

Atomic Radii for Selected Atoms



Trends in Atomic Size



Ionic Size/radius Trends

- When atom gains an electron (anion), the size increases i.e. sizes of ion is greater than neutral atom.

$$X^{3-} > X^{2-} > X^{-} > X$$

  - ✓ Reason: When electrons are added mutual repulsion between electrons increases. Electrons push each other apart

- When electrons are removed (cation) the size decreases i.e. cation size is smaller than the neutral atom.

$$A^{3+} < A^{2+} < A^{+} < A$$

  - ✓ Electron-electron repulsions reduce when electrons are removed allowing remaining electrons to be drawn closer around the nucleus.

CONCEPT CHECK!

1. Which should be the larger atom? Why?

   Na Cl

   Na should be the larger atom because the electrons are not bound as tightly due to a smaller effective nuclear charge.

   Li **Cs**

   Cs should be the larger atom

   Size of the atom is determined by the size of its valence shell
   For elements in a given Group (i.e. a column of the periodic table):
   The larger the principal quantum number (*n*) of its valence shell, the larger the shell, and the larger the atom

2. Which is larger?
   - ❑ **The hydrogen 1s orbital**
   - ❑ The lithium 1*s* orbital

   The hydrogen 1s orbital is larger because the electrons are not as tightly bound as the lithium 1s orbital

   Lithium has a higher effective nuclear charge and will thus draw in the inner electrons more closely.

3. Which is lower in energy?
   - ❑ The hydrogen 1*s* orbital
   - ❑ **The lithium 1*s* orbital**

   The lithium 1s orbital is lower in energy because the effective nuclear charge is larger and the electrons are closer to the nucleus.

4. Arrange the elements oxygen, fluorine, and sulfur according to increasing:
   - ❑ Ionization energy
   - ❑ Atomic size

   • Ionization energy
   S, O, F

   IE increases as we go up a column and to the right across a period

   • Atomic size
   F, O, S

   Atomic radius increases as we go left across a period and down a column

Electronegativity

- The different affinities of atoms for the electrons in a bond are described by a property called **electronegativity**
- Measure of the attraction of an atom for the electrons in a chemical bond.
- Flourine rules here: the closer you get to F the more electronegative it is.
- The range of electronegativity values is from 4.0 for fluorine (the most electronegative) to 0.7 for cesium (the least electronegative).
- Valence electrons hold atoms together in compounds.
- In many compounds, the negative charge of the electrons is concentrated closer to one atom than another.

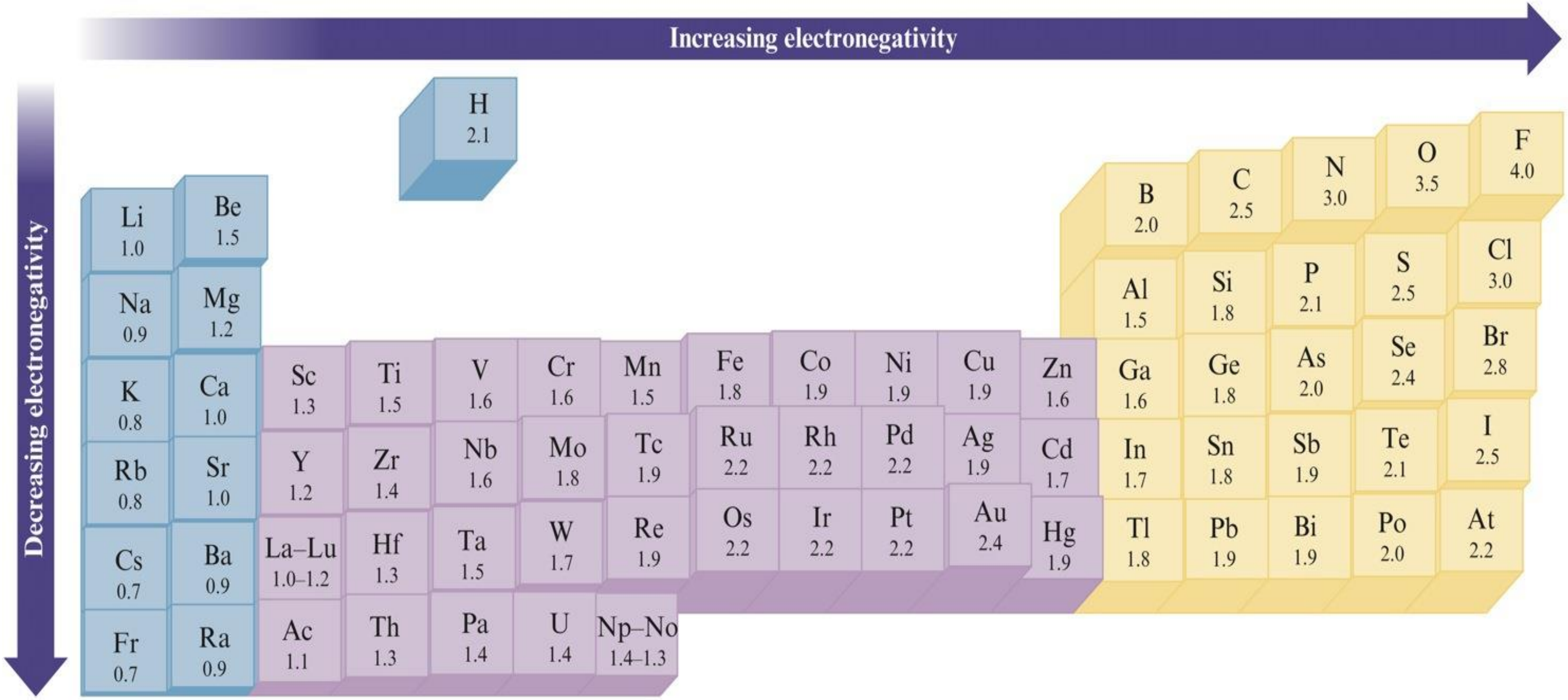
Electronegativity

- The higher the electronegativity of an atom, the greater its attraction for bonding electrons.
- It is related to ionization energy.
- Elements with low ionization energies have low electronegativities (nuclei do not exert a strong attractive force an electrons.)
- Those with high ionisation energies have high electronegativities (strong pull exerted on electrons by the nucleus (effective nuclear charge)

Electronegativity

- Electronegativity generally *increases across rows,* & *decreases down a group*
- It is measured on an arbitrary scale that ranges from 0 to 4.
- The units of electronegativity are Paulings.
- Generally, It is high for the nonmetals with fluorine as the highest. It is low for the metals.
  - ✓ metals are electron givers & have low electronegativities.
  - ✓ Nonmetals are electron takers and have high electronegativities

The Pauling Electronegativity Values



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.8	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac† 1.1														

below 1.0

1.0–1.4

1.5–1.9

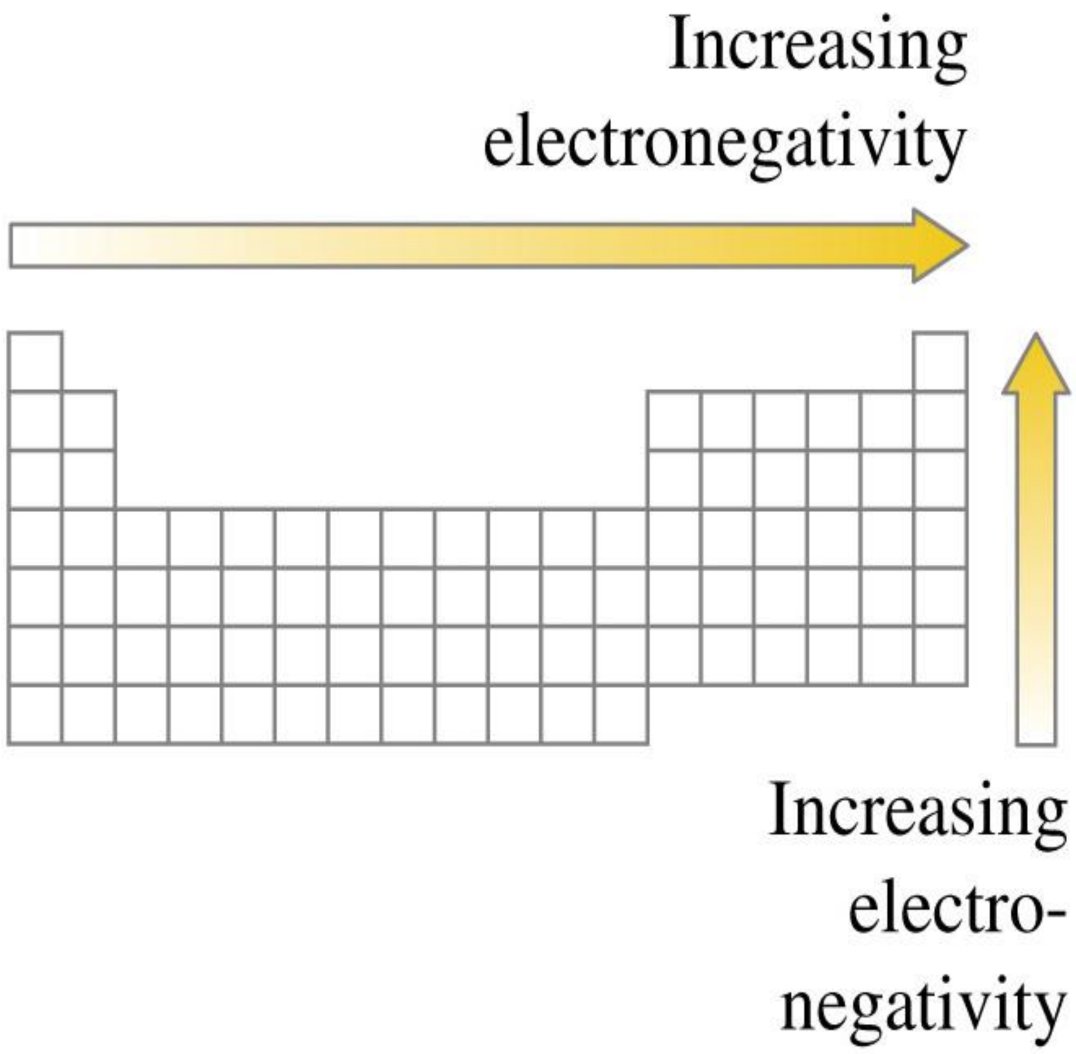
2.0–2.4

2.5–2.9

3.0–4.0

*Lanthanides: 1.1–1.3

†Actinides: 1.3–1.5



CONCEPT CHECK!

If lithium and fluorine react, which has more attraction for an electron? Why?

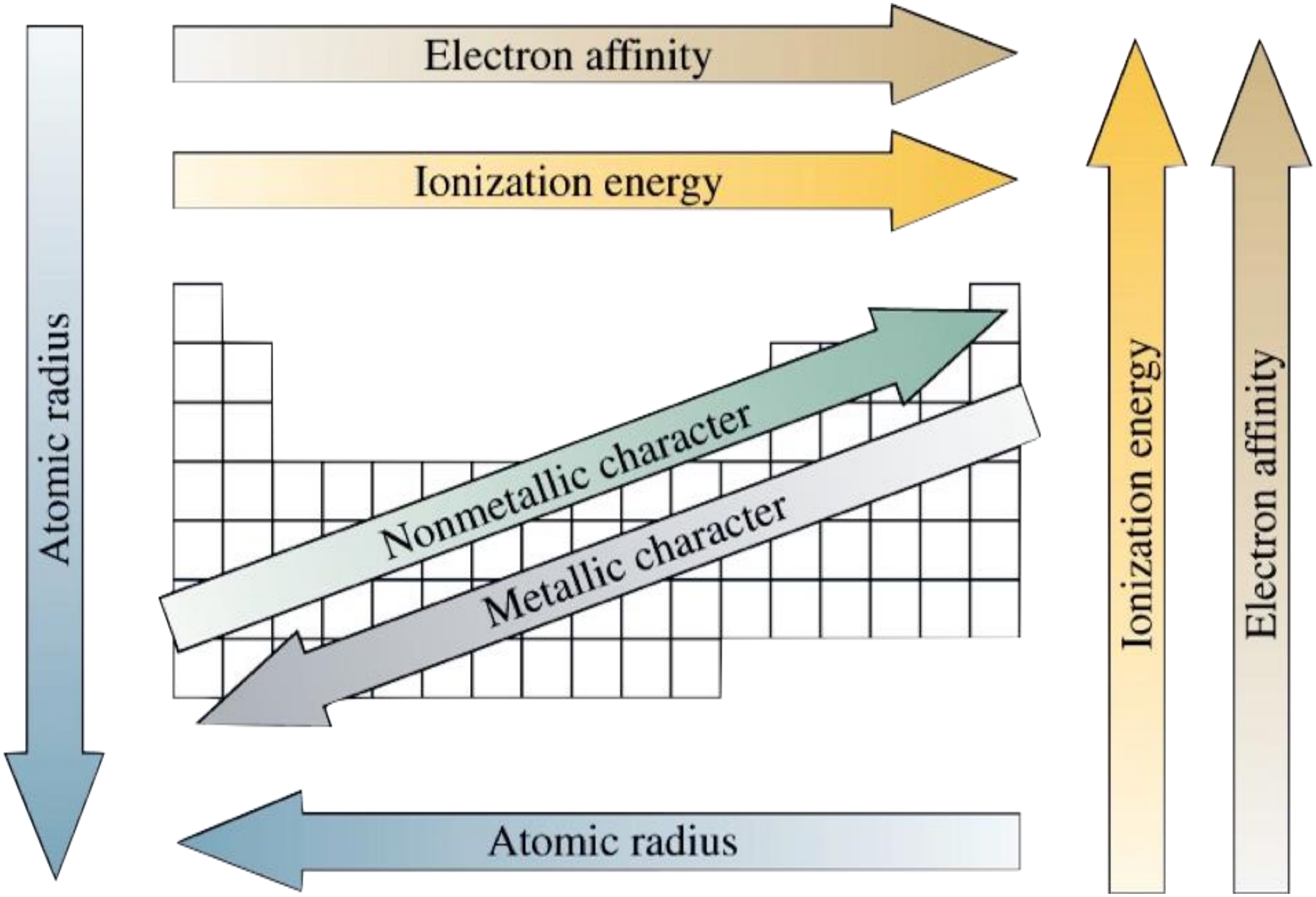
In a bond between fluorine and iodine, which has more attraction for an electron? Why?

What is the general trend for electronegativity across rows and down columns on the periodic table?

Explain the trend.

Summary of Key Concepts

- Electromagnetic Radiation: Wavelength like behavior.
- The Bohr Model: electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits.
- Quantum Mechanic model of an atom
- Heisenberg Uncertainty Principle: Position and momentum cannot be determined precisely at a given time.
- Quantum Numbers: Principal QN, Angular momentum QN, Magnetic QN, an Electron Spin QN.
- Orbital Shapes and Energies: s, p, and d orbitals.
- Pauli Exclusion Principle:
- Aufbau Principle:
- Hund's Rule
- Periodic Table:
- Periodic Trends:
  - ✓ Ionization Energy:
  - ✓ Electron Affinity
  - ✓ Atomic Radius

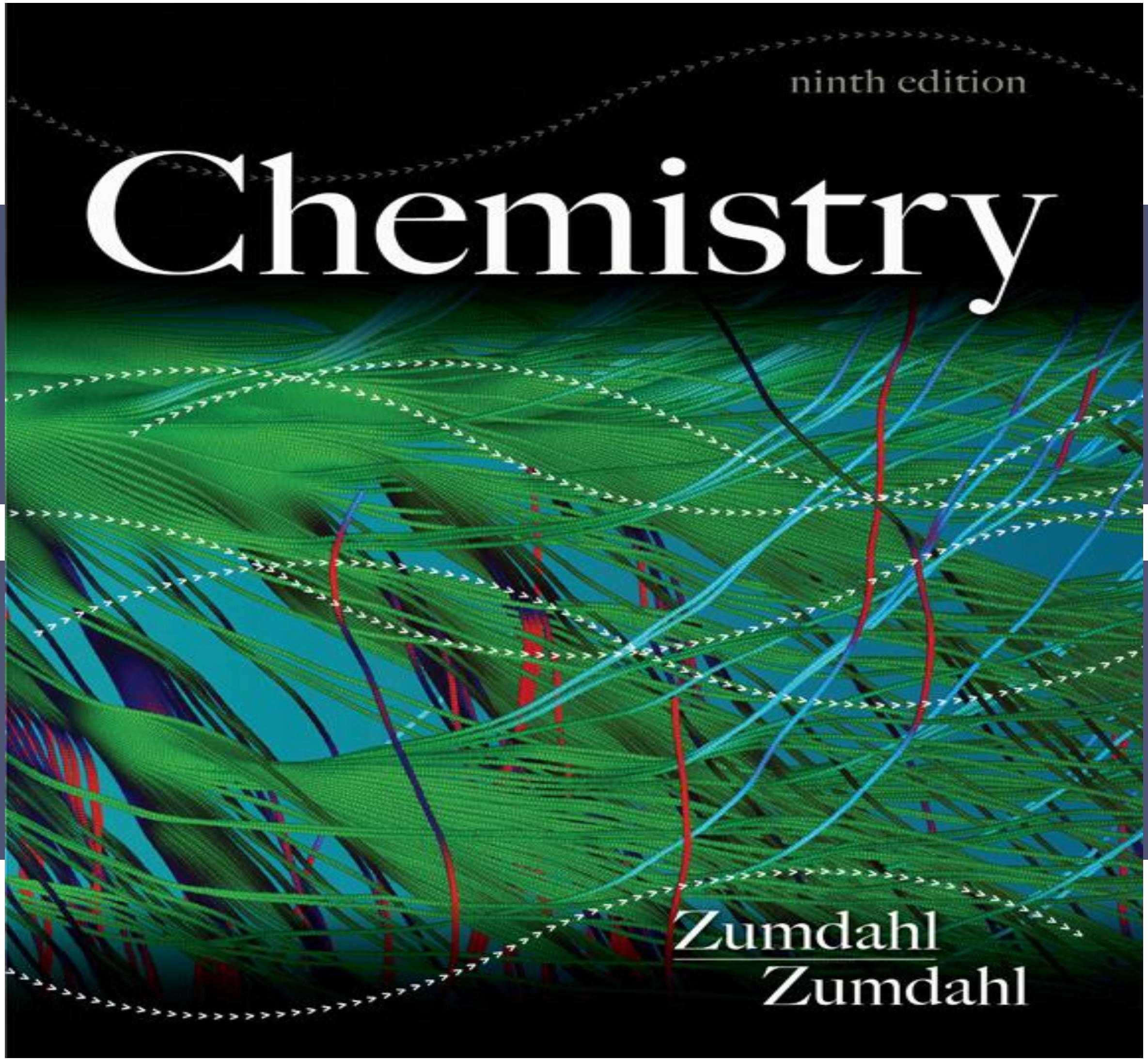


Electron affinity
Ionization energy
Atomic radius
Nonmetallic character
Metallic character
Atomic radius
Ionization energy
Electron affinity

Okanagan

Key Equations

- $u = \lambda \nu$ (7.1) Relating speed of a wave to its wavelength and frequency.
- $E = h\nu$ (7.2) Relating energy of a quantum (and of a photon) to the frequency.
- $E_n = -R_H\left(\frac{1}{n^2}\right)$ (7.4) Energy of an electron in the *n*th state in a hydrogen atom.
- $\Delta E = h\nu = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ (7.5) Energy of a photon emitted as the electron undergoes a transition from the n_i level to the n_f level.
- $\lambda = \frac{h}{mu}$ (7.7) Relating wavelength of a particle to its mass m and velocity u.
- $\Delta x \Delta p \geq \frac{h}{4\pi}$ (7.8) Calculating the uncertainty in the position or in the momentum of a particle.



Chapter 8

Bonding: General Concepts

Objectives

- To learn about ionic and covalent bonds and explain how they are formed
- To learn about the polar covalent bond
- To understand the nature of bonds and their relationship to electronegativity
- To understand bond polarity and how it is related to molecular polarity
- To learn about stable electron configurations
- To learn to predict the formulas of ionic compounds
- To learn about ionic structures
- To understand factors governing ionic size
- To learn to write Lewis structures
- To learn how to write Lewis structures for molecules with multiple bonds
- To understand molecular structure and bond angles
- To learn to predict molecular geometry from the number of electron pairs
- To learn to apply the VSEPR model to molecules with double bonds

CHEMICAL BONDING

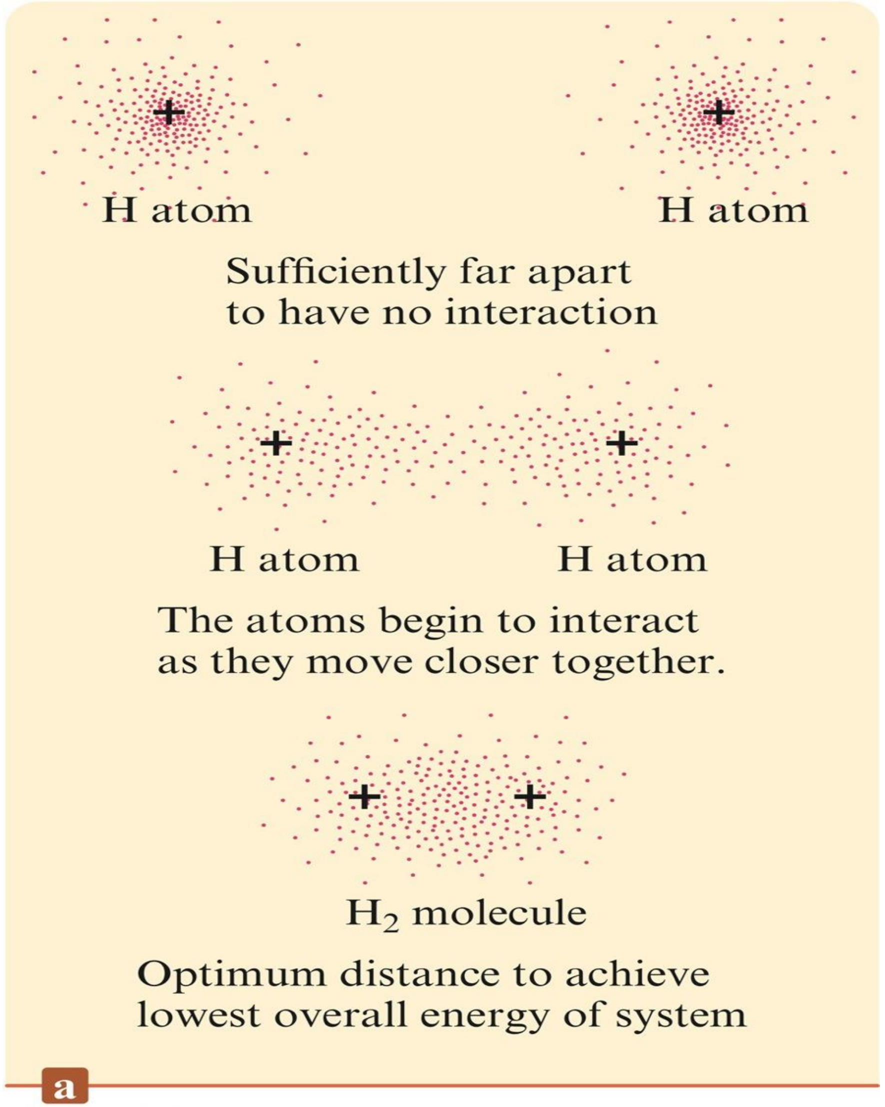
Questions to Consider

- What is meant by the term “chemical bond”?
- Why do atoms bond with each other to form compounds?
- How do atoms bond with each other to form compounds?

A Chemical Bond

- No simple, and yet complete, way to define this.
- Forces that hold groups of atoms together and make them function as a unit.
- A bond will form if the energy of the aggregate is lower than that of the separated atoms.
- Chemical bonding is at the heart of understanding chemistry
- Chemical bonds are strong attractive forces hold atoms and ions together in compounds/molecules
- Properties of substances are (in part) determined by chemical bonds

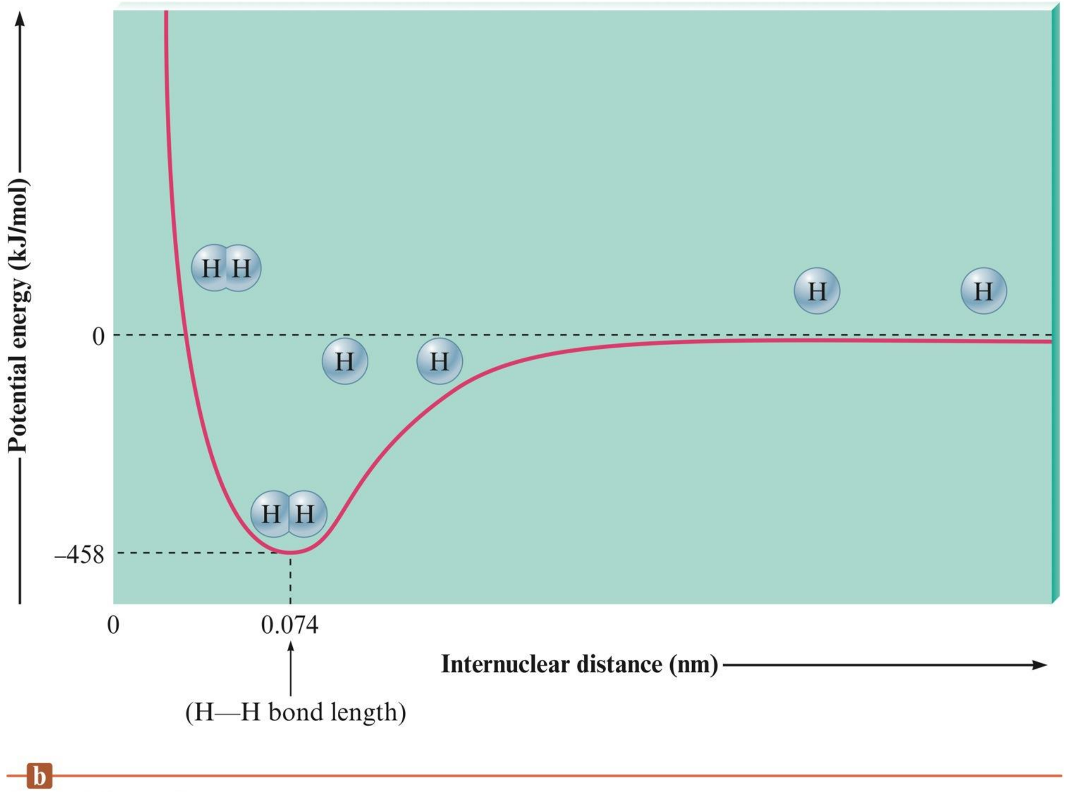
The attraction between two atoms or ions that holds them together to form chemical bond .



Fundamental questions:

Why a chemical bond is formed?

- formed by an atom to get **more stability**. Every atom tries to get more stability by lowering its potential energy. This can be achieved by making a bond.
- The potential energy decreases when two atoms attract each other.
- Hence energy is liberated during the formation of a chemical bond i.e., it is an exothermic process.



What is the connection between stability and electronic configuration?

- The noble gas atoms with octet configuration in their outer shells are very stable. Hence every atom tries to get octet configuration either by losing or gaining or sharing electrons. This is also called as **octet rule**.
- However this rule may not be followed always by the atoms.

TYPES OF CHEMICAL BONDS : A BRIEF INTRODUCTION

Key Ideas in Bonding

The chemical bonds are broadly divided into:

- Ionic Bonding – electrons are transferred
- Covalent Bonding – electrons are shared equally by nuclei
- *What about intermediate cases?*

Ionic bond

- These oppositely charged ions come closer to each other due to electrostatic force of attraction and thus by forming an ionic bond.
- An ionic bond is formed between two atoms when their electronegativity difference is **greater than 1.7 on Pauling's scale.**
- In general, an ionic bond is formed between a metal atom and a nonmetal atom. E.g., NaCl, LiF, $MgCl_2$ etc.,

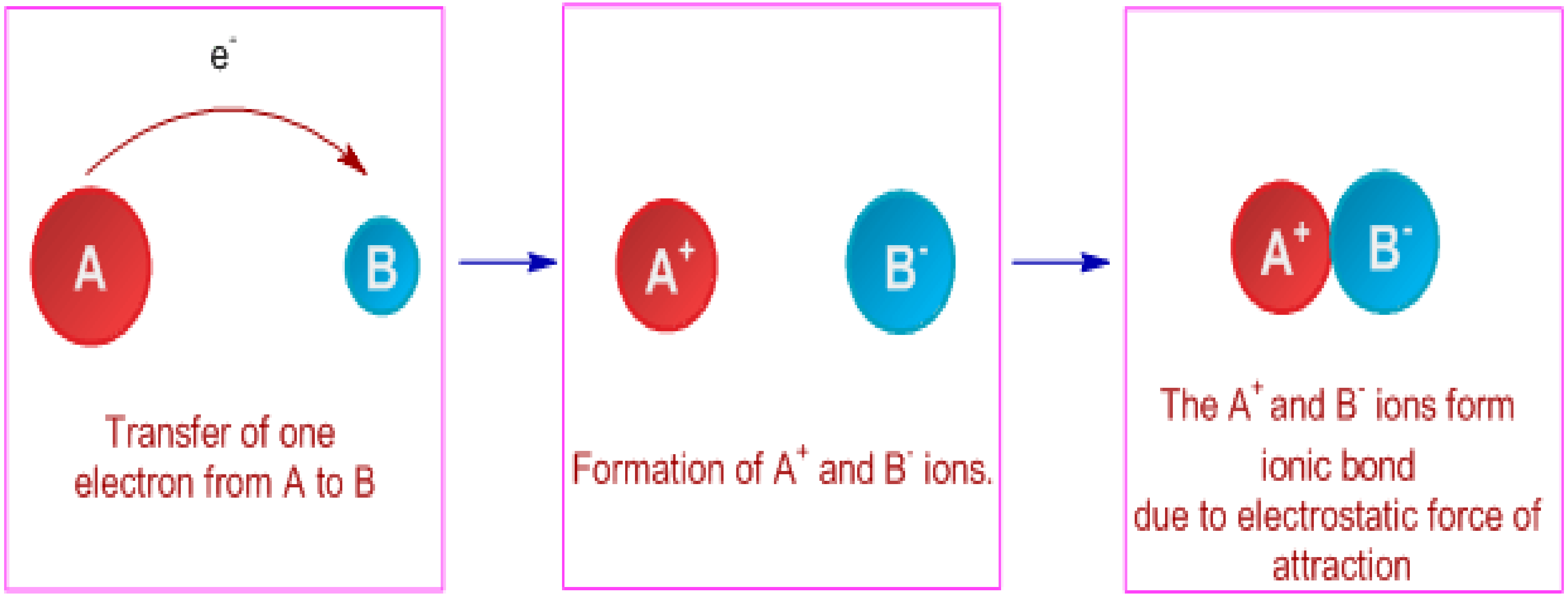
The steps involved in the formation of ionic bond can be summarized as:

a) An electropositive atom (metal) loses electron(s) to form a positively charged ion called as cation.

b) An electronegative atom accepts the electron(s) to form a negatively charged ion, otherwise known as anion.

c) Thus formed oppositely charged ions come closer to each other due to electrostatic force of attraction and get stability.

The formation of ionic bond between two atoms can be visualized as follows:



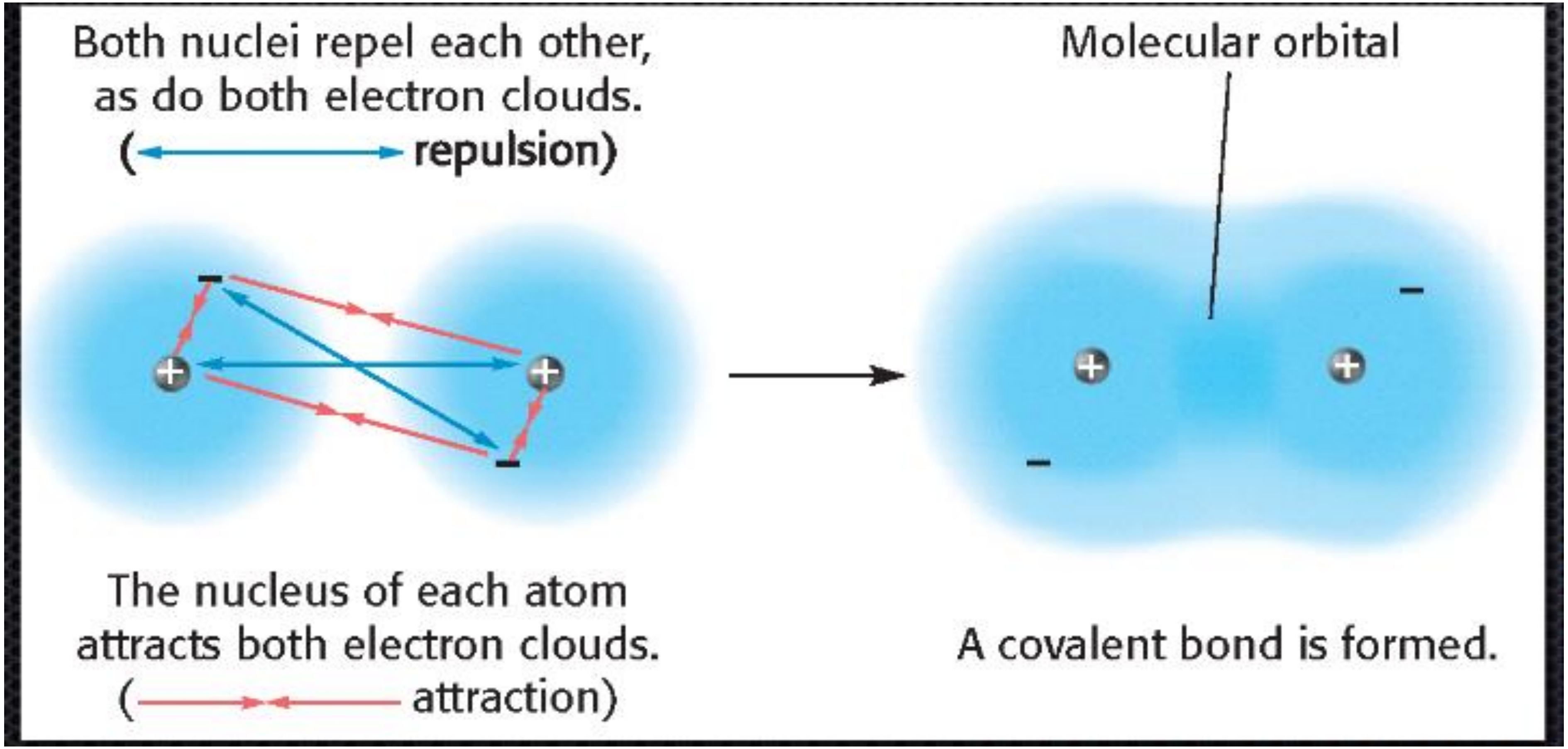
Note that there is decrease in size from A to A^+ and increase in size from B to B^-

Covalent Bond

- The chemical bond formed between two atoms due to the sharing of electron pair(s) is called covalent bond.
- It is formed between two atoms for which the electronegativity difference is less than 1.7 on Pauling's scale.
- Usually two nonmetal atoms form a covalent bond. E.g. H_2, F_2, HCl, H_2O etc.
- The shared pair of electrons, also known as bond pair
- It is either formed due:
  - ✓ to equal contribution of electrons by each atom participating in the bond formation; ..
  - ✓ or contribution by only one atom. This bond is also known as co-ordinate covalent bond or dative bond. ‼

A covalent bond is formed beween two atoms when their electronegativity difference is <u>less than 1.7 on Pauling's scale.</u>

Usually it is formed between two nonmetals.



Polar Covalent Bond

- Unequal sharing of electrons between atoms in a molecule.
- Results in a charge separation in the bond (partial positive and partial negative charge).

δ^- or δ^+

- The Effect of an Electric Field on Hydrogen Fluoride Molecules

For a molecule HX, the relative electronegativities of the H and X atoms are determined by comparing the measured H–X bond energy with the "expected" H–X bond energy.

indicates a positive or negative fractional charge.x

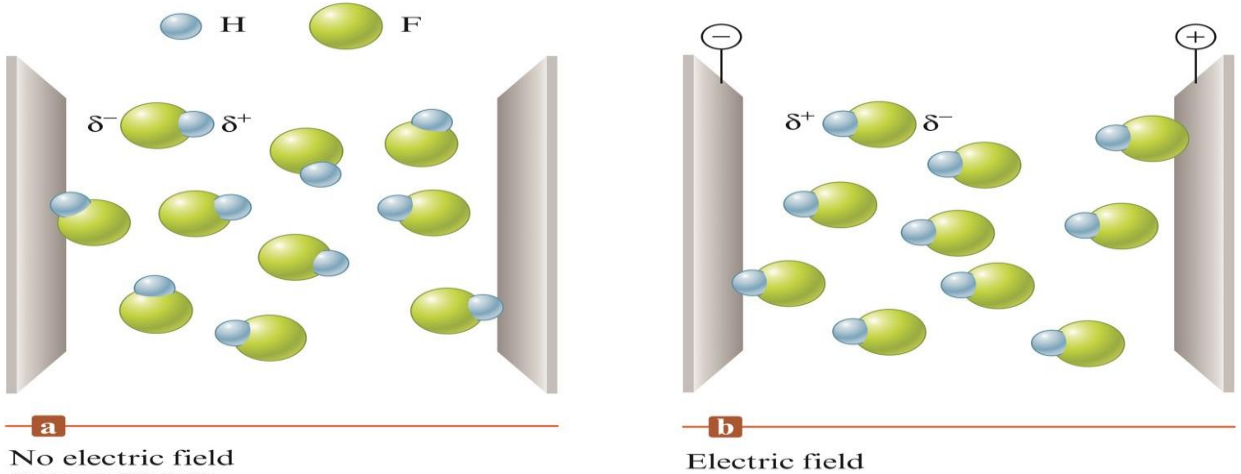
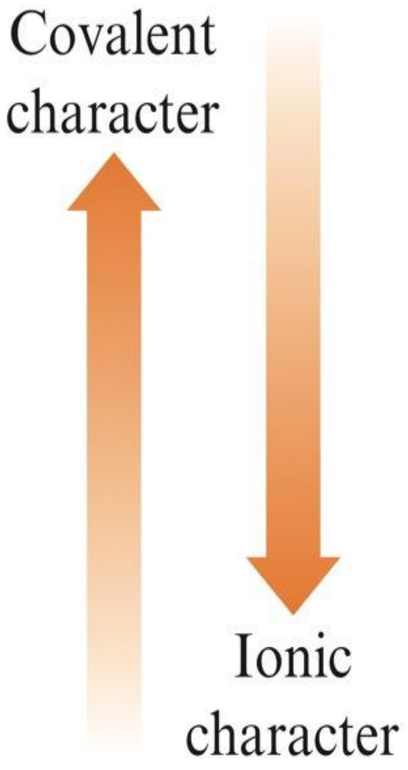


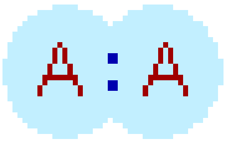
Table 8.1 | The Relationship Between Electronegativity and Bond Type

Electronegativity Difference in the Bonding Atoms	Bond Type
Zero	Covalent
↓	↓
Intermediate	Polar covalent
↓	↓
Large	Ionic



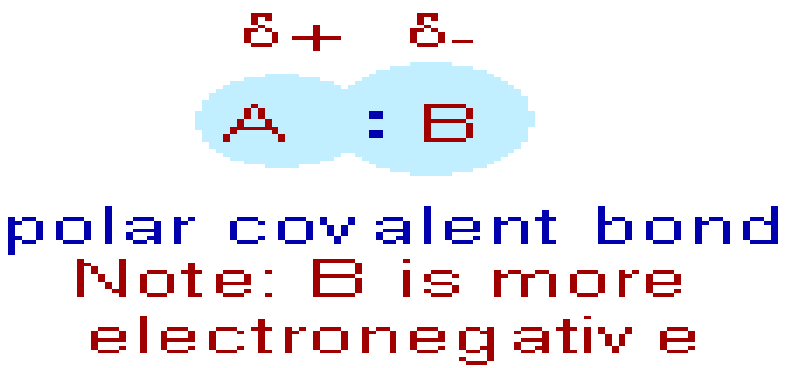
Polarity of covalent bond

- The bond pair is ***equally shared*** in between two atoms *when the electronegativity difference between them is zero or nearer to zero.*
- neither of the atoms gets excess of electron density and hence carry **no** charge.
- This is called **non polar covalent bond**.
- This is true for all *homonuclear diatomic molecu*les, such as H_2, O_2, N_2, F_2, and Cl_2, because the two identical atoms have identical electronegativities.



non polar covalent bond

- When there is a considerable difference in the electronegativity,..
- The bond pair is no longer shared equally between the atoms.
- It is shifted slightly towards the atom with higher electronegativity by creating **partial negative charge** (represented by δ-) over it.
- the atom with less electronegativity gets partial positive charge (represented by δ+).
- This type of bond is also referred to as **polar covalent bond**.



Covalent bonds can have ionic character

Electronegativity

Atoms	Difference		Type of Bond
N-N	3.0 - 3.0 =	**0.0**	Nonpolar covalent
Cl-Br	3.0 - 2.8 =	**0.2**	Nonpolar covalent
H-Si	2.1 - 1.8 =	**0.3**	Nonpolar covalent

- A ***polar bond*** has separate centers of positive and negative charge.

Polar Bond

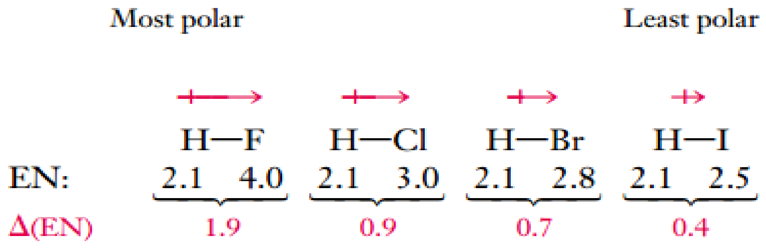
- A ***molecule*** with separate centers of positive and negative charge is a ***polar molecule.***
- The difference in electronegativity between two atoms gives a measure of the polarity between two atoms.
- A polar molecule has a polar bond with a moderate electronegativity difference (0.5 to 1.7) between the two atoms involved in the polar bond.
- In HF, in which the electron pairs are shared unequally are called polar covalent bonds can be represented as:

$$\overset{\delta+}{\mathrm{H}}\!-\!\overset{\delta-}{\mathrm{F}} \quad \text{or} \quad \overset{+\!\!\longrightarrow}{\mathrm{H}\!-\!\mathrm{F}}$$

- This means that the F end of the molecule is somewhat more negative than the H end.

Electric Dipole

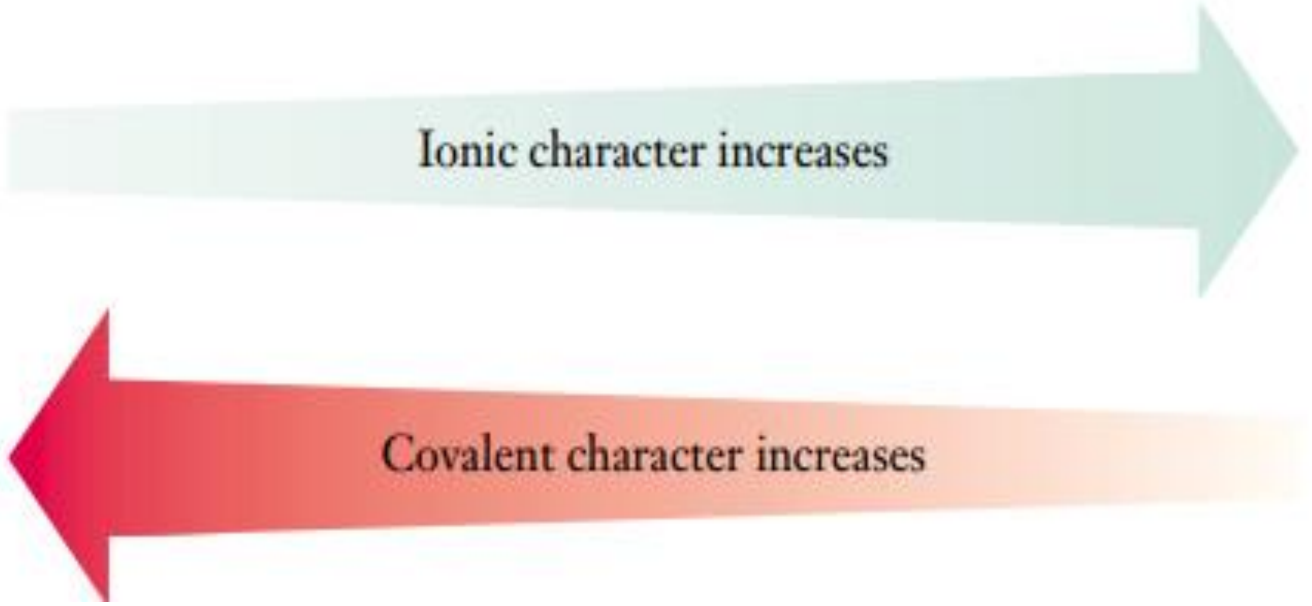
- The separation of charge in a polar covalent bond creates an **electric dipole**.
- We expect the dipoles in the covalent molecules HF, HCl, HBr,& HI to be different because F, Cl, Br, and I have different electronegativities.
- This tells us that atoms of these elements have different **tendencies to attract an electron pair that they share with hydrogen.**



- The longest arrow indicates the largest dipole, or greatest separation of electron density in the molecule

In summary, we can describe chemical bonding as a continuum that may be represented as

Δ(EN) for the bonding atoms	zero	⟶	intermediate	⟶	large
Bonding types	nonpolar covalent	⟶	polar covalent	⟶	ionic



EXAMPLE!

Arrange the following bonds from most to least polar:

a) N–F O–F C–F
b) C–F N–O Si–F
c) Cl–Cl B–Cl S–Cl

a) C–F, N–F, O–F
b) Si–F, C–F, N–O
c) B–Cl, S–Cl, Cl–Cl

CONCEPT CHECK!

Which of the following bonds would be the least polar yet still be considered polar covalent?

Mg–O C–O O–O S–iO **[N–O]**

Which of the following bonds would be the most polar without being considered ionic?

Mg–O C–O O–O **[Si–O]** N–O

DIPOLE MOMENTS

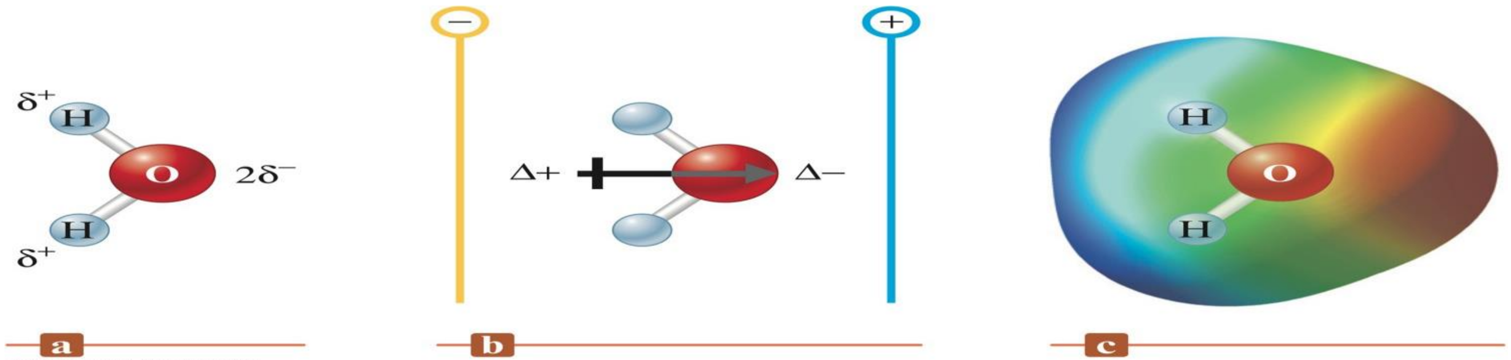
- We indicate the polarity of a molecule by its **dipole moment,** which measures the separation of charge within the molecule.
- The ***dipole moment*** *(μ)* of a molecule is the product of the magnitude of the charge (q) and the distance (*d*) that separates the centers of positive and negative charge. **Note: *q*** is Coulomb and ***d*** in m

$$\mu = d \times q$$

- A unit of dipole moment is the ***debye (D)***. One debye (D) is equal to 3.34 x 10^{-30} C m.

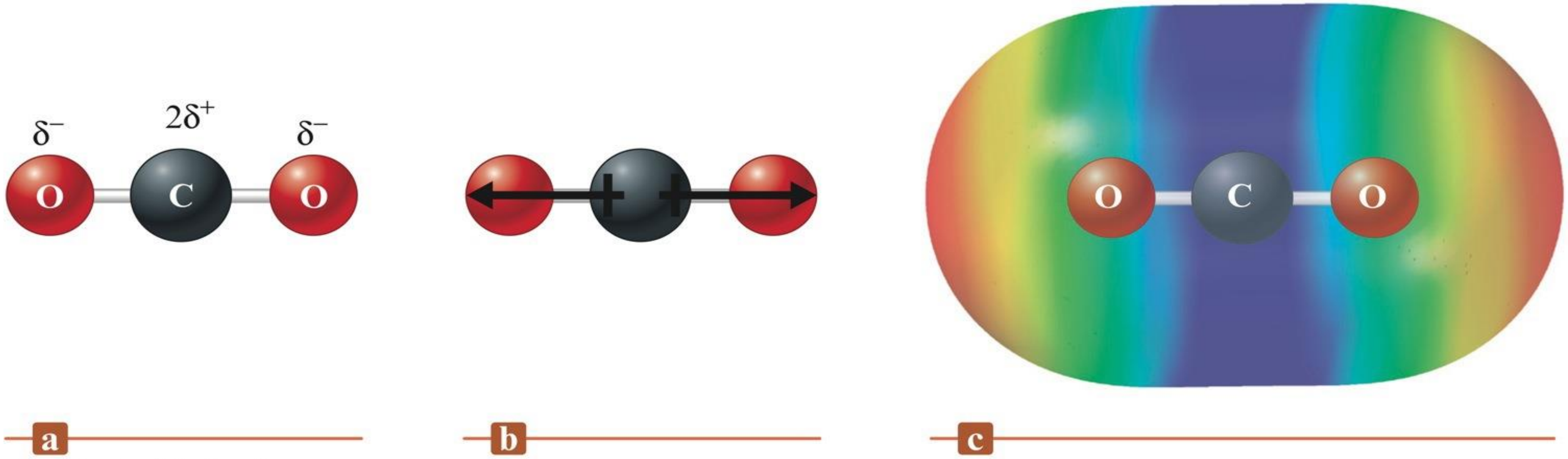
Bond Polarity and Dipole Moment

- Property of a molecule whose charge distribution can be represented by a center of positive charge and a center of negative charge.
- Bond dipoles have both a ***magnitude*** and a ***direction*** (they are ***vector*** quantities).
- Use an arrow to represent a dipole moment.
  - ✓ Point to the negative charge center with the tail of the arrow indicating the positive center of charge.



No Net Dipole Moment (Dipoles Cancel)

- ❖ Ordinarily, a polar molecule must have polar bonds, *BUT … polar bonds are not sufficient.*
- ❖ *A molecule may have polar bonds and be a nonpolar molecule – IF the bond dipoles cancel*



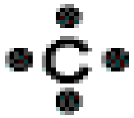
Localized Electron Bonding Model

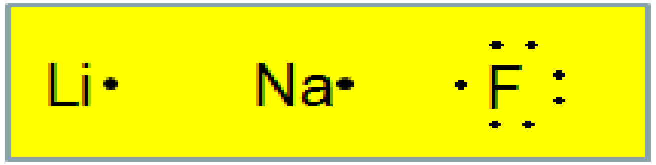
- A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms
- Electron pairs are assumed to be localized on a particular atom or in the space between two atoms:
  - *Lone pairs* – pairs of electrons localized on an atom
  - *Bonding pairs* – pairs of electrons found in the space between the atoms

1. Description of valence electron arrangement (Lewis structure).
2. Prediction of geometry (VSEPR model).
3. Description of atomic orbital types used by atoms to share electrons or hold lone pairs.

LEWIS STRUCTURE

- **Lewis Theory** was Formulated by Gilbert Newton Lewis and other two scientists (Walther Kossel, and Irving Langmuir)
- They came up with a theory to explain chemical bonding (**Between 1916 and 1919**)
- Lewis structures are visual representations of the bonds between atoms and illustrate the lone pairs of electrons in molecules
- A **Lewis structure** (or Lewis dot symbols) is a chemical symbol of an element surrounded by dots, each representing one of the s and/or p *valence electrons of the atom.*
- The electrons in the valence shell of the atom are shown as dots around it

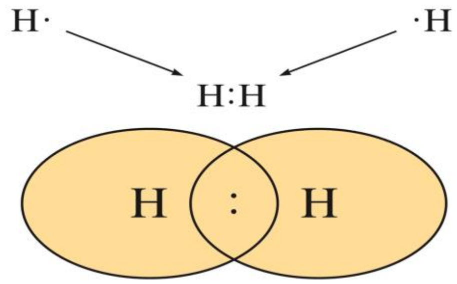




- The **Lewis Structure** Shows how valence electrons are arranged among atoms in a molecule.
- Reflects central idea that stability of a compound relates to noble gas electron configuration.

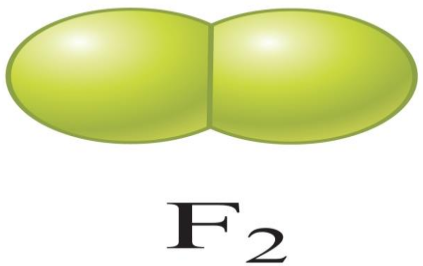
Duet Rule

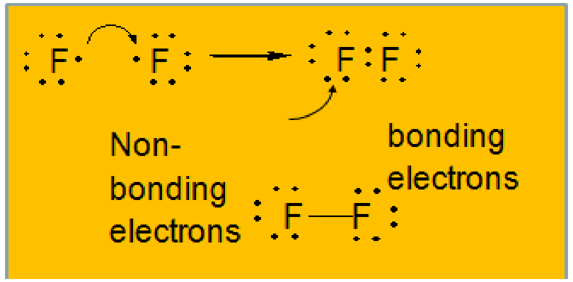
- ✓ Hydrogen forms stable molecules where it shares two electrons



Octet Rule

- ✓ Elements form stable molecules when surrounded by eight electrons





Single Covalent Bond

- A covalent bond in which two atoms share one pair of electrons.

$$H{-}H$$

Double Covalent Bond

- A covalent bond in which two atoms share two pairs of electrons.

$$O{=}C{=}O$$

Triple Covalent Bond

- A covalent bond in which two atoms share three pairs of electrons.

$$N \equiv N$$

Steps for Writing Lewis Structures

1. Sum the valence electrons from all the atoms.
2. Identify the central atom, its often the atom with the lowest electronegativity. Hydrogen, is never a central atom.
   - ✓ The least electronegative atom is usually the one requiring the most electrons to fill its octet.
3. Write the skeletal structure, & Use a pair of electrons to form a bond in the structure by single covalent bonds
4. For each single bond thus formed, subtract two from the total number of the valence electrons.
5. Atoms usually have noble gas configurations. Arrange the remaining electrons to satisfy the octet rule (or duet rule for hydrogen).
6. If at this stage, the central atom (s) lacks an octet, form multiple covalent bonds by converting lone pair electrons from terminal atoms into bond pairs.
7. Oxygen atoms do not bond to each other except in O_2 and O_3 molecules; hydrogen peroxide, H_2O_2, and its derivatives, the peroxides, which contain the O_2^{2-} group

Steps for Writing Lewis Structures

Example: H_2O

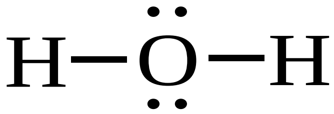
1. Sum the valence electrons from all the atoms. (Use the periodic table.)

$$2\,(1\ e^-) + 6\ e^- = 8\ e^-\ \text{total}$$

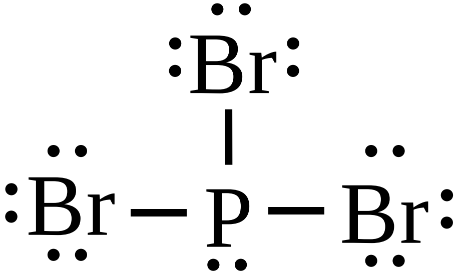
2. Use a pair of electrons to form a bond between each pair of bound atoms.

H–O–H

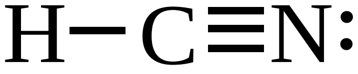
3. Atoms usually have noble gas configurations. Arrange the remaining electrons to satisfy the octet rule (or duet rule for hydrogen).



PBr_3



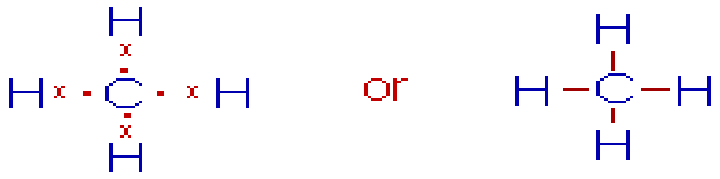
HCN



Steps for Writing Lewis Structures

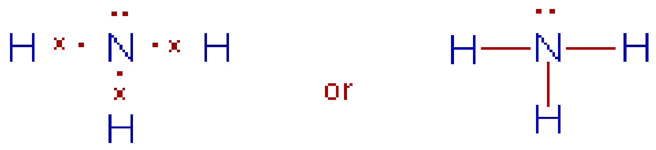
Example: Methane (CH_4):

- ✓ The C atom forms 4 covalent bonds by contributing four of its valence electrons. It forms 4 bonds with four H atoms. Thus it gets octet configuration



Example: Ammonia (NH_3)

- ✓ the nitrogen atom contributes 3 of its valence electrons to form three bond pairs which are shared with hydrogen atoms.



Steps for Writing Lewis Structures

For Multiple Covalent Bonds

Example: Dinitrogen (N_2)

- ✓ each nitrogen atom contributes 3 electrons to form 3 bond pairs, which in turn are shared by two nitrogen atoms. Each nitrogen also contains one lone pair.

Example: Carbon dioxide(CO_2):

- ✓ The carbon atom contributes four of its valence electrons, whereas each oxygen atom contributes two electrons
- ✓ There are two electron pairs shared between carbon and one of the oxygen atom i.e., a double bond, C=O is formed. There are two such C=O bonds in CO_2 molecule

CONCEPT CHECK!

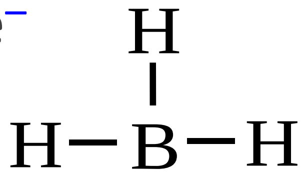
Draw a Lewis structure for each of the following molecules:

H_2 F_2 HF CCl_4

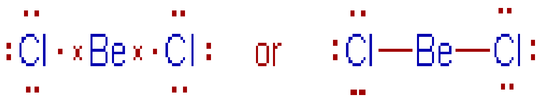
Exceptions of the Octet Rule

- Boron and Beryllium tends to form compounds in which the atoms has fewer than eight electrons around it (it does not have a complete octet).

$BH_3 = 6e^-$

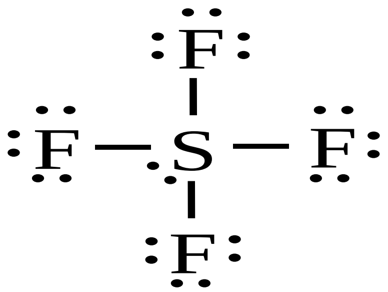


$BeCl_2 = 4e$

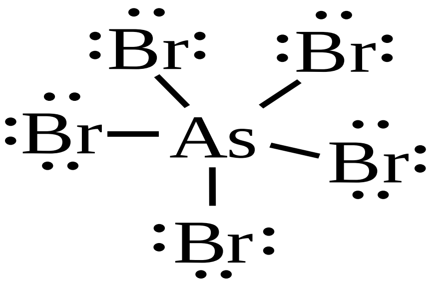


- When it is necessary to exceed the octet rule for one of several third-row (or higher) elements, place the extra electrons on the central atom.

$SF_4 = 34e^-$



$AsBr_5 = 40e^-$



CONCEPT CHECK!

Draw a Lewis structure for each of the following molecules:

BF_3

PCl_5

SF_6

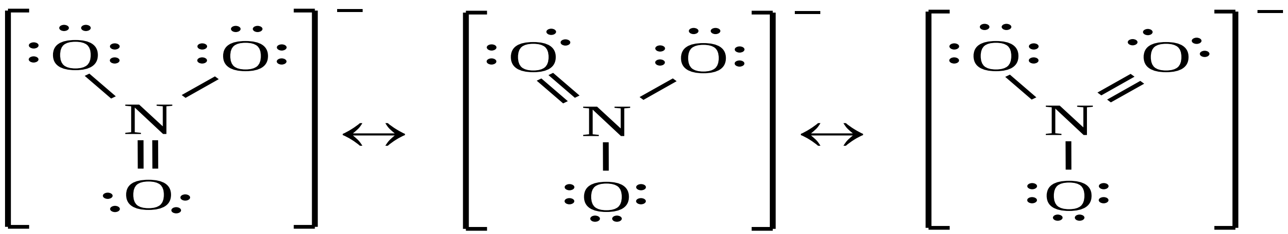
Let's Review

- C, N, O, and F should always be assumed to obey the octet rule.
- B and Be often have fewer than 8 electrons around them in their compounds.
- Second-row elements never exceed the octet rule.
- Third-row and heavier elements often satisfy the octet rule but can exceed the octet rule by using their empty valence *d* orbitals.
- When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first. If electrons remain after the octet rule has been satisfied, then place them on the elements having available *d* orbitals (elements in Period 3 or beyond).

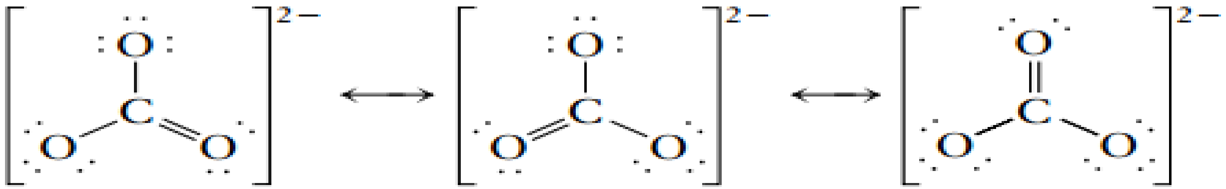
Resonance

- More than one valid Lewis structure can be written for a particular molecule.

$NO_3^- = 24e^-$



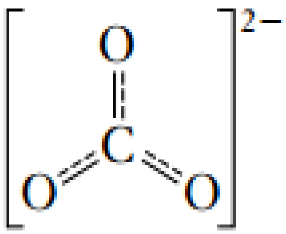
$CO_3^{2-} = 24e$



- Actual structure is an average of the resonance structures.
- Electrons are really delocalized – they can move around the entire molecule.

Resonance

- The three structures above are resonance structures of the carbonate ion.
- The relationship among them is indicated by the double-headed arrows.
- This symbol does not mean that the ion flips back and forth among these three structures. The true structure can be described as an average, **or hybrid**, The true structure of the three.



(lone pairs on O atoms not shown)

CONCEPT CHECK!

Draw a Lewis structure for each of the following molecules:

CO CO_2

CH_3OH OCN^-

Formal Charge

- Used to evaluate nonequivalent Lewis structures.
- Atoms in molecules try to achieve formal charges as close to zero as possible.
- Any negative formal charges are expected to reside on the most electronegative atoms & positive on the least electronegative atoms
    - Formal charge = (# valence e^- on free neutral atom) – (# valence e^- assigned to the atom in the molecule).

Calculation

FC = No. valence electrons in isolated atom – No. bonds to atom – *No. unshared electrons*

- Assume:
    - Lone pair electrons belong entirely to the atom in question.
    - Shared electrons are divided equally between the two sharing atoms.

Rules Governing Formal Charge

To calculate the formal charge on an atom:

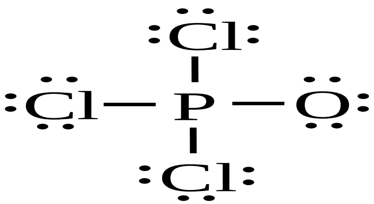
1. Take the sum of the lone pair electrons and one-half the shared electrons.
2. Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom.
3. The sum of the formal charges of the atoms in the Lewis structure must equal to zero for a neutral atom or equal to the ionic charge for a polyatomic ion

Example: Consider the Lewis structure for $POCl_3$. Assign the formal charge for each atom in the molecule.

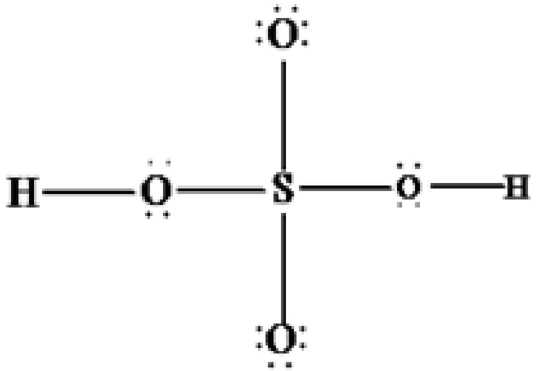
P: 5 – 4 = +1

O: 6 – 7 = –1

Cl: 7 – 7 = 0



Find the formal charges of all the atoms in the sulphuric acid structure.



Formal charge on S = 6 – (4 + 0) = + 2

An isolated S atom has 6 electrons

There are no. unshared pairs on the S

Sulfur: FC = 6 – (4 + 0) = + 2

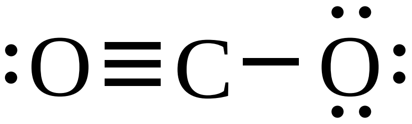
Hydrogen: FC = 1 – (1+0) = 0

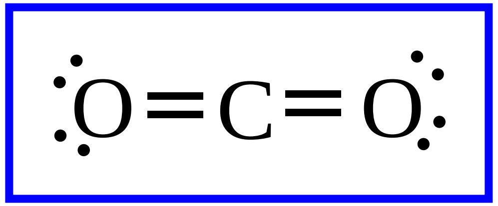
Hydroxyl oxygen: FC = 6 – (2 +4) = 0

Oxygen not bonded to hydrogen: FC = 6 – (1 +6) = –1

Rules Governing Formal Charge

- The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species.
- If nonequivalent Lewis structures exist for a species, those with formal charges closest to zero and with any negative formal charges on the most electronegative atoms are considered to best describe the bonding in the molecule or ion.





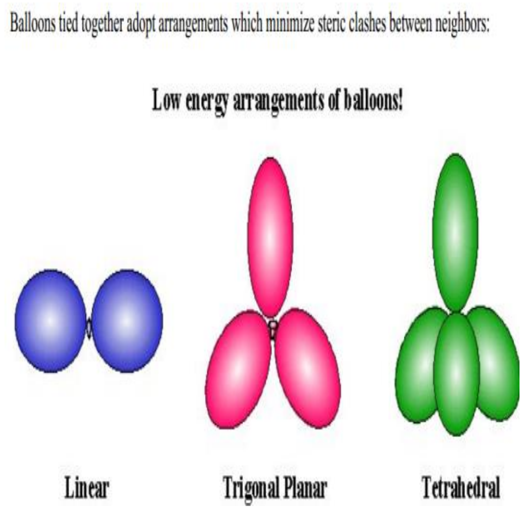
DRAWBACKS OF LEWIS THEORY

- Lewis theory could not explain the geometry of molecules & bond angle in them.
- It could not explain why some molecules are violating the octet rule.
- This is a qualitative explanation for **covalent bond only.**
- To fulfill these gaps and to explain the covalent bond formation quantitatively, the **Valence bond theory (VBT)** was put forward**.**
- However it is important to learn **VSEPR theory,** another qualitative model, which was put forward to explain the shapes of molecules, before moving on to Valence bond theory.

Molecular Structure: The VSEPR Model

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

- Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of theelectron pairs in the valence shell of the atoms
- Helps us to understand & predict the spatial arrangement of atoms in a polyatomic molecule or ion
- VSEPR theory uses Lewis structures to predict the molecular geometry of covalently bonded molecules (molecular shape)
- The structure around a given atom is determined principally by minimizing electron pair repulsions in the valence shell.
- Molecular shape offers insight into a wide range of important physical properties (polarity, solubility, volatility, chirality, etc).



The main postulates of VSEPR theory are as follows:

- The electron pairs in the valence shell around the **central atom** of a molecule **repel each other** & tend to orient in space so as to minimize the repulsions & maximize the distance between them.
- There are two types of valence shell electron pairs viz.
  - ✓ **Bond pairs** are shared by two atoms & are attracted by two nuclei. Hence they occupy less space and cause less repulsion.
  - ✓ **Lone pairs** are not involved in bond formation & are in attraction with only one nucleus. Hence they occupy more space. As a result, the lone pairs cause more repulsion.
- The order of repulsion between different types of electron pairs is as follows:

Lone pair - Lone pair > Lone Pair - Bond pair > Bond pair - Bond pair

Note: The bond pairs are usually represented by a solid line, whereas the lone pairs are represented by a lobe with two electrons.

The main postulates of VSEPR theory are as follows:

- In VSEPR theory, the multiple bonds are treated as if they were single bonds.
  - ✓ The electron pairs in multiple bonds are treated collectively as a **single super pair.**
  - ✓ The repulsion caused by bonds increases with increase in the # of bonded pairs between two atoms i.e.,
  - ✓ A triple bond causes more repulsion than a double bond which in turn causes more repulsion than a single bond.
- The shape of a molecule can be predicted from the number and type of valence shell electron pairs around the central atom.
  - ✓ When the valence shell of central atom contains only bond pairs, the molecule assumes symmetrical geometry due to even repulsions between them.
  - ✓ However the symmetry is distorted when there are also lone pairs along with bond pairs due to uneven repulsion forces.
  - ✓ The best spatial arrangement of the bonding pairs of electrons in the valence orbitals is one in which the repulsions are minimized

Steps to Apply the VSEPR Model

1. Draw the Lewis structure for the molecule.
2. Count total number of electron pairs around the central atom. Arrange them to minimize the electron shell repulsion
3. Count the electron pairs and arrange them in the way that minimizes repulsion (put the pairs as far apart as possible.
4. Determine the positions of the atoms from the way electron pairs are shared (how electrons are shared between the central atom and surrounding atoms).
5. Determine the name of the molecular structure from positions of the atoms.

Example!

Determine the shape for each of the following molecules, and include **bond angles**:

HCN PH_3 SF_4 O_3 KrF_4

- ✓ **Solutions**

  HCN – linear, 180º

  PH_3 – trigonal pyramid, 109.5º (107º)

  SF_4 – see saw, 90º, 120º

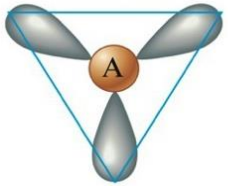
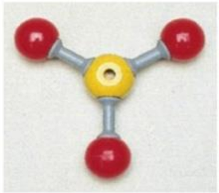
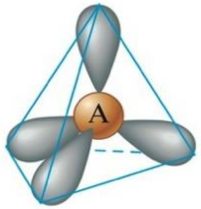
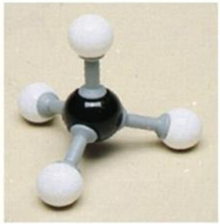
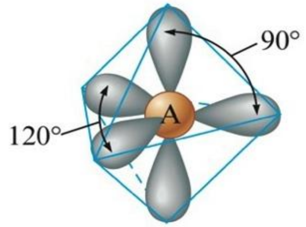
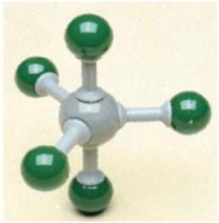
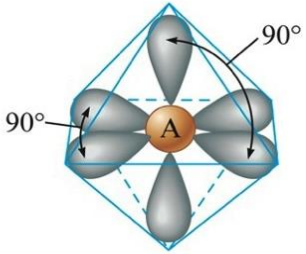
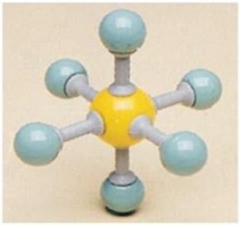
  O_3 – bent, 120º

  KrF_4 – square planar, 90º, 180º

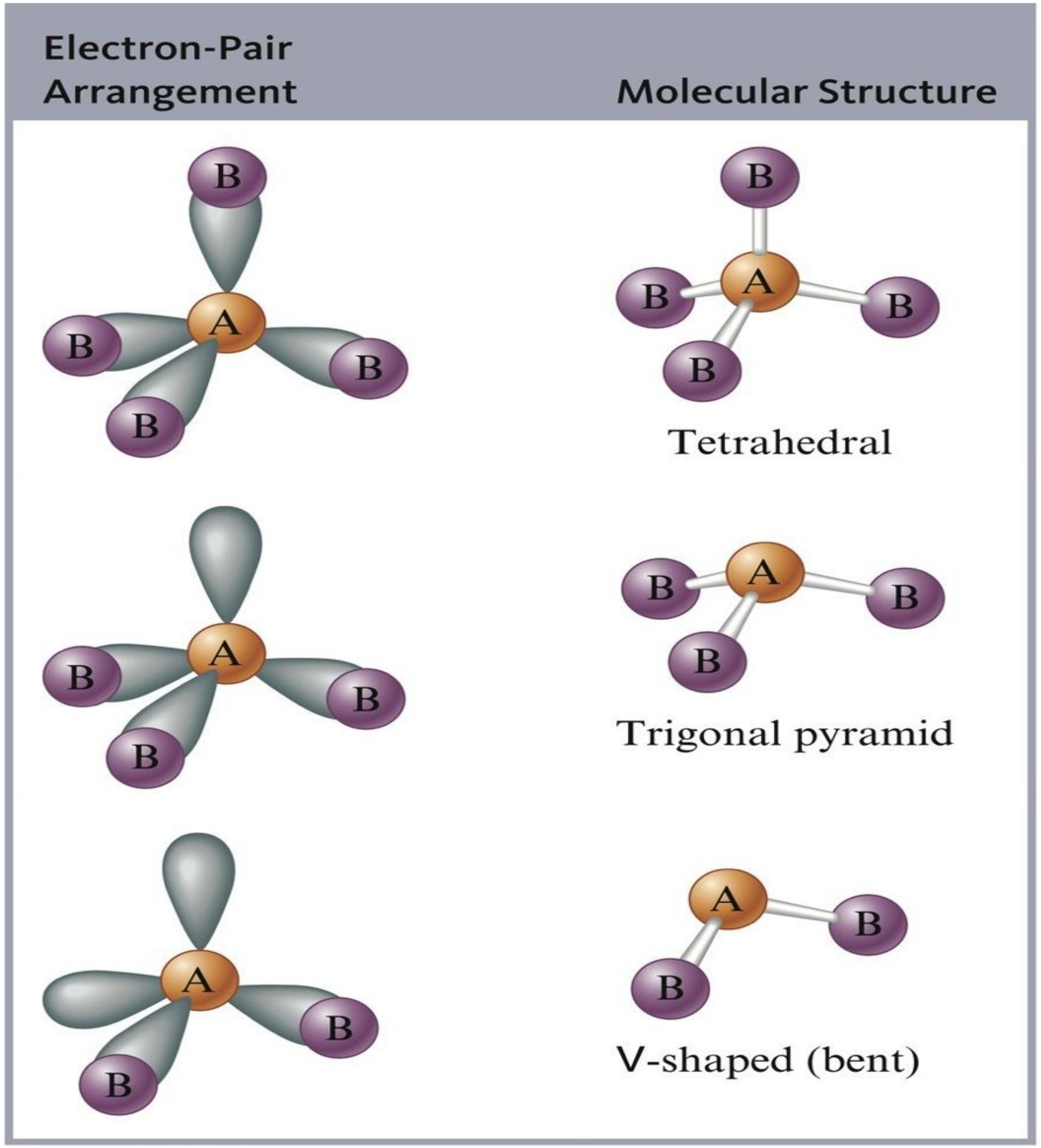
Let's Think About It

- Draw the Lewis structure for XeF_4.
- Does XeF_4 contain lone pairs?
- Is the molecule polar or nonpolar overall? Why?

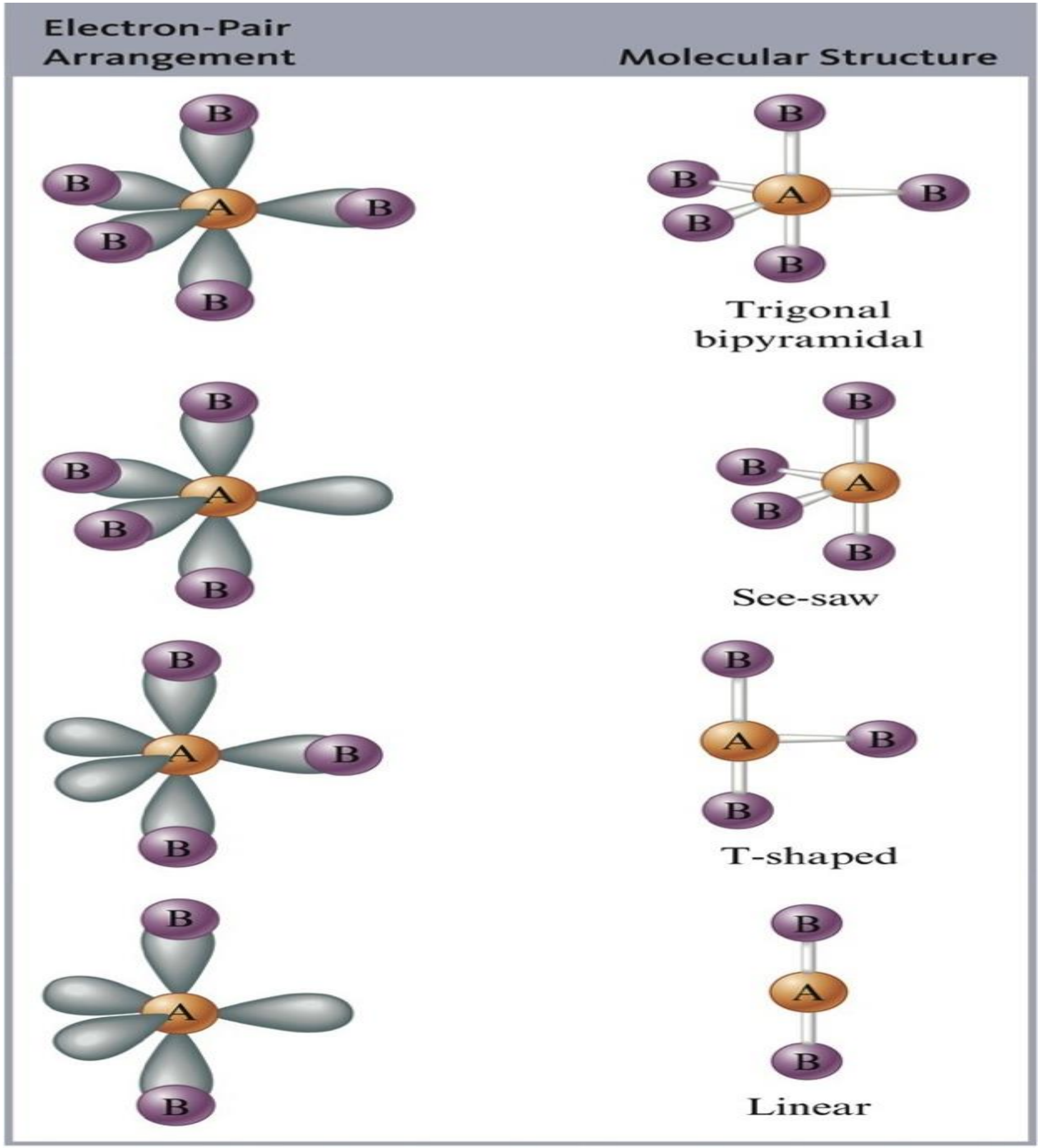
Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

Number of Electron Pairs	Arrangement of Electron Pairs		Example
2	Linear		
3	Trigonal planar		
4	Tetrahedral		
5	Trigonal bipyramidal		
6	Octahedral		

Structures of Molecules That Have Four Electron Pairs Around the Central Atom



Structures of Molecules with Five Electron Pairs Around the Central Atom



RELATION BETWEEN NUMBER & TYPE OF VALENCE ELECTRON PAIRS WITH THE SHAPE OF MOLECULE

- The shape of molecule and also the approximate bond angles can be predicted from the number and type of electron pairs in the valence shell of central atom as tabulated below.

  In the following table the molecule is represented by "AXE" notation, where:

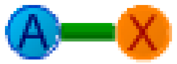
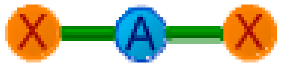
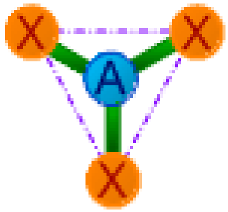
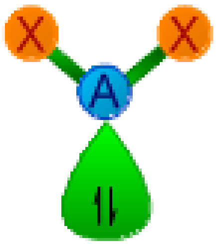
  A = Central atom

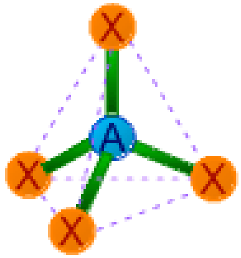
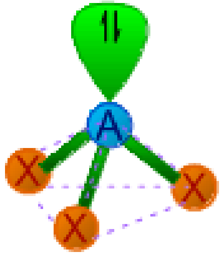
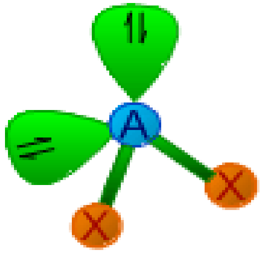
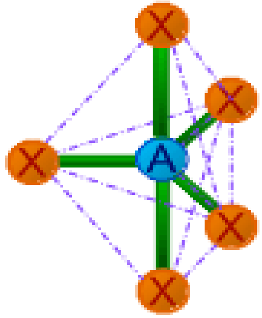
  X = atom bonded to the central atom either by a single bond or by multiple bond;**indicating a bond pair**.

  E = Lone pair

Note:

- The sum of # of ligand atoms (**X**) and # of lone pairs (**E**) is also known as **steric number.**
  - ✓ The bond pairs are shown as green colored thick lines,
  - ✓ whereas the lone pairs are shown as point charges using green colored lobes.

Steric number	Number of Bond pairs	Number of Lone pairs	Formula	Shape of molecule		Approximate Bond angles	Examples
1	1	0	AX	Linear		-	ClF, BrF, BrCl, HF, O_2
2	2	0	AX_2	Linear		180°	$BeCl_2$, $HgCl_2$, CO_2
3	3	0	AX_3	Trigonal planar		120°	BF_3, CO_3^{2-}, NO_3^-, SO_3
	2	1	AX_2E	Angular		120°	SO_2, $SnCl_2$, O_3, NSF, NO_2^-

4	4	0	AX_4	Tetrahedral		109°28'	CH_4, $SiCl_4$, NH_4^+, PO_4^{3-}, SO_4^{2-}, ClO_4^-
	3	1	AX_3E	Trigonal pyramidal		around 109°28'	NH_3, PCl_3, XeO_3
	2	2	AX_2E_2	Angular		around 109°28'	H_2O, SCl_2, Cl_2O, OF_2
	5	0	AX_5	Trigonal bipyramidal		120° & 90°	PCl_5, SOF_4

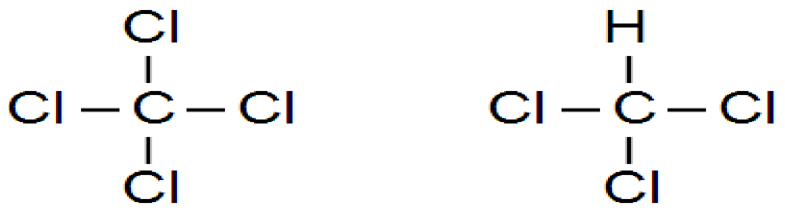
Molecular Shapes, Dipole Moments and polarity of molecules

To predict molecular polarity:

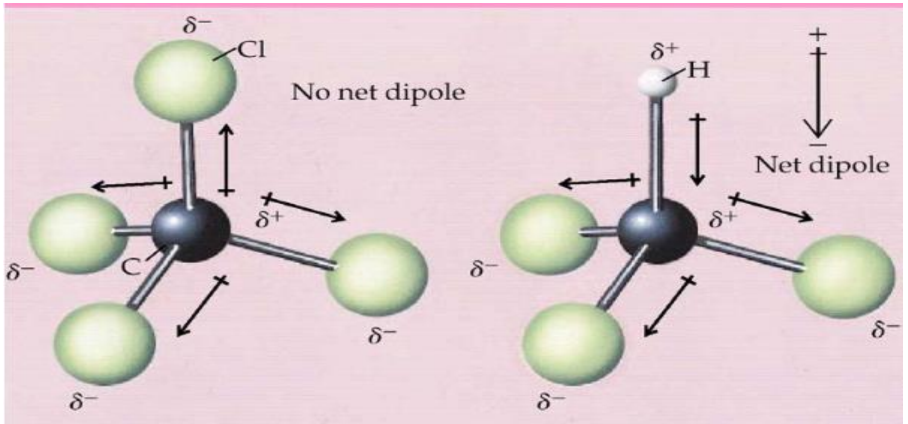
- Use electronegativity values to predict bond dipoles.
- Use the VSEPR method to predict the molecular shape.
- From the molecular shape, determine whether bond dipoles cancel to give a nonpolar molecule, or combine to produce a **resultant dipole moment for the molecule.!!**

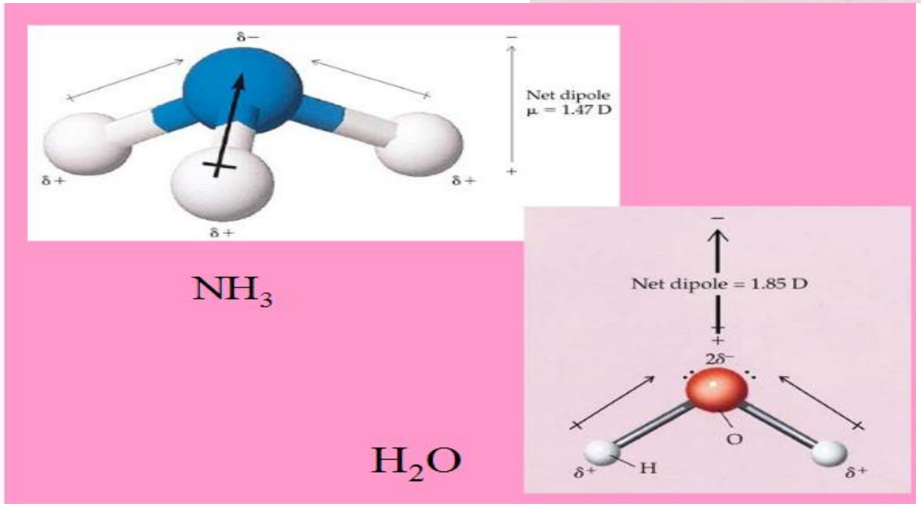
Note: Lone-pair electrons can also make a contribution to dipole moments.

Polar or non-polar?



Which molecule is polar? You must look at the geometry to decide.





CONCEPT CHECK!

True or false:

A molecule that has polar bonds will always be polar.

-If true, explain why.

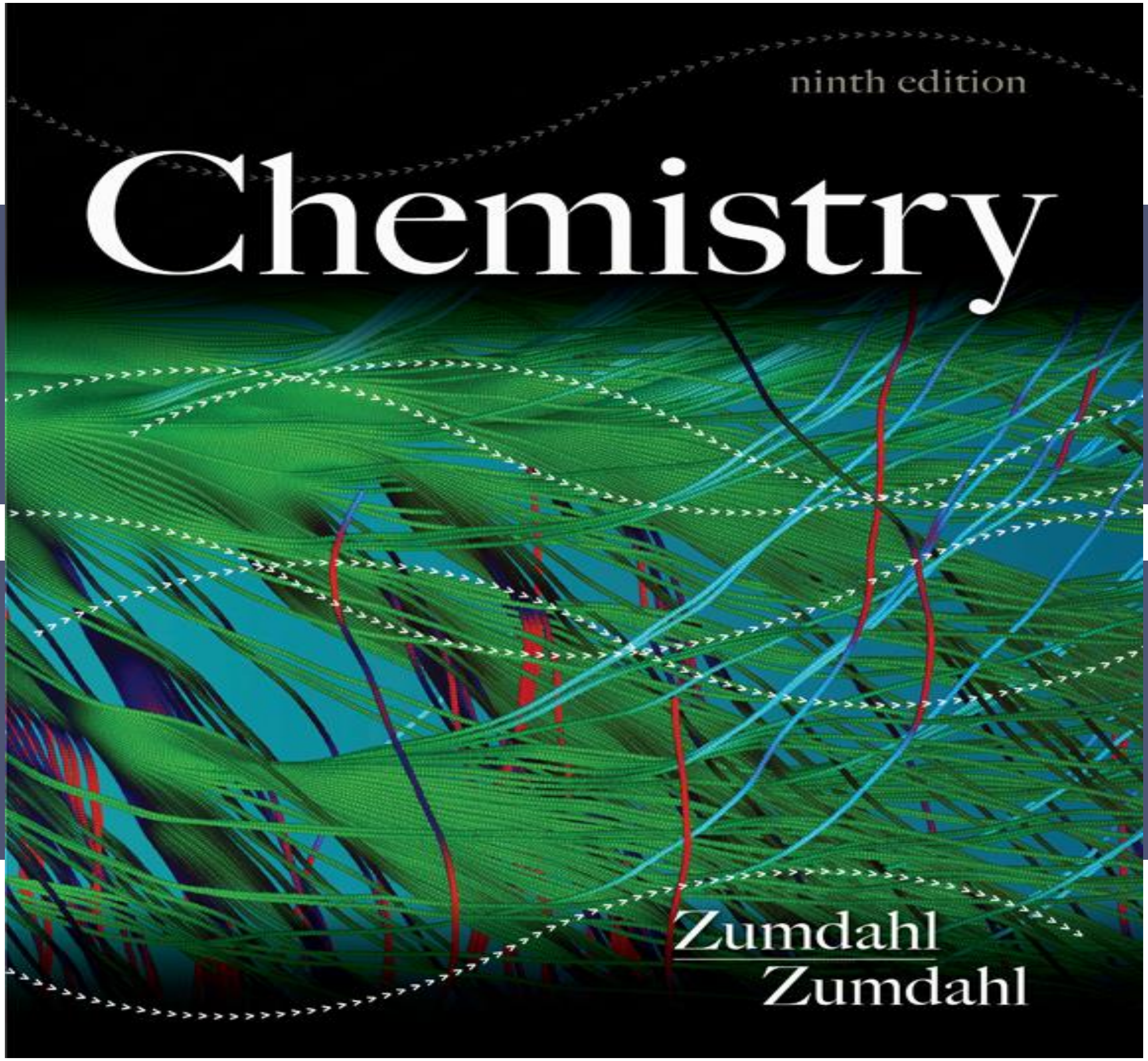
-If false, provide a counter-example

True or false:

Lone pairs make a molecule polar.

-If true, explain why.

-If false, provide a counter-example.



Chapter 9

Covalent Bonding: Orbitals

The Nature of Chemical Bonding

The Nature of Chemical Bonding

There are many types of experiments we can perform to determine the fundamental nature of chemical bonding in materials. For example:

- we can study physical properties such as melting point, hardness, and electrical and thermal conductivity.
- We can also study solubility characteristics and the properties of the resulting solutions.
- To determine the charge distribution in a molecule,
- we can study its behavior in an electric field.
- We can obtain information about the strength of a bonding interaction by measuring the **bond energy,** which is the energy required to break the bond

The Nature of Chemical Bonding

Types of chemical bonds

- Ionic: electrons are transferred to form ions
- Covalent: equal sharing of electrons
- Polar covalent: unequal electron sharing
- Metallic Bonding.

The Nature of Covalent Bonding

Will look into the following concerning **Covalent Bonding**

- The Valence Bond Theory,
- Hybridization and molecular shapes.
- Simple Molecular Orbital Theory,
- Overlap Integral for Simple Diatomic Molecules.

THEORIES OF COVALENT BONDING

1. **Lewis Theory**
   - Show how the valence electron pairs are arranged among the atoms in a molecule or polyatomic ion.
   - The ***Lewis structure (or Lewis formula)***- is two-dimensional structural formula consists of electron-dot symbols that depict each atom and its neighbors, the bonding pairs that hold them together, and the lone pairs that fill each atom's outer level (valence shell) - **octet rule**
2. **Valence Shell Electron Pair Repulsion (VSEPR) Theory and Molecular Geometry**
   - Based on the idea that electron pairs will be arranged around a central atom in a way that minimizes the electron repulsions
   - Can be used to predict the geometric structure of most molecules
   - The theory predicts the shape of covalent compounds in which valence shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thus minimizing the electron pair repulsion

The Valence Bond Theory (VBT) and Orbital Hybridization

History

- The **Valence Bond Theory** (VBT) was proposed by Heitler & London to explain the formation of **covalent bond quantitatively using *quantum mechanics.***
- Later on, Linus Pauling improved this theory by introducing the concept of **hybridization**.
- At present Valence Bond Theory is one of the two quantum mechanical theories used to describe covalent bond formation and the electronic structure of molecules

The Valence Bond Theory

The main postulates of this theory are as follows:

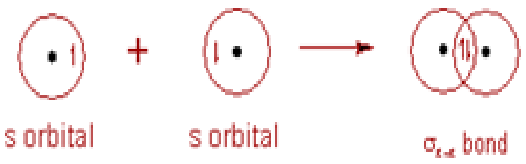
- A covalent bond is formed by the ***overlapping of two half filled valence atomic orbitals***of two different atoms
- The electrons in the overlapping orbitals get paired & confined between the nuclei of two atoms.
- The electron density **between two bonded atoms** increases due to overlapping. **This confers stability to the molecule.**
- The greater the extent of overlapping, **stronger is the bond formed.**
- The direction of the covalent bond is along the region of overlapping of the atomic orbitals **i.e., covalent bond is directional.**
- Based on the pattern of overlapping, there are two types of covalent bonds: sigma bond (σ-bond) and a pi bond (π-bond).

There are two types of covalent bonds based on the pattern of overlapping as follows:

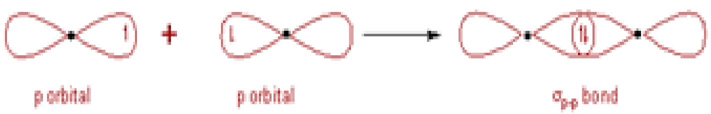
(i) Sigma (σ)-bond

- The covalent bond formed due to overlapping of atomic orbital along the inter nucleus axis is called σ-bond.
- Electron pair is shared in an area centered on a line running *between* the atoms
- This **head-on overlap** of orbitals is referred to as a sigma bond.
- It is a stronger bond and cylindrically symmetrical.
- Depending on the types of orbitals overlapping, the σ-bond is divided into following types:

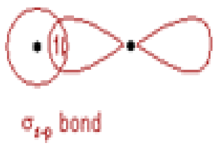
$\sigma_{s\text{-}s}$ bond:

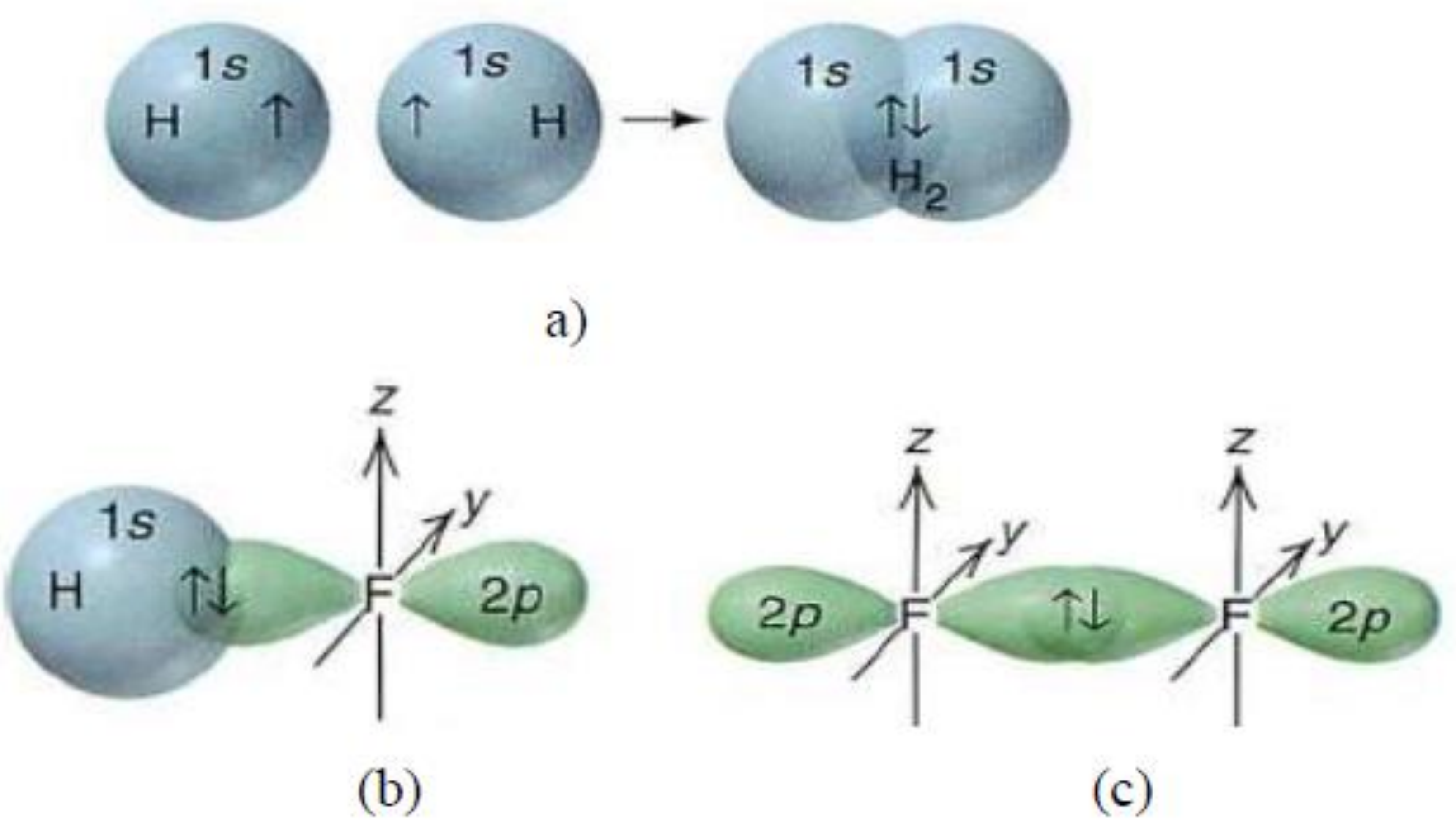


$\sigma_{p\text{-}p}$ bond:



$\sigma_{s\text{-}p}$ bond:

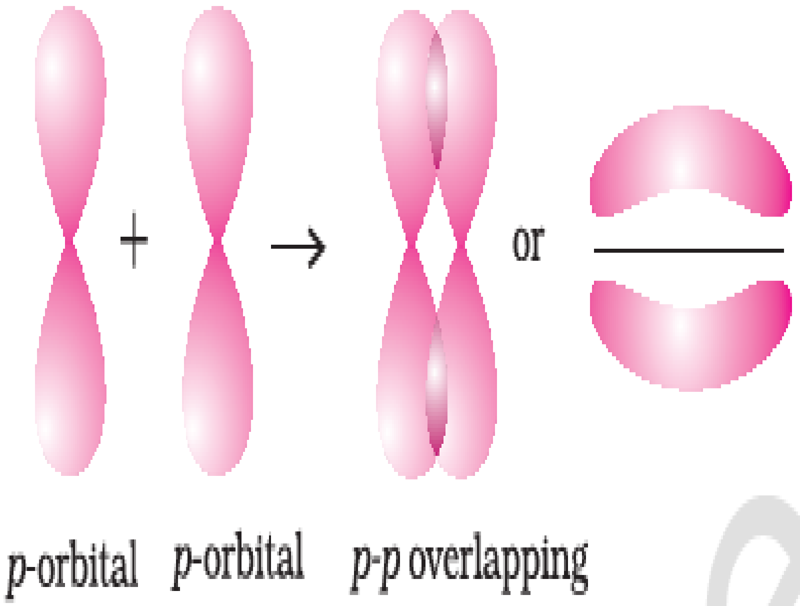




(a) $\sigma_{s\text{-}s}$ overlapping on the formation of H_2 molecule (b) $\sigma_{s\text{-}p}$ overlapping on the formation of HF molecule and (c) $\sigma_{p\text{-}p}$ overlapping on the formation of F_2 molecule

(ii) Pi (π)-Bond:

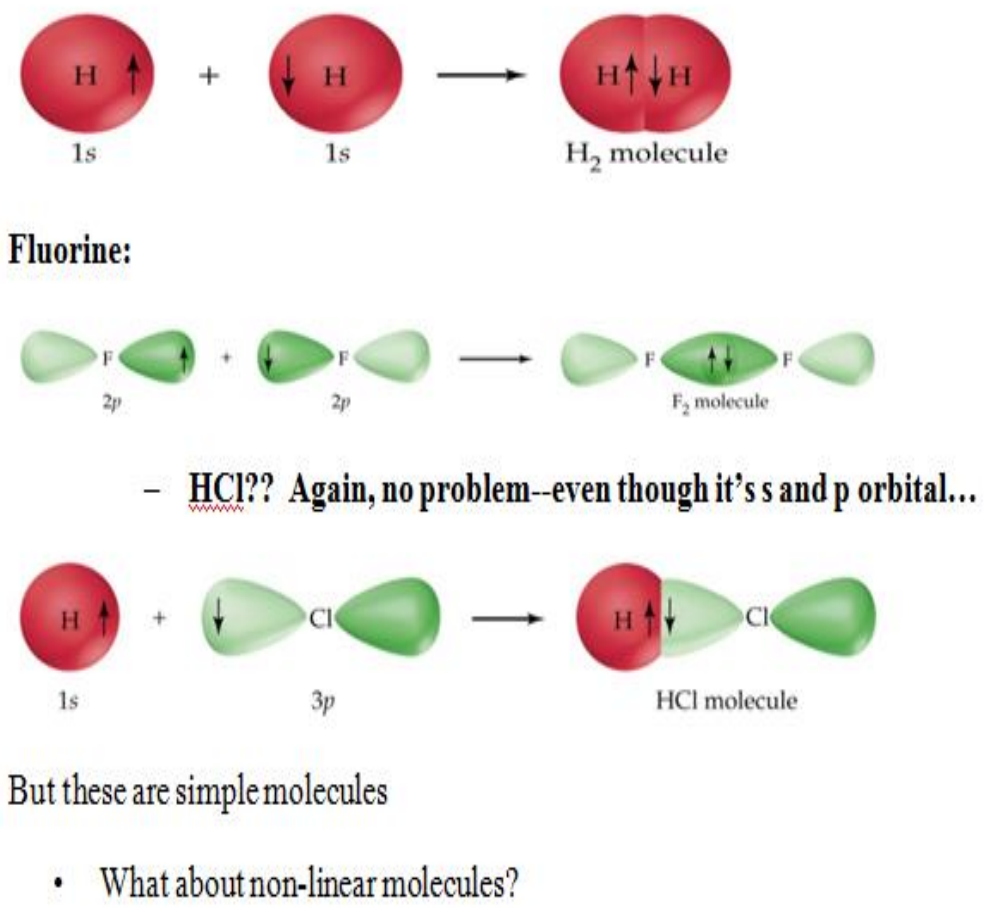
- The covalent bond formed by **sidewise overlapping** of atomic orbitals is called π- bond.
- In this bond, the electron density is present above & below the **inter nuclear axis.**
- It is relatively a weaker bond since the electrons are not strongly attracted by the nuclei of bonding atoms.
- Forms double and triple bonds by sharing electron pair(s) in the space above and below the σ bond.
- Uses the unhybridized *p* orbitals.



The Restriction of the VBT

Note:

- The 's' orbitals can only form σ-bonds, whereas the p, d & f orbitals can form both σ and π-bonds.
- The valence bond method predicts molecule shapes from the shapes and orientation of the atomic orbitals and their overlap regions when two atoms approach.



The VBT

- The old version of valence bond theory is limited to diatomic molecules only.
- Forexample, the covalent bond in H_2, O_2, Cl_2, N_2, HCl, *etc*. molecule can be explained by theorbital overlapping of the two atoms.
- It could not explain the structures and bond angles of molecules with more than three atoms.

  E.g. It could not explain the structures and bond angles of H_2O, NH_3 etc.
- In order to explain the structures and bond angles of molecules, Linus Pauling modified thevalence bond theory using **hybridization concept**.

Hybridization and Molecular Shapes

- In most cases the orbitals that overlap are **reconfigured orbitals**, called **hybrid orbitals**, having different shapes & orientations than **pure orbitals.**
- Generally It is define as:
  - ✓ ***the intermixing of two or more pure atomic orbitals of an atom with almost same energy to give same number of identical & degenerate new type of orbitals.***
- Mathematical concept based on quantum mechanics, the wave functions, Ψ of **valence-shell** of atomic orbitals of same atom are combined to give new wave functions corresponding to **hybrid orbitals**
- The number of hybrid orbitals formed is equal to the number of pure atomic orbitals undergoing hybridization.
  - ✓ E.g. If three atomic orbitals intermix with each other, the number of hybrid orbitals formed will be equal to 3.

Important conditions for hybridisation

1. The orbitals present in the valence shell of the atom are hybridised.
2. The orbitals undergoing hybridization should have almost equal energy.
3. Promotion of electron is not essential condition prior to hybridisation.
4. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridization

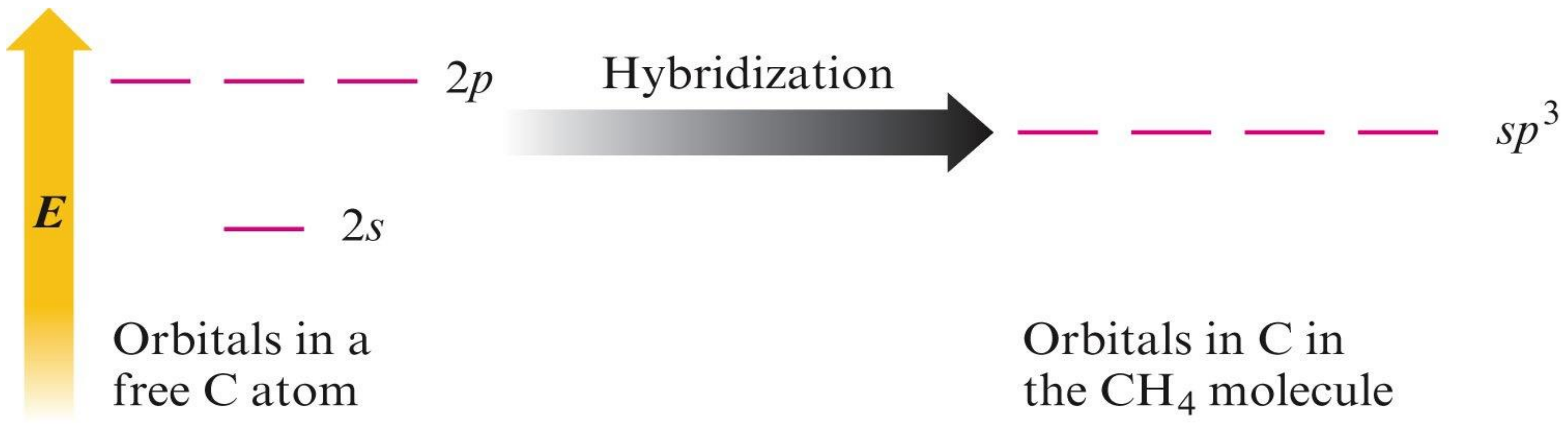
Types of Hybridisation

- There are various types of hybridization involving s, p and d orbitals

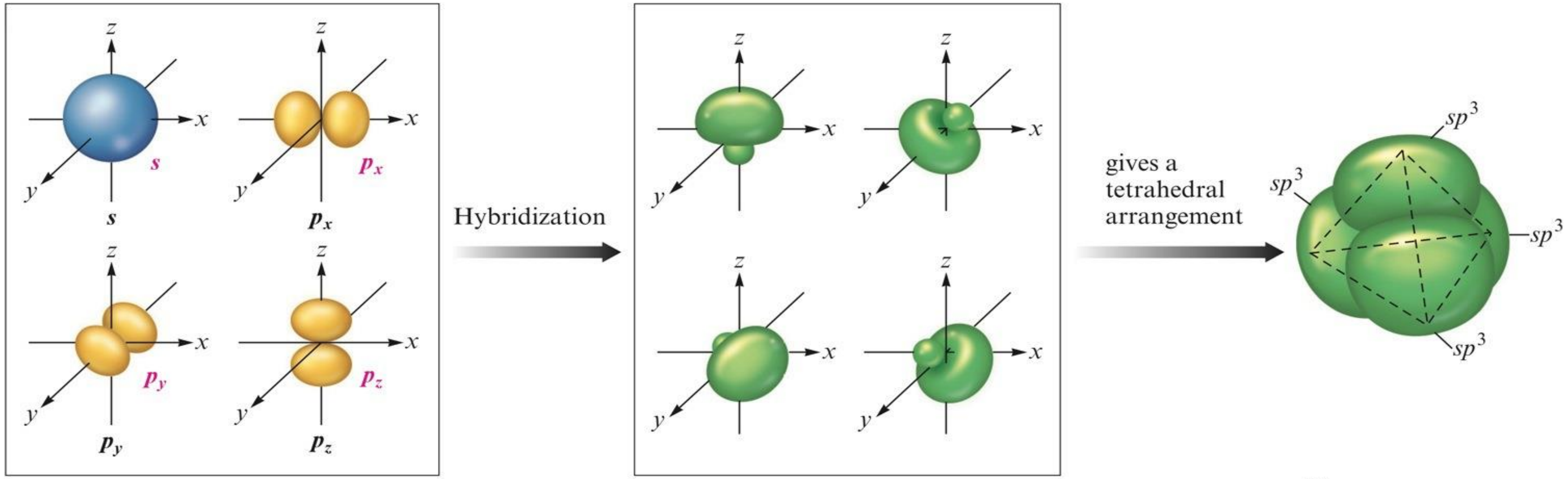
1. sp^3 Hybridization (4 hybrid orbitals)

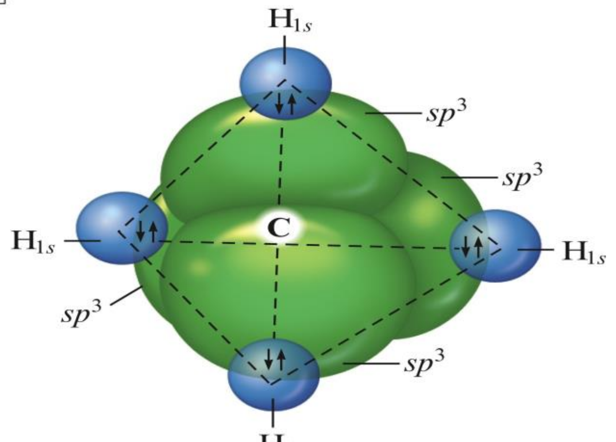
- Combination of one *s* and three *p* orbitals.
- Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, the localized electron model assumes that the atom adopts a set of sp^3 orbitals; the atom becomes sp^3 hybridized.
- The four orbitals are identical in shape.

An Energy-Level Diagram Showing the Formation of Four sp^3 Orbitals



The Formation of *sp*^{3} Hybrid Orbitals



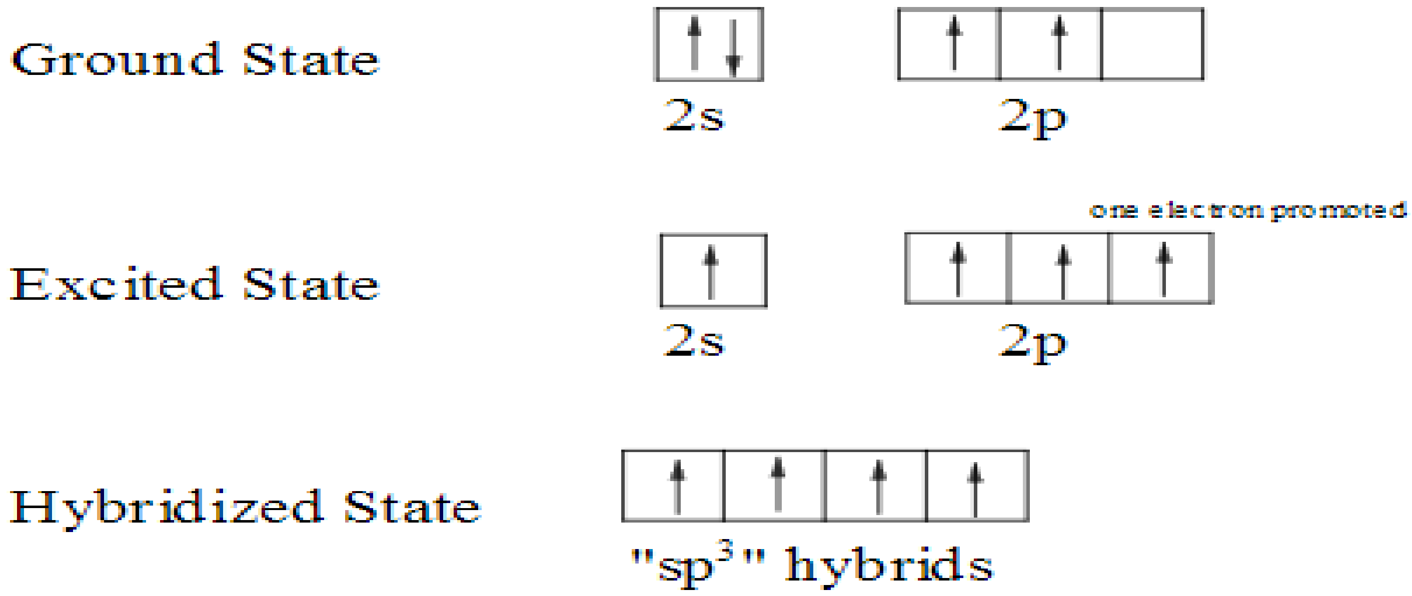


Tetrahedral Set of Four *sp*^{3} Orbitals

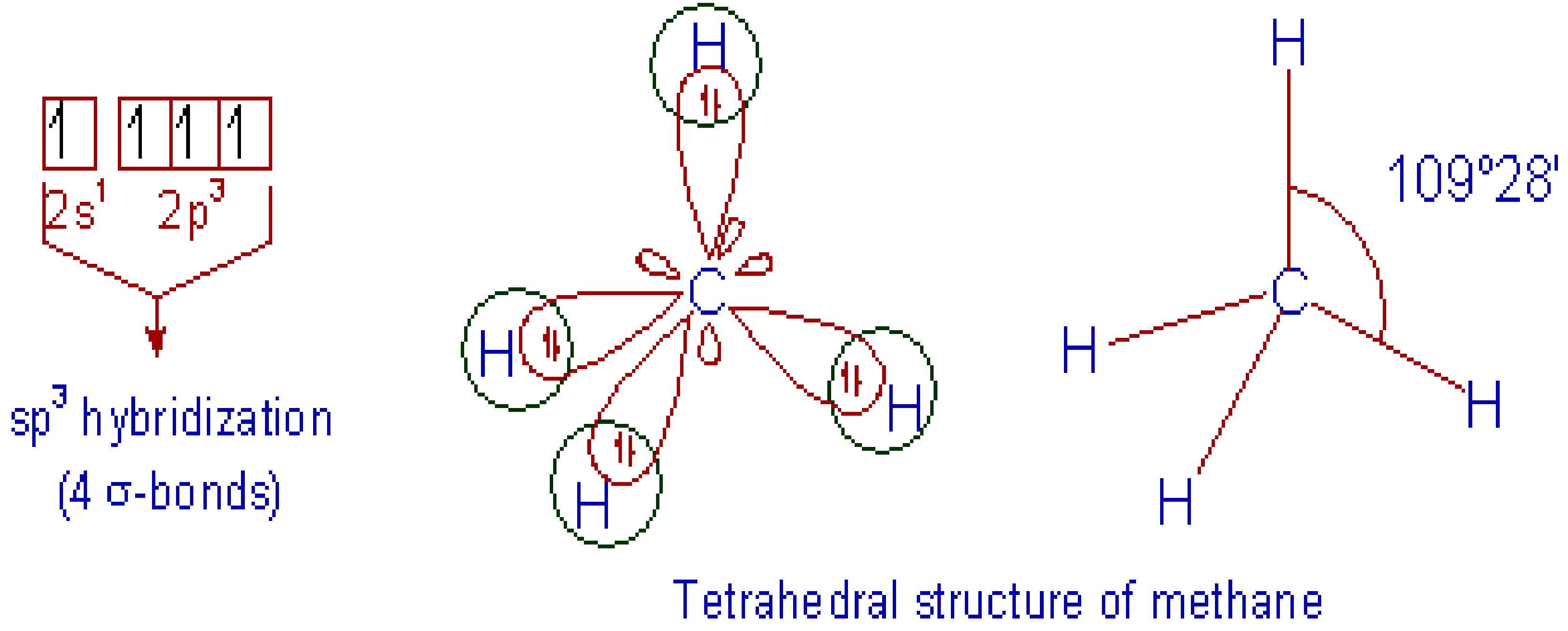
EXAMPLE!

Methane CH_4, Ethane, C_2H_6

- The ground state of C reveals a pair of electrons in the 2s and two single electrons in the 2p.
- This is not consistent with the need for four single electrons required to form the four bonds with the hydrogens
- so again, electrons are promoted into the p subshell just prior to bonding.



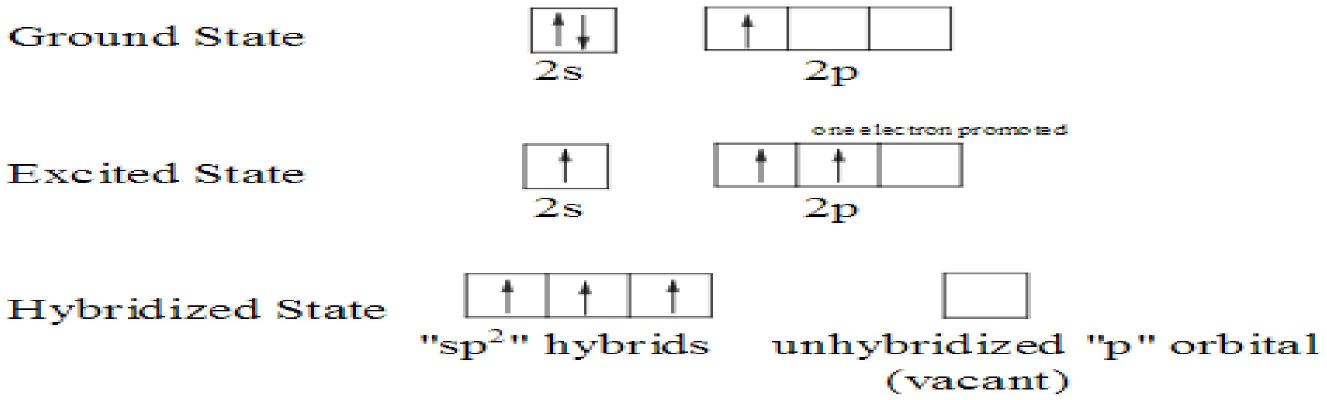
- These four orbitals arrange themselves in a tetrahedral geometry in order to minimize repulsion effects.



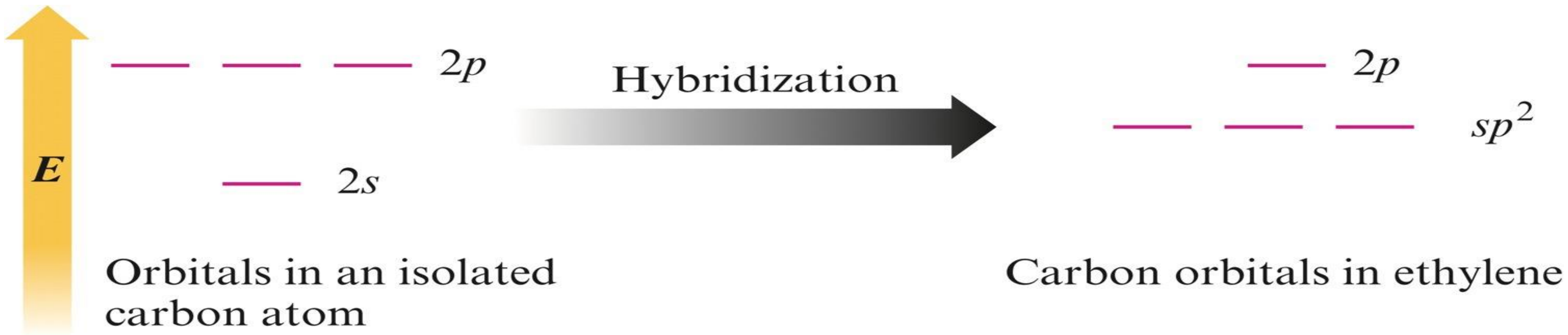
- **The sp^3 hybrid orbitals have 25% ‘s’ character and 75% 'p' character.**

2. *sp*² Hybridization

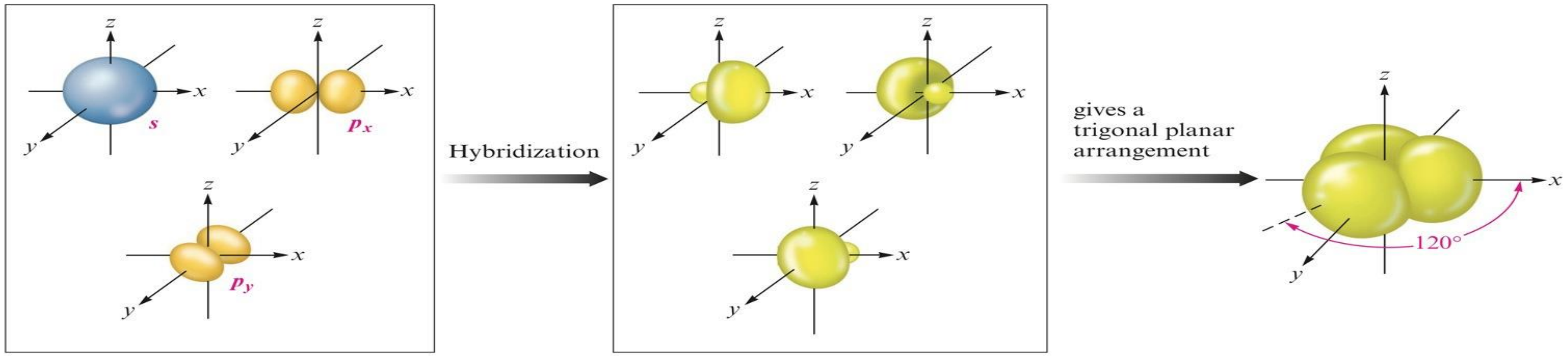
- Combination of one *s* and two *p* orbitals.
- Gives a trigonal planar arrangement of atomic orbitals.
- One *p* orbital is not used.
  - ✓ Oriented perpendicular to the plane of the sp^2 orbitals.
  - ✓ the mixing of one s and two p orbitals of the central atom to give three hybrid orbitals that point toward the vertices of equilateral triangle , their axes at 120 angle apart are used
- would arrange themselves as far apart as possible forming a **trigonal planar** electron arrangement.
- **The sp^2 hybrid orbitals have 33.3% 's' character and 66.6% 'p' character**.



An Orbital Energy-Level Diagram for sp^2 Hybridization



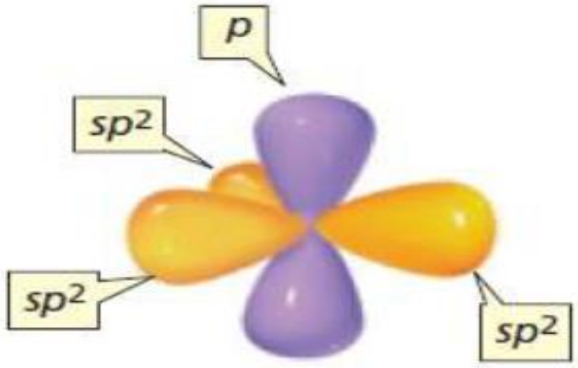
The Hybridization of the s, p_x, and p_y Atomic Orbitals

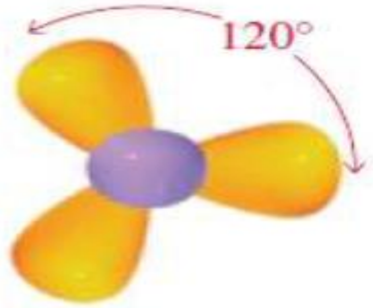


EXAMPLE!

Boron Trifloride **BF_3**

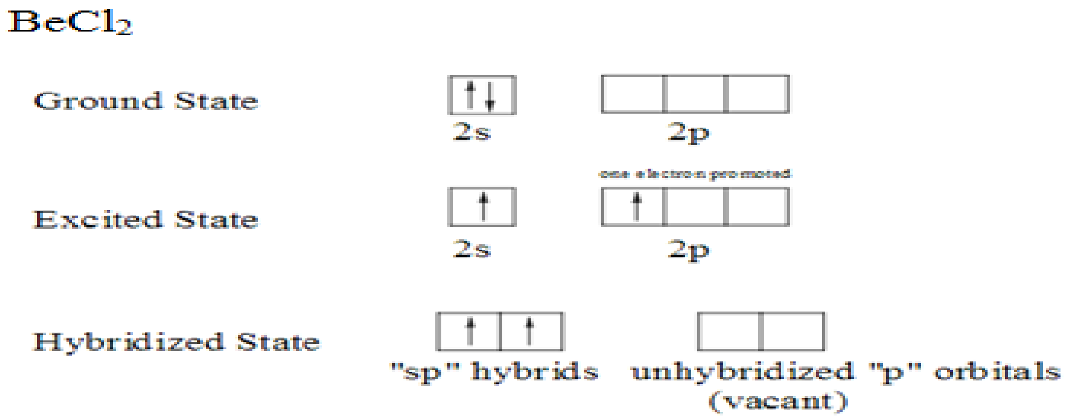
- VB theory proposes that the central B atom in the molecule is sp^2 hybridized.
- Each sp^2 orbital overlaps the 2p orbital of an F atom, and the six valence electrons- three from B and one from each of the three F atoms-form three bonding pairs.
- Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital
- The figure below shows the three-sp^2 orbitals in the **trigonal plane**, with the third 2p orbital unhybridized and perpendicular to this plane.



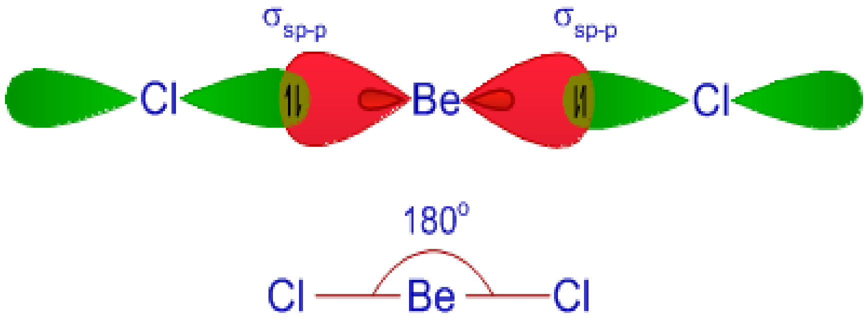


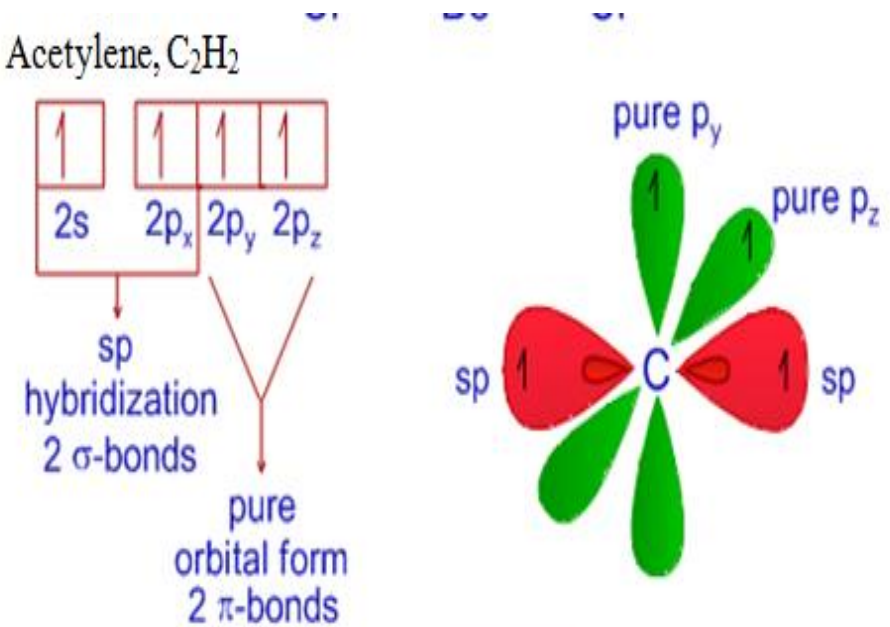
3. *sp* Hybridization

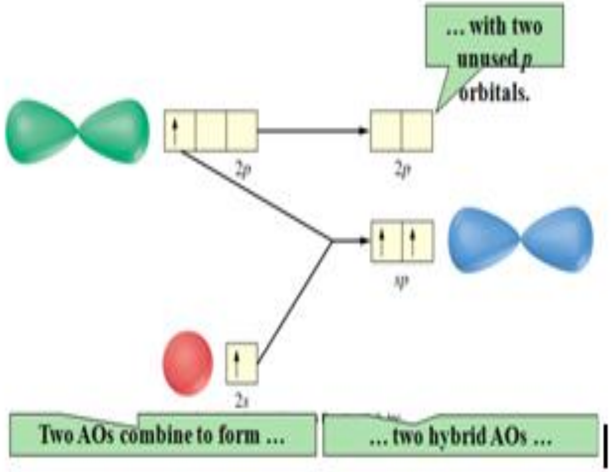
- Combination of one *s* and one *p* orbital.
- Gives a linear arrangement of atomic orbitals.
- Two *p* orbitals are not used.
  - ✓ Needed to form the π bonds.
- These sp-hybrid orbitals are arranged linearly at by making 180º of angle.
- They possess 50% 's' and 50% 'p' character.



- Note that any left-over "p" orbitals are referred to as "unhybridized orbitals".
- These unhybridized orbitals are used to form any double or triple (Pi) bonds in a molecule and since this structure shows no multiple bonding, these unhybridized orbitals are vacant.
- **It should be noted that the "sp" hybrid orbitals will arrange themselves in a linear geometry.**



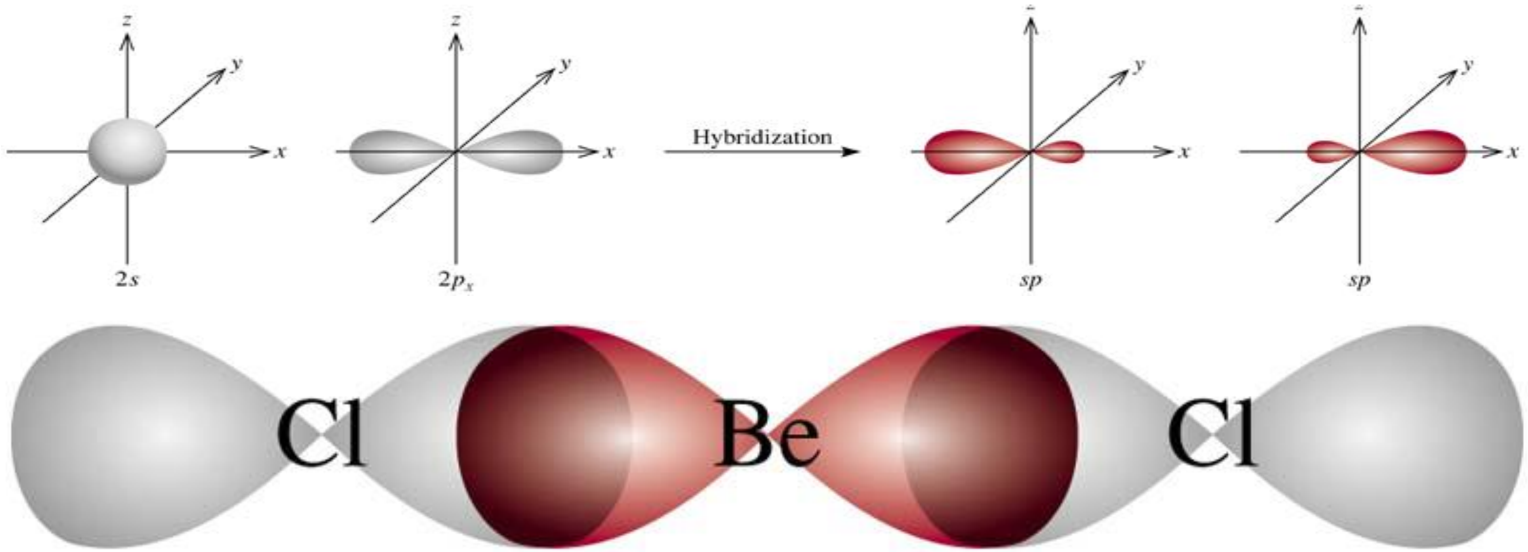




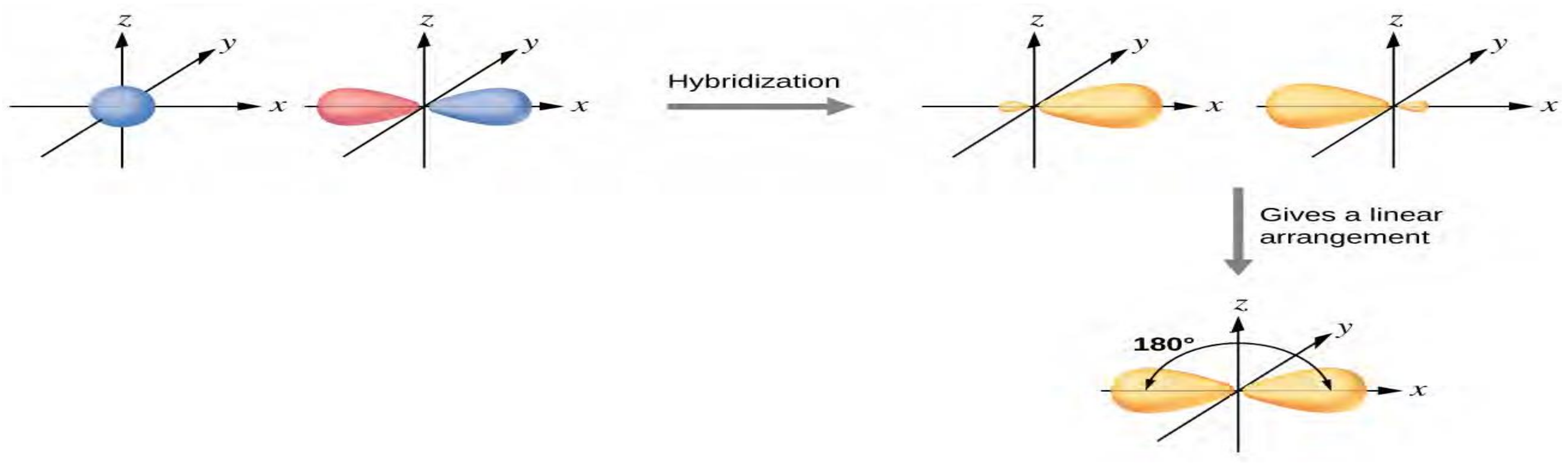
EXAMPLE!

CO_2, $BeCl_2$ etc

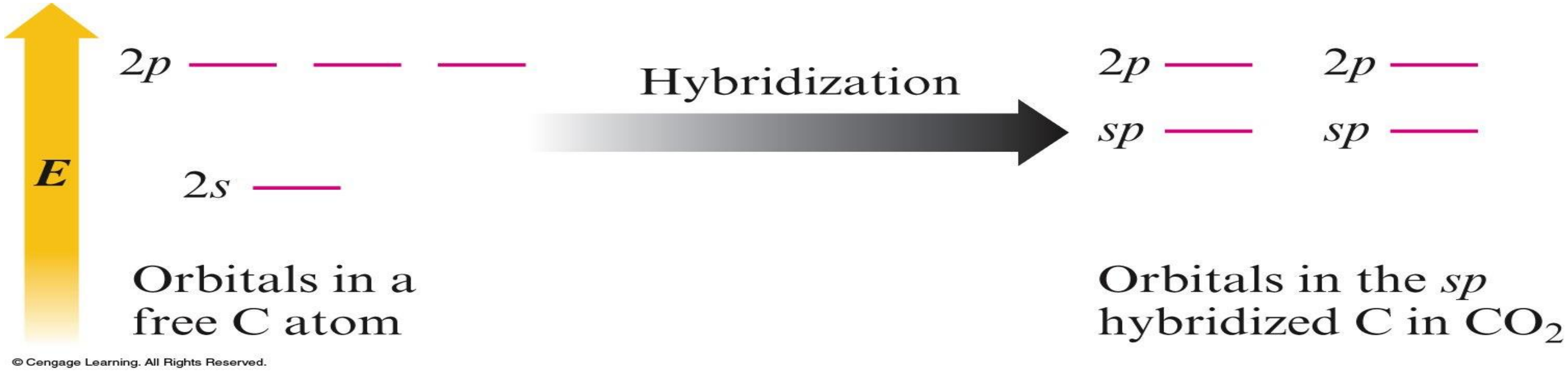
- When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals.
- The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons.
- Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.



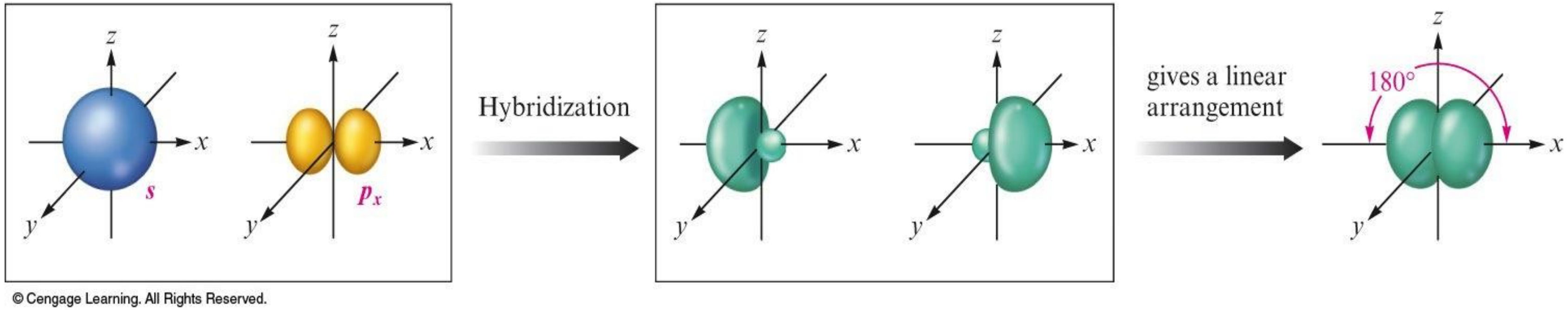
- Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (purple).
- Each hybrid orbital is oriented primarily in just one direction.
- Note: each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains



The Orbital Energy-Level Diagram for the Formation of *sp* Hybrid Orbitals on Carbon



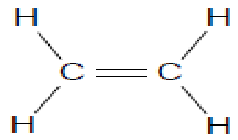
When One *s* Orbital and One *p* Orbital are Hybridized, a Set of Two *sp* Orbitals Oriented at 180 Degrees Results



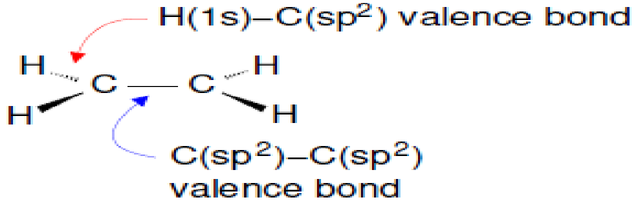
Multiple Bonds

Hybridization in molecules containing double and triple bonds

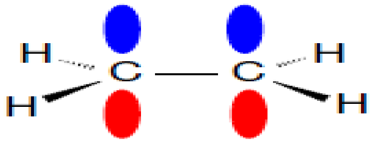
1. Ethene C_2H_4



- Trigonal planar carbons $\Longrightarrow$ sp^2 hybridization
- sp^2 hybrids used to make σ bonds to H atoms (with their 1s orbitals) and between the C atoms:

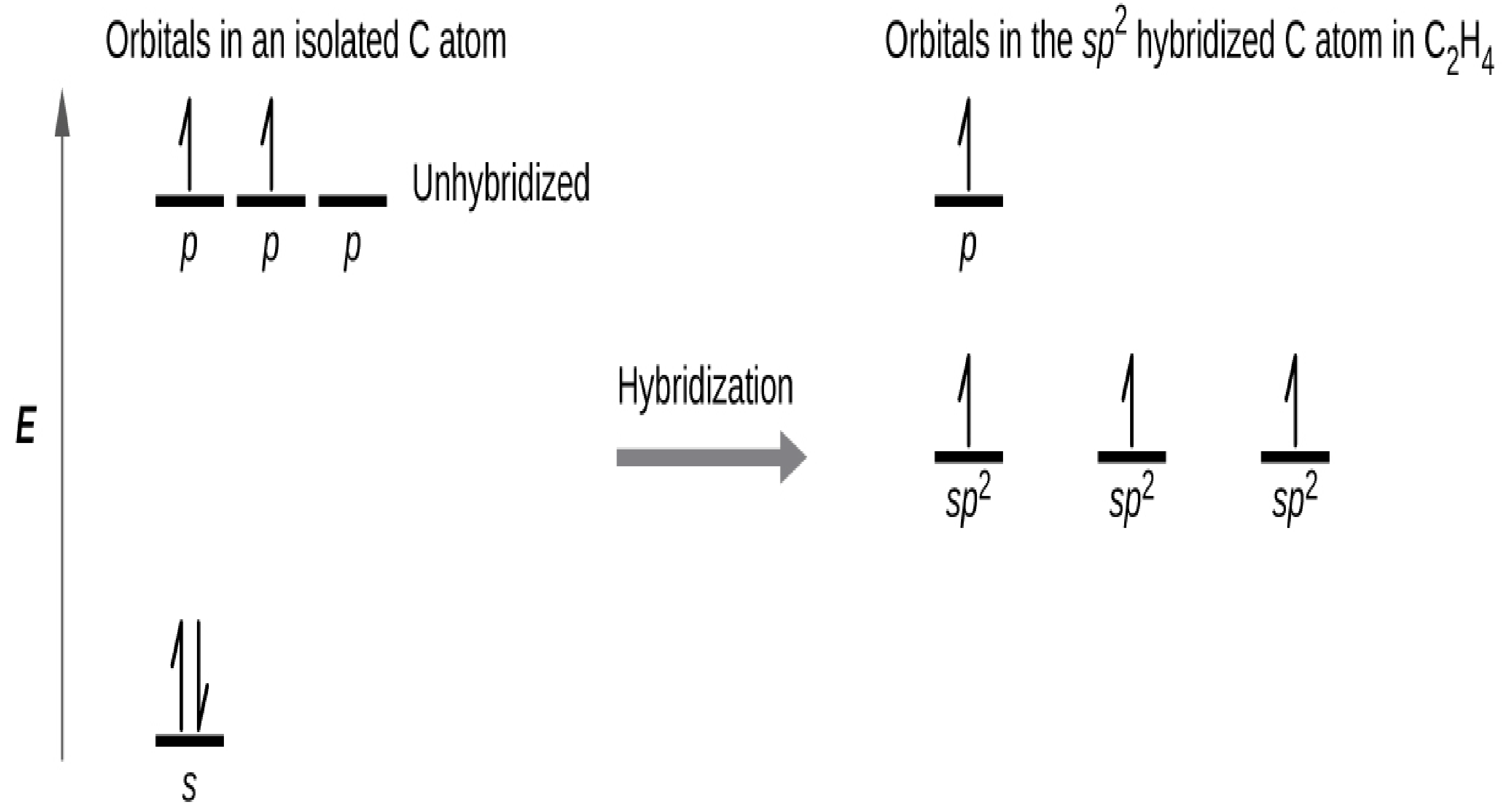


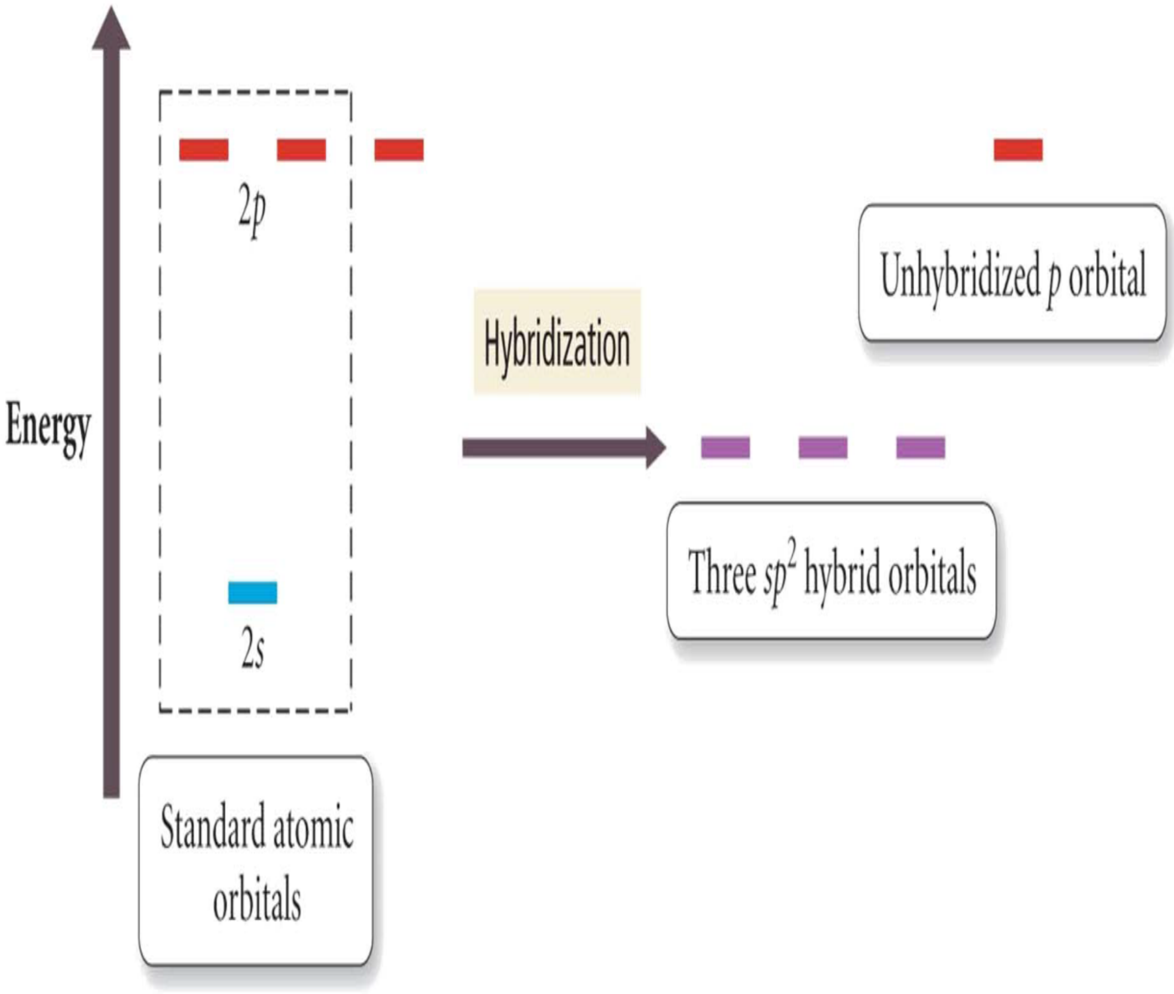
- This leaves one unused p orbital on each carbon atom:

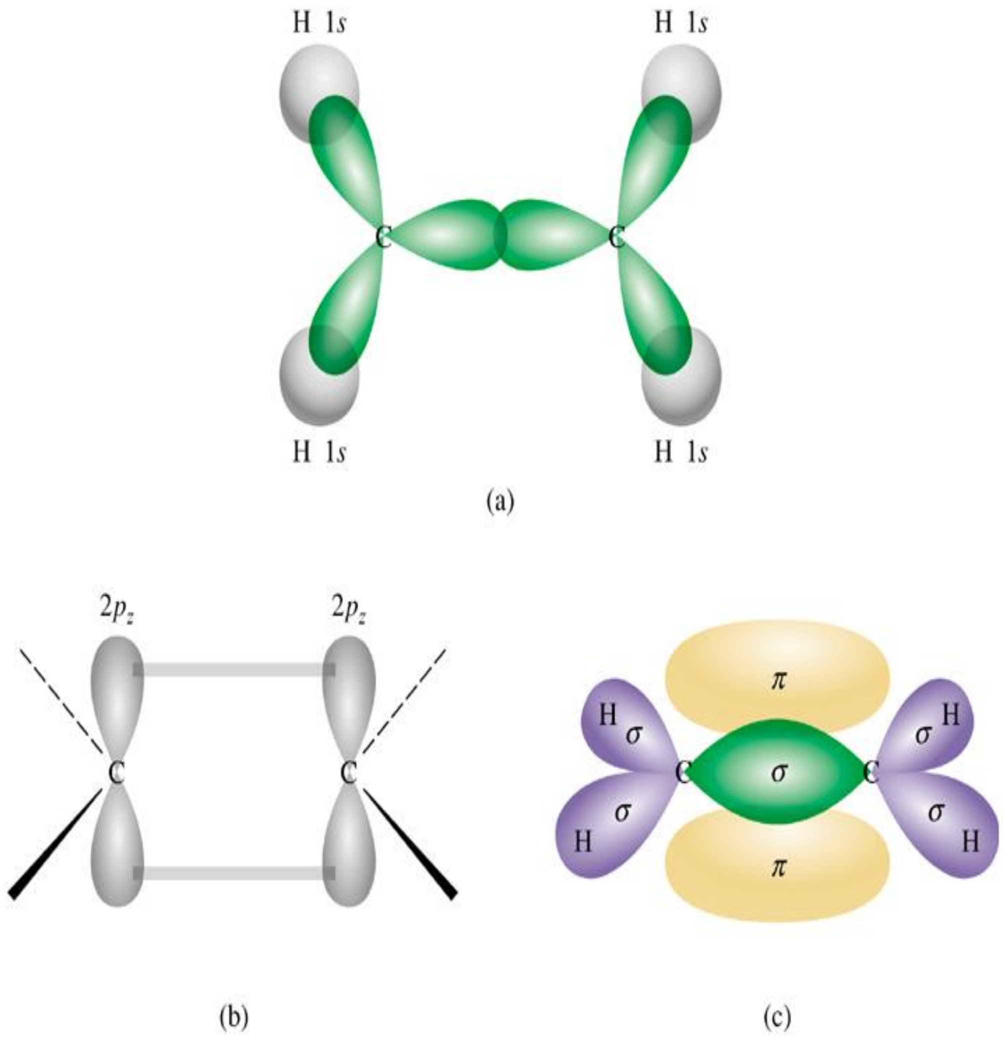


- The overlap of these p orbitals forms a π valence bond.
- VB description of the π bond: C(2p)-C(2p).

- In ethene, each carbon atom is *sp*2 hybridized, and the *sp*2 orbitals and the *p* orbital are singly occupied.
- The hybrid orbitals overlap to form σ bonds, while the *p* orbitals on each carbon atom overlap to form a π bond.

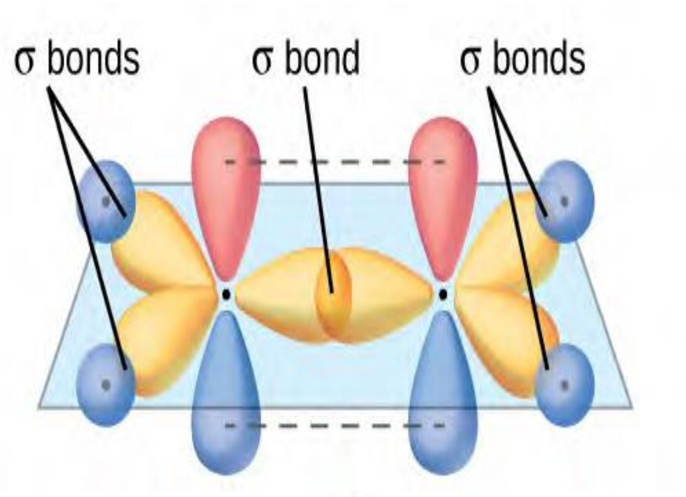



Energy
2p
2s
Hybridization
Unhybridized p orbital
Three sp2 hybrid orbitals
Standard atomic orbitals

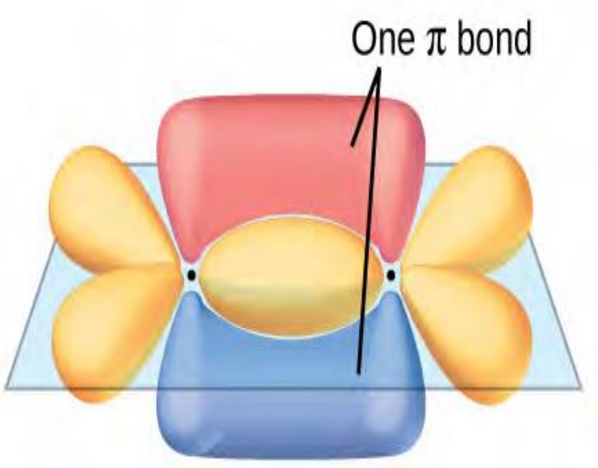

H 1s
H 1s
H 1s
H 1s
C
C
(a)
2pz
2pz
C
C
(b)
π
π
σ
σ
σ
σ
σ
H
H
H
H
C
C
(c)

In the ethene molecule, C2H4, there are

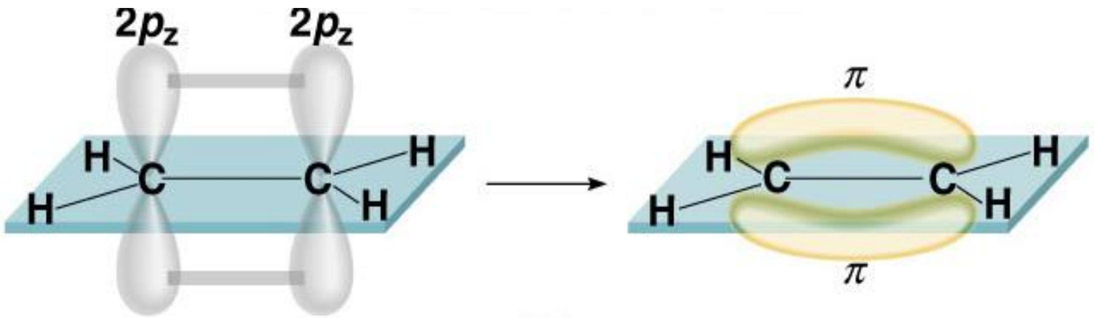
- five σ bonds shown in purple. One C–C σ bond results from overlap of *sp*2 hybrid orbitals on the carbon atom with one *sp*2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the *sp*2 orbitals with *s* orbitals on the hydrogen atoms.
- (The π bond is formed by the side-by-side overlap of the two unhybridized *p* orbitals in the two carbon atoms, which are shown in red. The two lobes of the π bond are above and below the plane of the σ system.



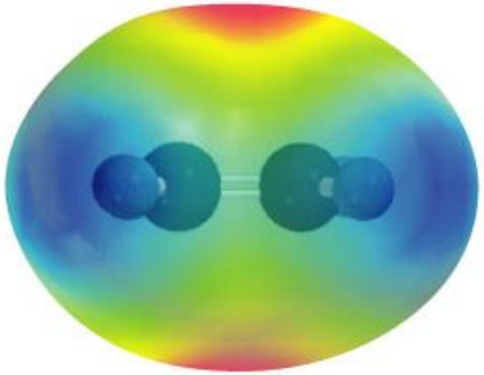
(a)



(b)



(a)

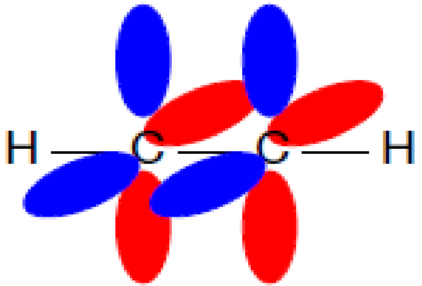


Multiple Bonds

Ethyne C_2H_2

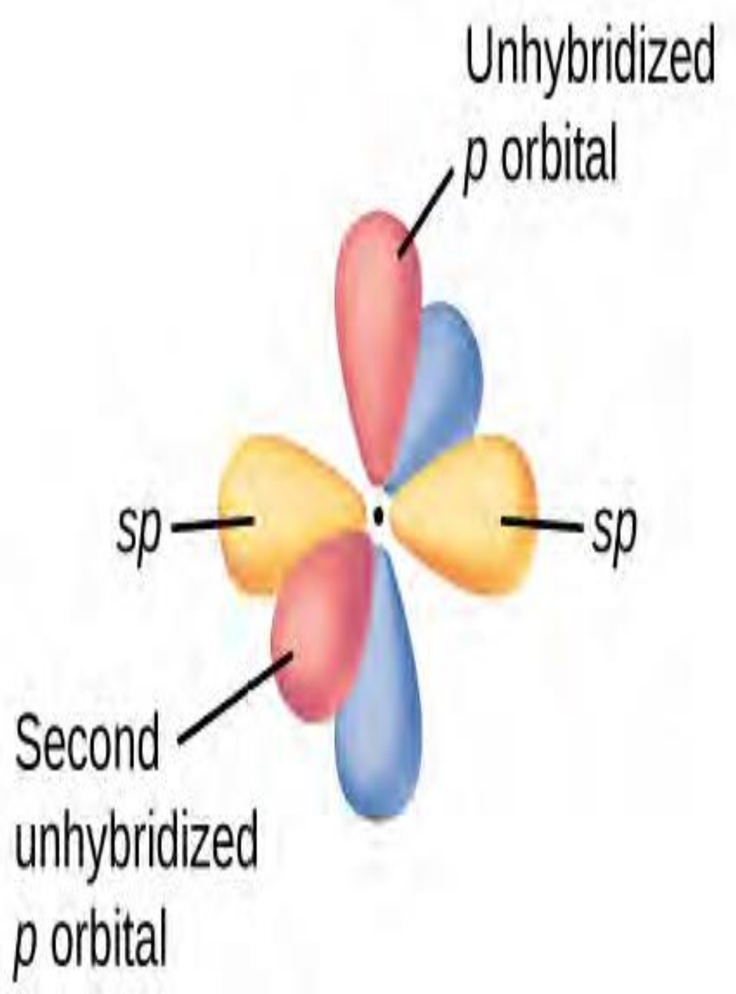
$$H-C\equiv C-H$$

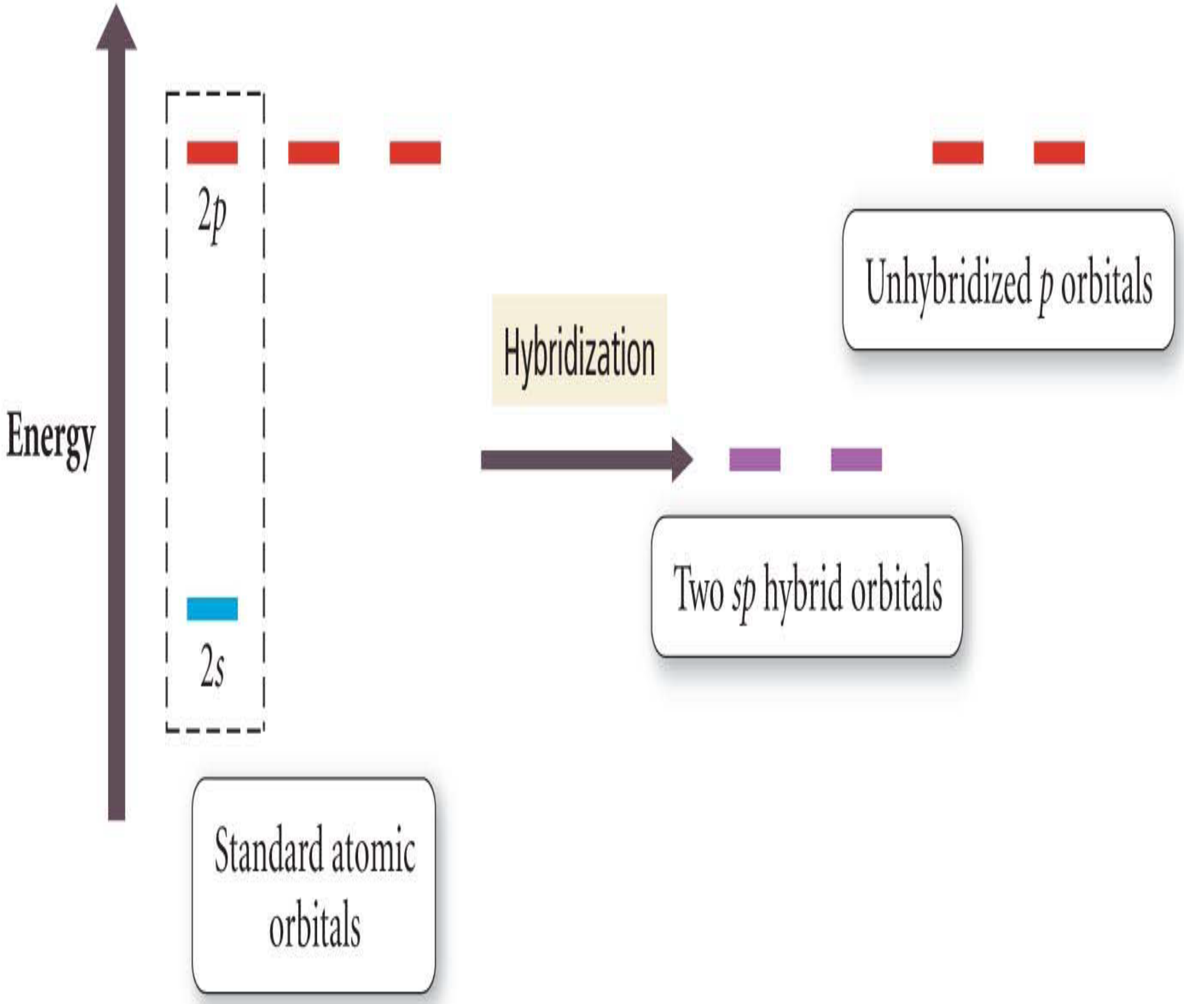
- Linear geometry around each carbon $\Longrightarrow$ sp hybridization
- Each carbon atom has two p orbitals left over:

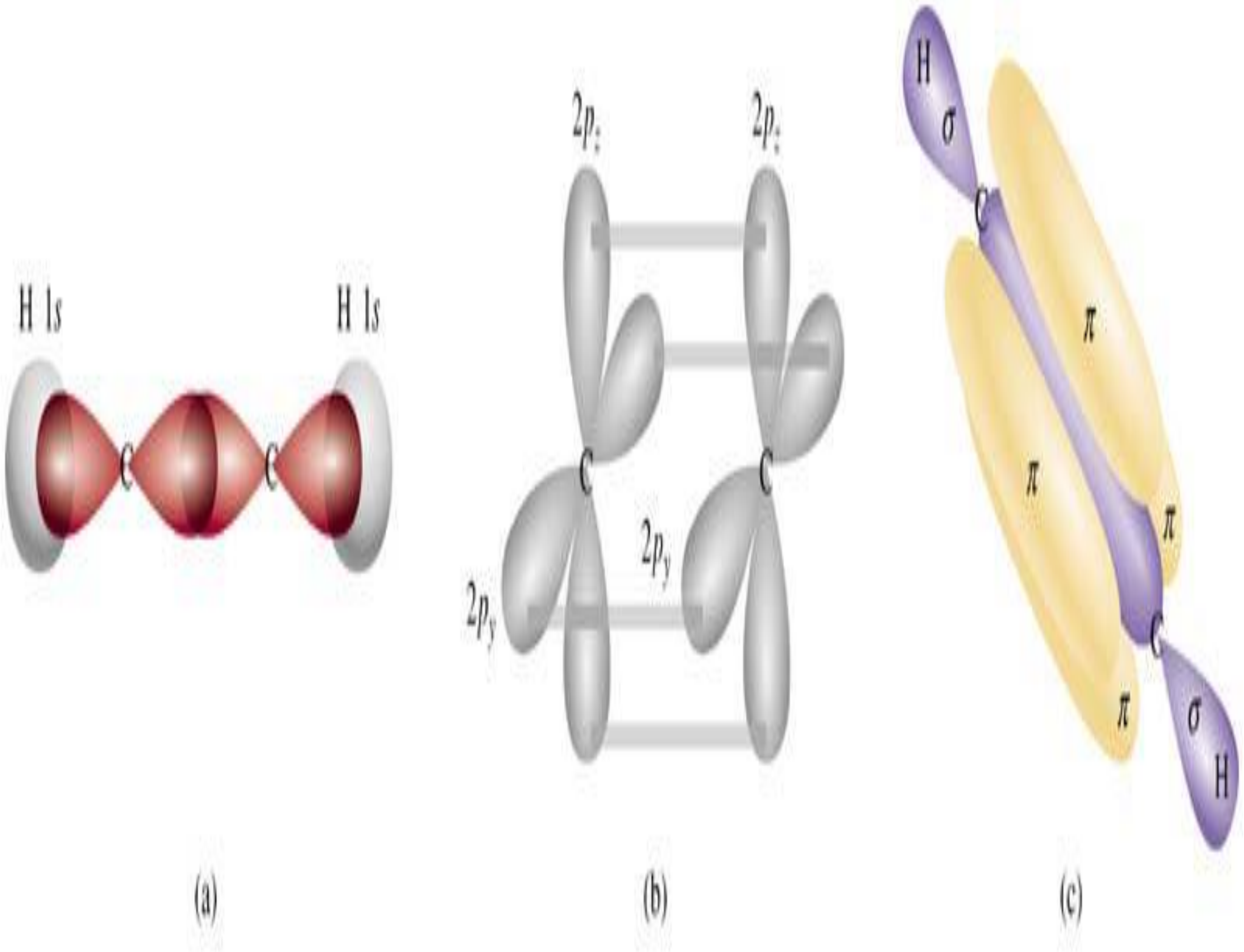


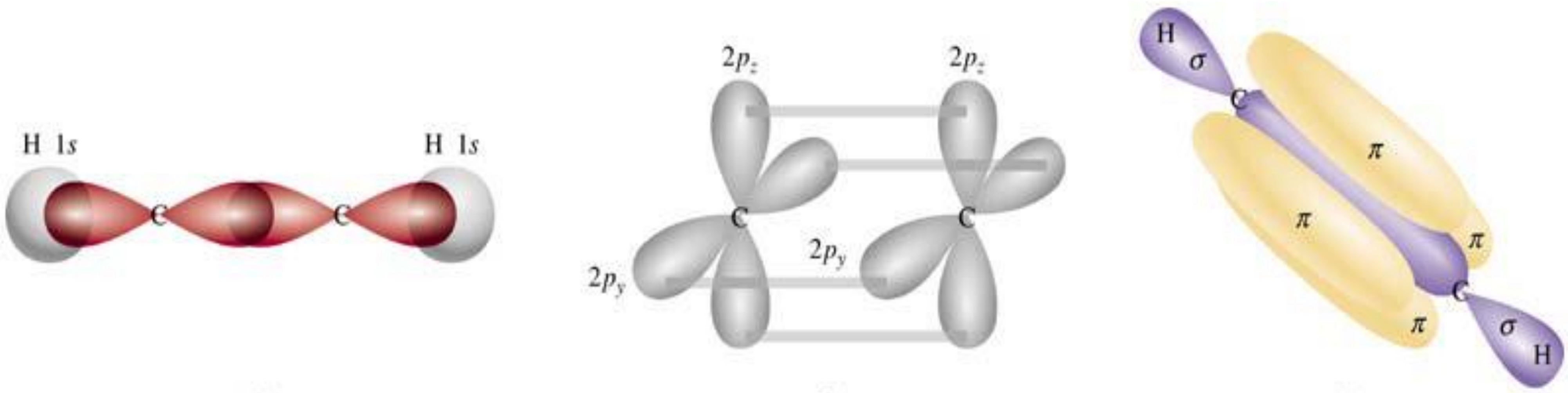
- These p orbitals combine into two π bonds.

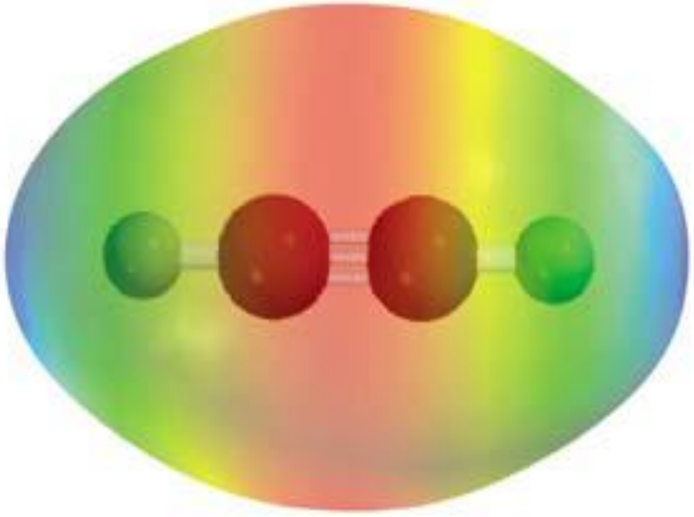
- In molecules with *sp* hybrid orbitals, two unhybridized *p* orbitals remain on the atom.
- We find this situation in acetylene, H−C≡C−H, which is a linear molecule.
- The *sp* hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms.
- The remaining *sp* orbitals form σ bonds with hydrogen atoms.
- The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds.
- The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.




Energy
2p
2s
Standard atomic orbitals
Hybridization
Two sp hybrid orbitals
Unhybridized p orbitals

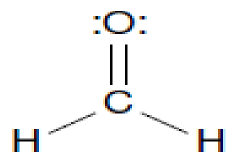

H 1s
C
C
H 1s
(a)
2pz
2pz
C
C
2py
2py
(b)
H
σ
C
π
π
π
π
C
σ
H
(c)



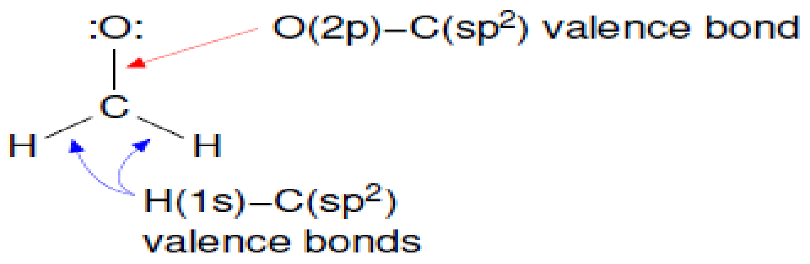


(d)

Formaldehyde



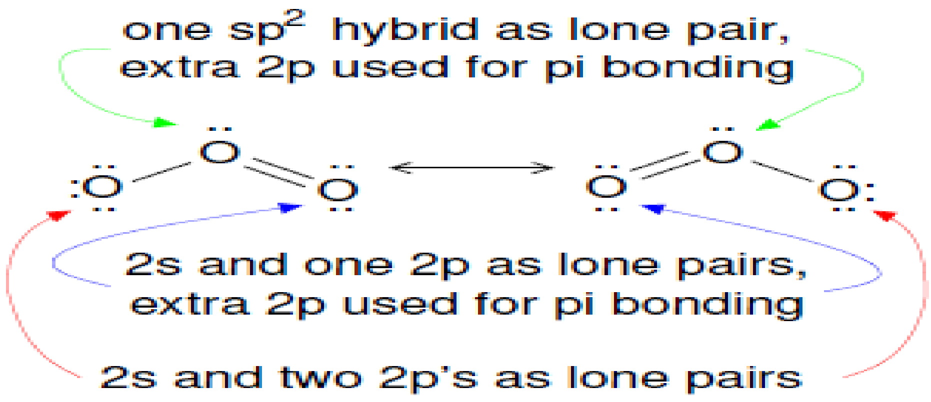
- Trigonal planar geometry at the carbon atom $\Longrightarrow$ sp^2 hybridization
- The O atom can form a σ bond using a p orbital.



- Why use the O(2p) rather than the O(2s) for bonding?
  - The general assumption in VB theory is that lone pairs go into the lowest-energy AO.
- The carbon atom has one p orbital left over which can combine with the corresponding orbital on O to form the π bond.

Ozone

- The sigma framework of ozone is easy:
  - The central O is sp^2 hybridized.
  - One of the sp^2 hybrids contains a lone pair.
  - The other two form σ bonds with one p orbital on each of the terminal O atoms.
- Construct VB wavefunctions corresponding to both of these structures and average these wavefunctions together:



EXAMPLE!

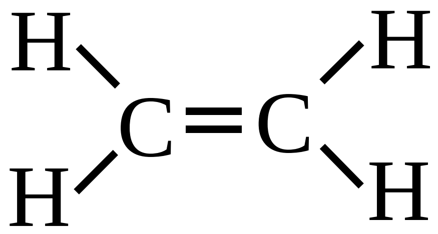
Draw the Lewis structure for C_2H_4 (ethylene)?

What is the shape of an ethylene molecule?

trigonal planar around each carbon atom

What are the approximate bond angles around the carbon atoms?

120^o



CONCEPT CHECK!

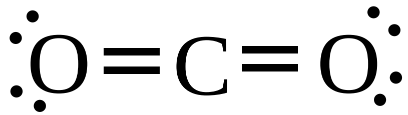
Why can't *sp*^{3} hybridization account for the ethylene molecule?

EXAMPLE!

Draw the Lewis structure for CO_2.

What is the shape of a carbon dioxide molecule?

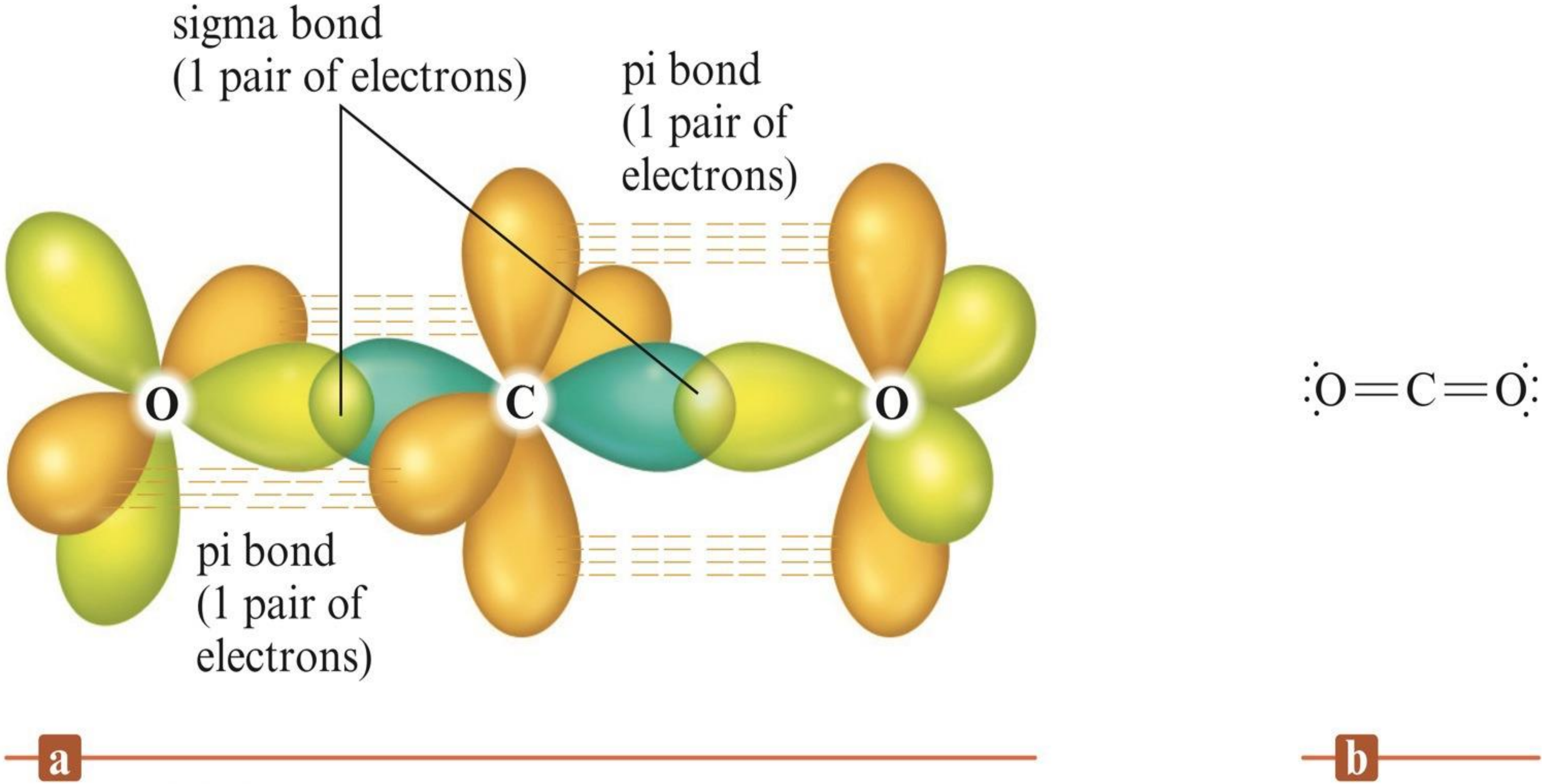
linear



What are the bond angles?

180º

The Orbitals for CO_2



EXERCISE!

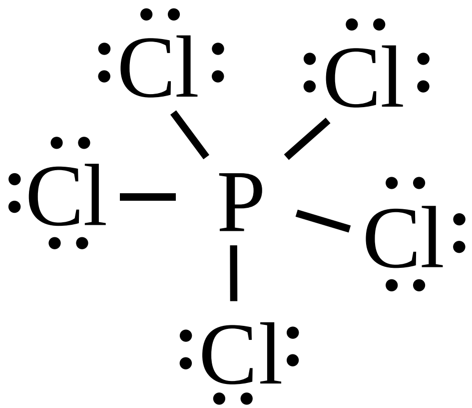
Draw the Lewis structure for PCl_5.

What is the shape of a phosphorus pentachloride molecule?

trigonal bipyramidal

What are the bond angles?

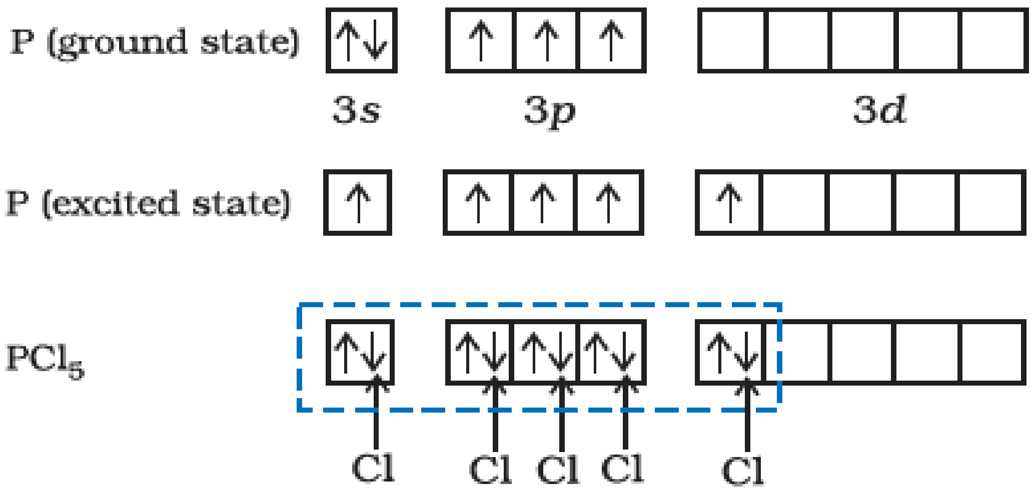
90^o and 120^o

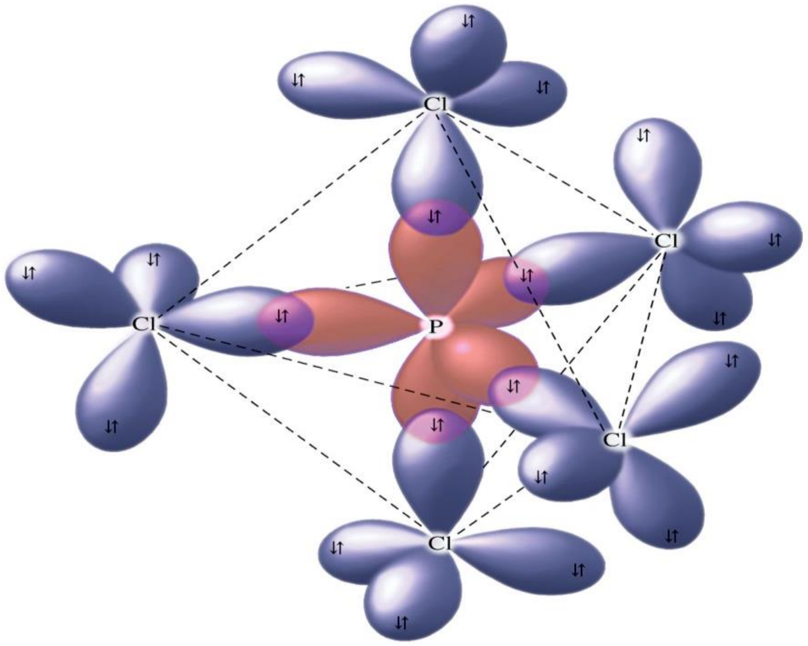


4. *dsp*^{3} Hybridization

- Combination of one *d*, one *s*, and three *p* orbitals.
- Gives a trigonal bipyramidal arrangement of five equivalent hybrid orbitals.

Example: The Orbitals Used to Form the Bonds





EXAMPLE!

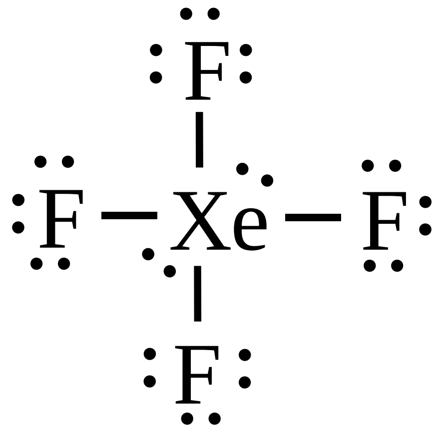
Draw the Lewis structure for XeF_4.

- What is the shape of a xenon tetrafluoride molecule?

  octahedral

- What are the bond angles?

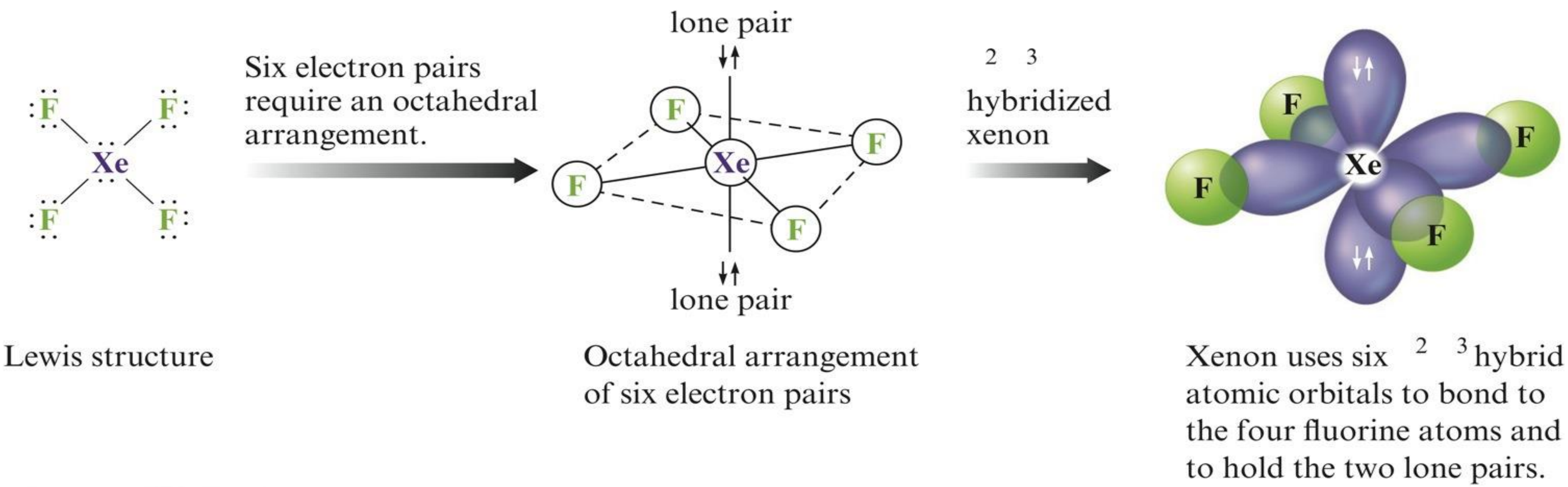
  90^o and 180^o



d^2sp^3 Hybridization

- Combination of two *d*, one *s*, and three *p* orbitals.
- Gives an octahedral arrangement of six equivalent hybrid orbitals.

How is the Xenon Atom in XeF_4 Hybridized?

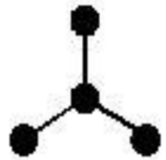
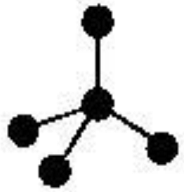
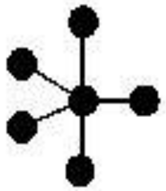
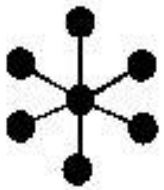


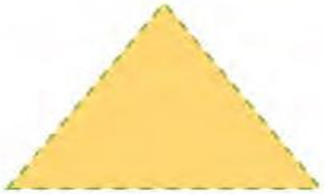
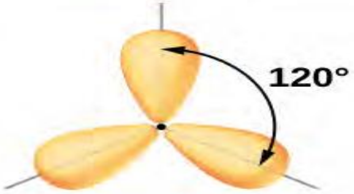
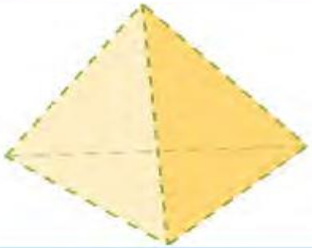
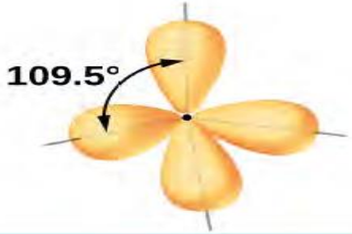
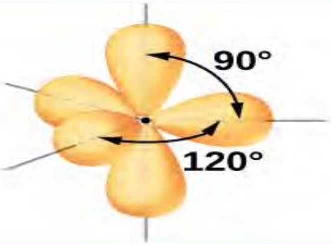
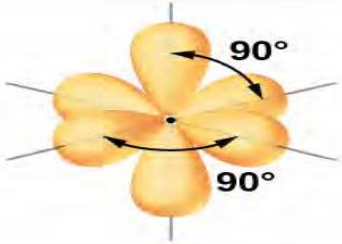
Shortcomings of VB theory

- A lot of things that fall out naturally in MO theory are hard in VB theory:
  - Explanation of photoelectron spectra
  - Explanation of paramagnetism of O2
- In its simplest form, VB theory only tells us what we already know based on Lewis diagrams and VSEPR. It only becomes a predictive theory in its most advanced forms.

The following table summarizes the five types of hybridization addressed in this exercise.

Number of required hybrid orbitals	Electron Pair Arrangement	Type of Hybridization	Atomic Orbitals used to create Hybrids
2	Linear	sp	one s, one p
3	Trigonal planar	sp^2	one s, two p's
4	Tetrahedral	sp^3	one s, three p's
5	Trigonal bipyramidal	sp^3d	one s, three p's, one d
6	Octahedral	sp^3d^2	one s, three p's, two d's

# electron groups	Bond angle	Base geometry	# lone pairs	Shape		Hybridization
2	180º	Linear	0	Linear		sp
3	120º	Trigonal planar	0	Trigonal planar		sp^2
			1	Bent		
4	109.5º	Tetrahedral	0	Tetrahedral		sp^3
			1	Trigonal pyramidal		
			2	bent		
5	90º/120º	Trigonal bipyramidal	0	Trigonal bipyramidal		sp^3d
			1	See-saw		
			2	t-shaped		
			3	Linear		
6	90º	Octahedral	0	Octahedral		sp^3d^2
			1	Square pyramidal		
			2	Square planar		

Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

CONCEPT CHECK!

Why atomic orbitals in a given atom undergo hybridization?

- ✓ The hybrid orbitals are oriented in space so as to minimize repulsions between them.

- ❖ This explains why the atomic orbitals undergo hybridization **before bond formation.**
- ❖ The reason for hybridization is to minimize the repulsions between the bonds that are going to be formed by the **atoms by using hybrid orbitals.**
- ❖ Remember that the:
  - ✓ hybridization is the process that occurs before bond formation.
  - ✓ The shape of the molecule is determined by the type of hybridization, number of bonds formed by them and the number of lone pairs.

Exercise!

Draw the Lewis structure for HCN.

Which hybrid orbitals are used?

Draw HCN:

- Showing all bonds between atoms.
- Labeling each bond as σ or π.

Determine the bond angle and expected hybridization of the central atom for each of the following molecules:

NH_3 SO_2 KrF_2 CO_2 ICl_5

NH_3 – 109.5°, sp^3

SO_2 – 120°, sp^2

KrF_2 – 90°, 120°, dsp^3

CO_2 – 180°, sp

ICl_5 – 90°, 180°, d^2sp^3

Using the Localized Electron Model

- Draw the Lewis structure(s).
- Determine the arrangement of electron pairs using the VSEPR model.
- Specify the hybrid orbitals needed to accommodate the electron pairs.

Molecular Orbital Theory

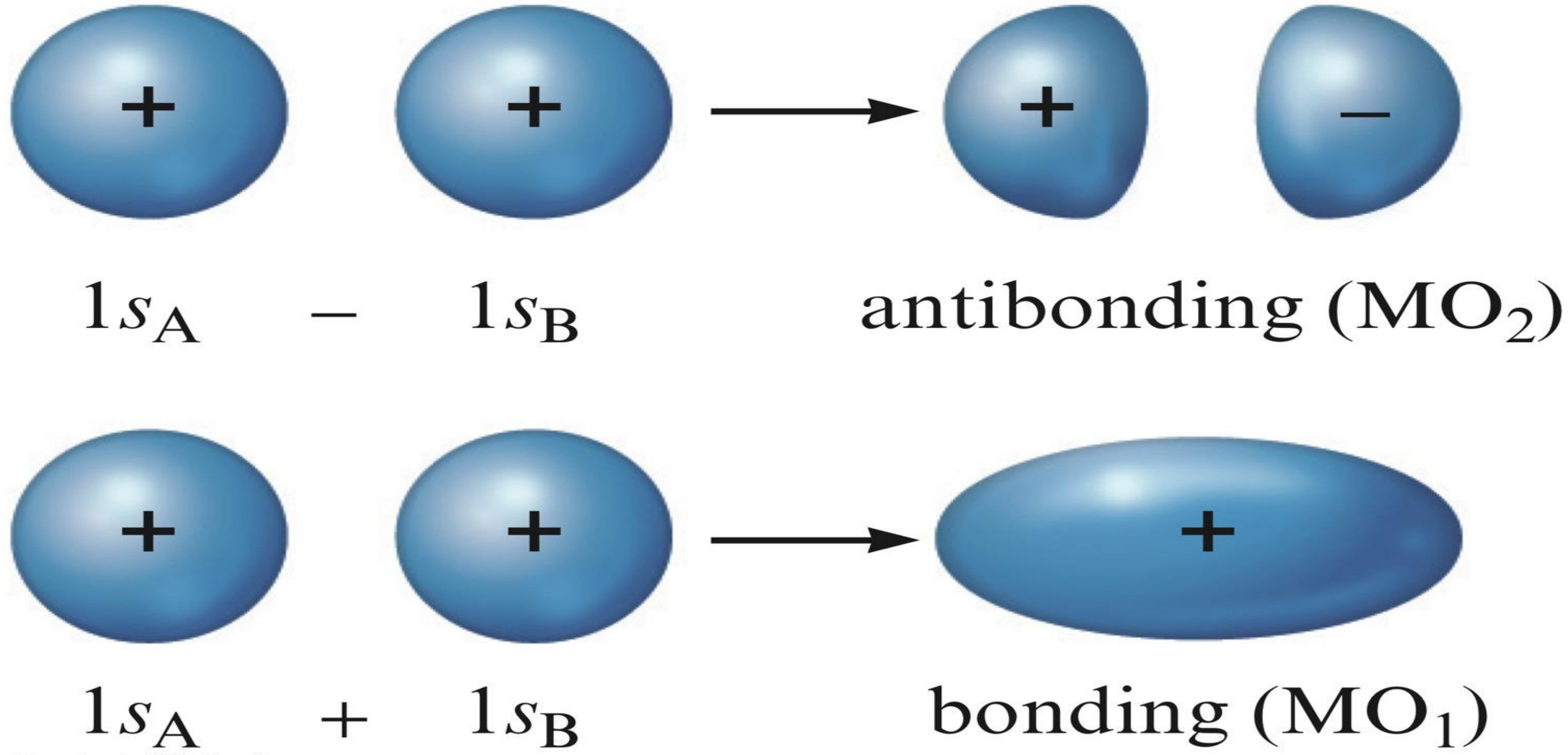
Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the:

- paramagnetism of the oxygen molecule.
- Explaination the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures.
- Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons.
- Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms.
- MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators

The Molecular Orbital Theory

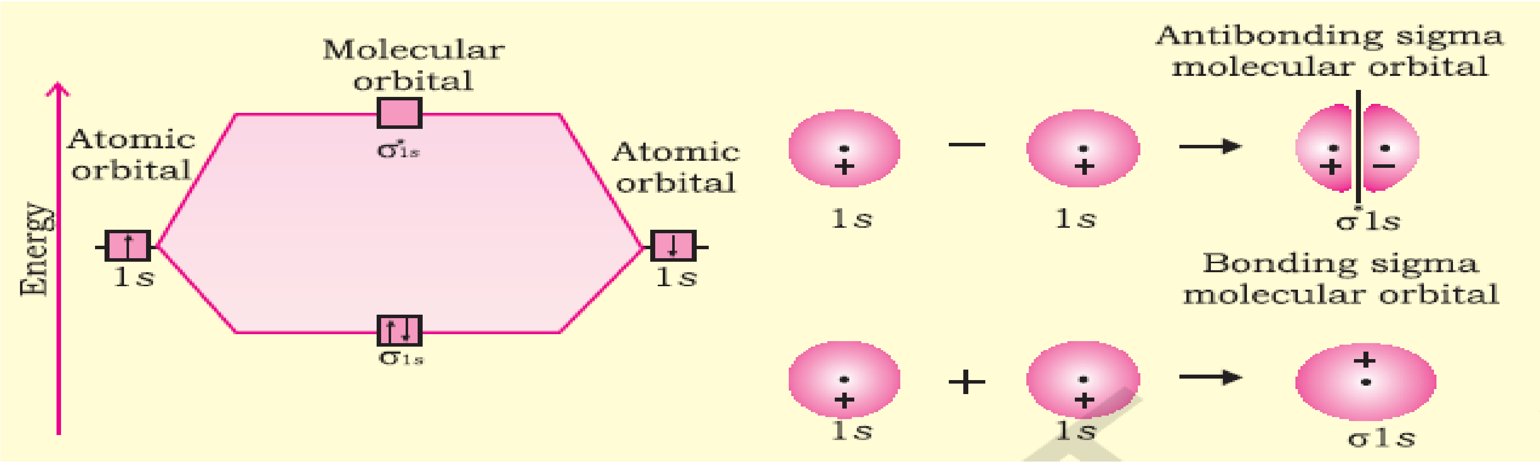
- Regards a molecule as a collection of nuclei and electrons, where the electrons are assumed to occupy orbitals much as they do in atoms, but having the orbitals extend over the entire molecule.
- The electrons are assumed to be delocalized rather than always located between a given pair of atoms.
- The electron probability of both molecular orbitals is centered along the line passing through the two nuclei.
    - ✓ Sigma (σ) molecular orbitals (MOs)
- In the molecule only the molecular orbitals are available for occupation by electrons.

Combination of Hydrogen 1*s* Atomic Orbitals to form MOs



Energy Level Diagram for Molecular Orbitals

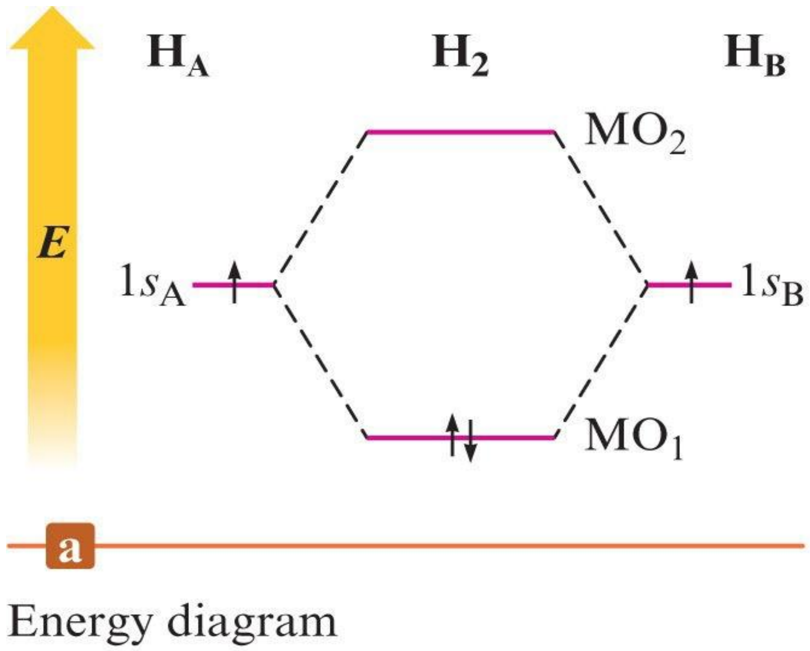
- We have seen that 1*s* atomic orbitals on two atoms form two molecular orbitals designated as σ1*s* and σ*1*s*.

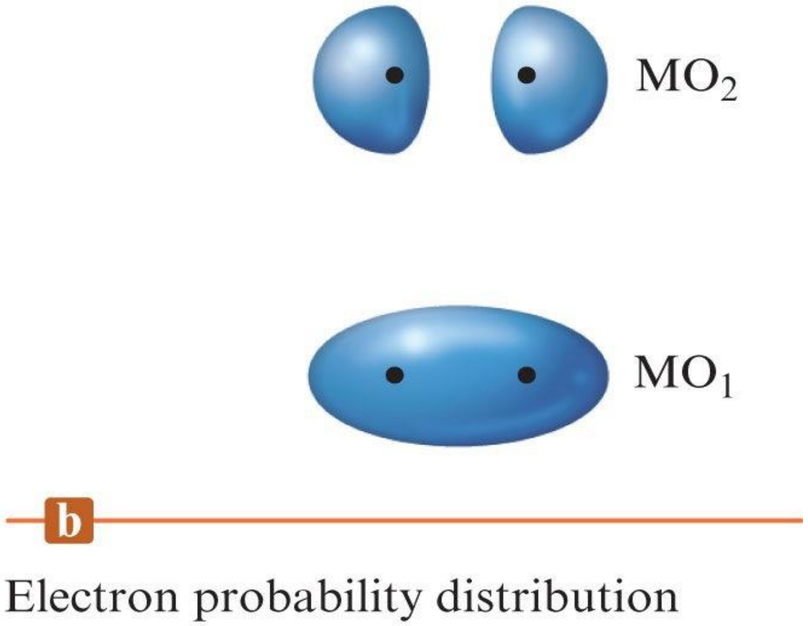


- In the same manner, the 2*s* and 2*p* atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals
  - Antibonding MOS   *σ*2s*   *σ*2pz*   *π*2px*   *π*2py*
  - Bonding MOs   *σ2s*   *σ2pz*   *π2px*   *π2py*

- MO_1 is lower in energy than the *s* orbitals of free atoms, while MO_2 is higher in energy than the *s* orbitals.
  - Bonding molecular orbital – lower in energy
  - Antibonding molecular orbital – higher in energy

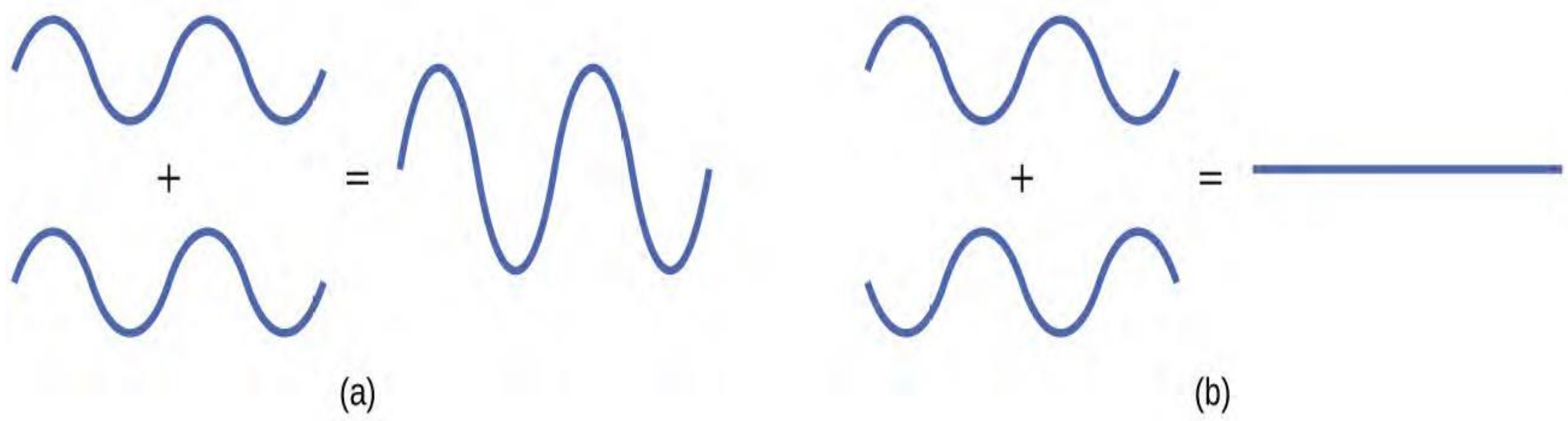
MO Energy-Level Diagram for the H_2 Molecule





- The molecular orbital model produces electron distributions and energies that agree with our basic ideas of bonding.
- The labels on molecular orbitals indicate their symmetry (shape), the parent atomic orbitals, and whether they are bonding or antibonding.
- Molecular electron configurations can be written in much the same way as atomic electron configurations.
- Each molecular orbital can hold 2 electrons with opposite spins.
- The number of orbitals are conserved.

- (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude.
- (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.



Types of MO

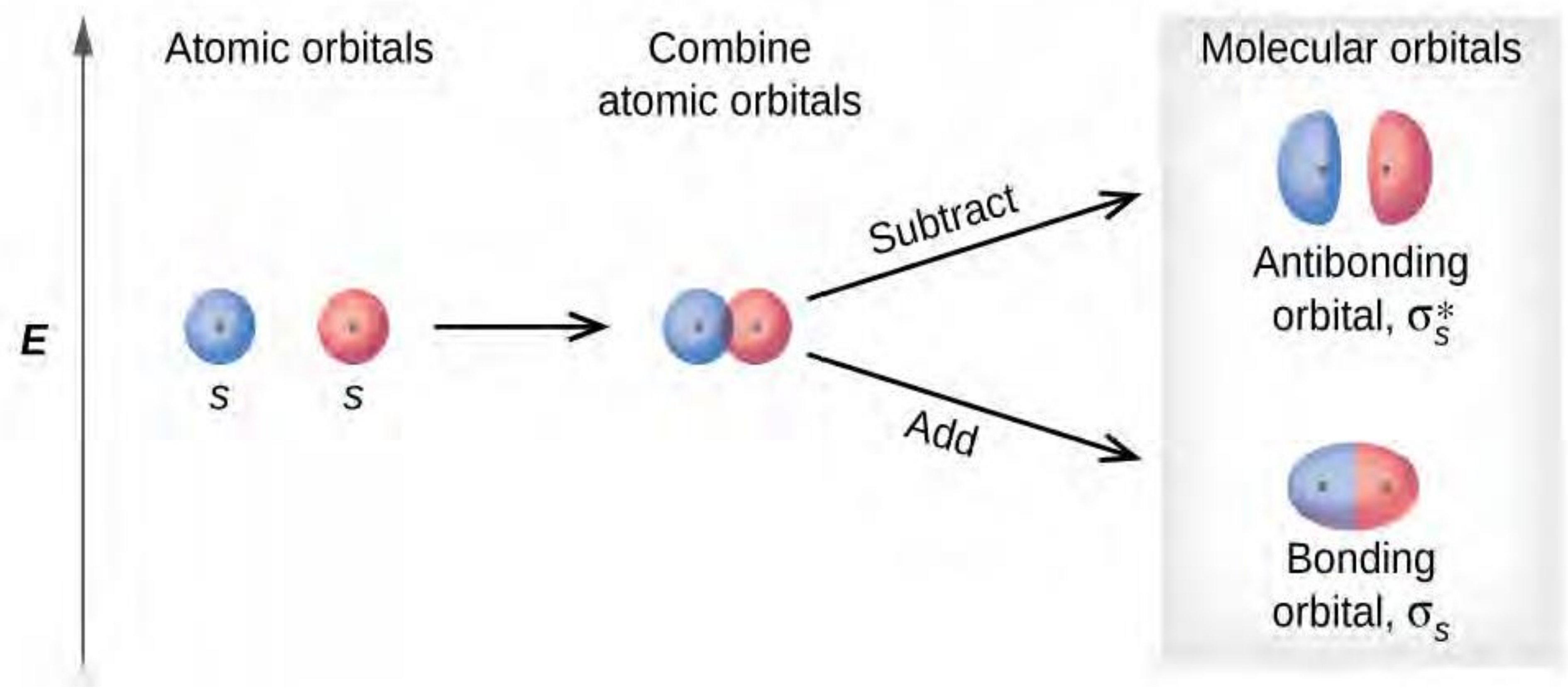
- There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms.

  The in-phase combination produces a lower energy **σs molecular orbital** (read as "sigma-s") in which most of the electron density is directly between the nuclei.

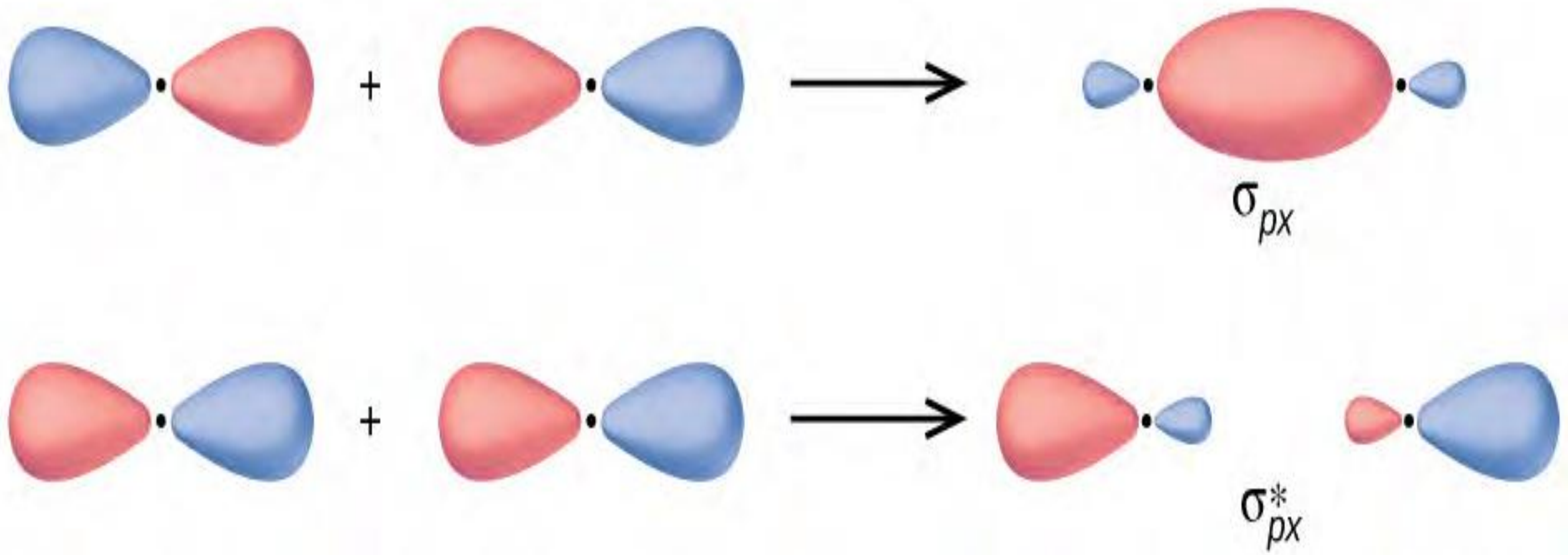
  The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy **molecular orbital** (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei.

  The asterisk signifies that the orbital is an antibonding orbital.

- Electrons in a σs orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals **bonding orbitals**.
- Electrons in the σs * orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called **antibonding orbitals**.
- Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

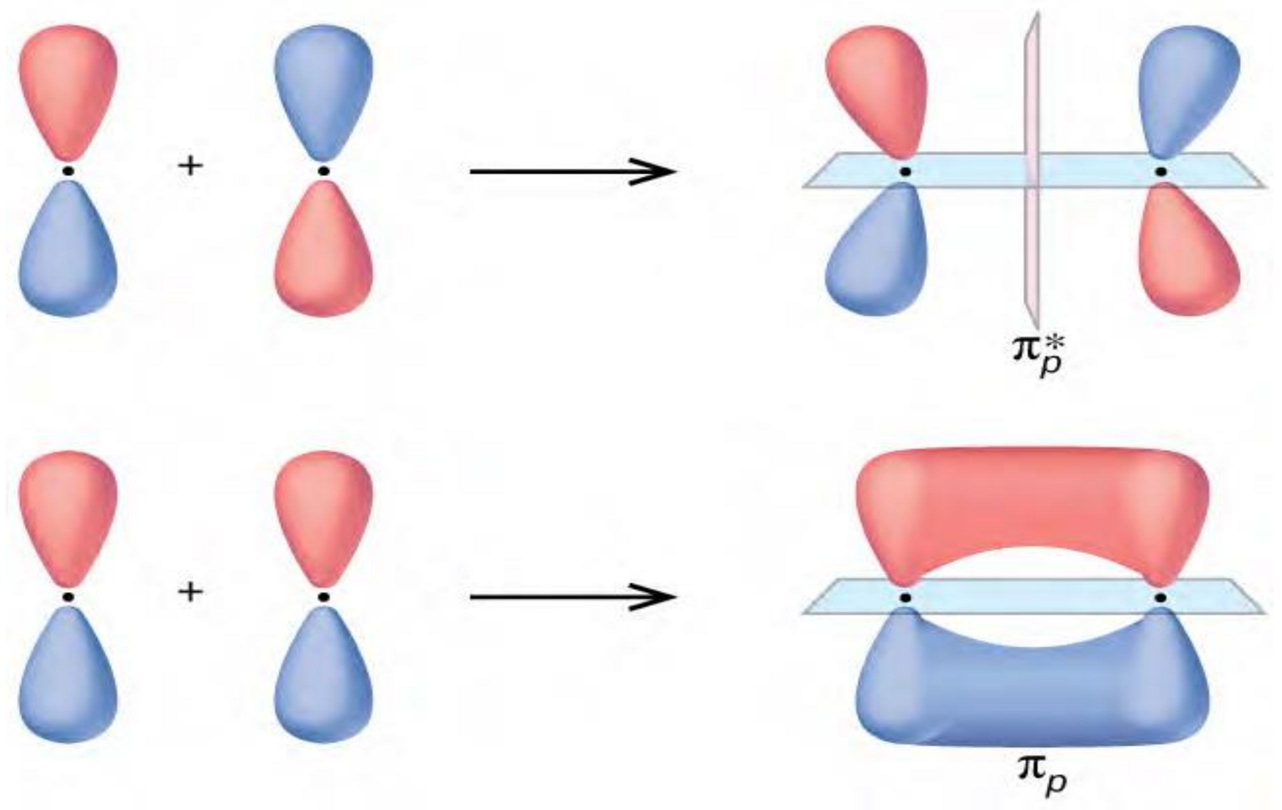

Atomic orbitals
Combine atomic orbitals
Molecular orbitals
E
s
s
Subtract
Add
Antibonding orbital, σ_s^*
Bonding orbital, σ_s

- In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors.
  - When orbital lobes of the same phase overlap, constructive wave interference increases the electron density.
  - When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes.
- When *p* orbitals overlap end to end, they create σ and σ* orbitals.
- If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two *px* orbitals overlap end to end and form *σpx* (bonding) and *σ*px*
- (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital


+
σ_{px}
+
σ^*_{px}

- The side-by-side overlap of two *p* orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibondingmolecular orbital**.
- In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node.
- In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons.
- Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital.
- For the out-of-phase combination, there are two nodal planes created, one along theinternuclear axis and a perpendicular one between the nuclei.

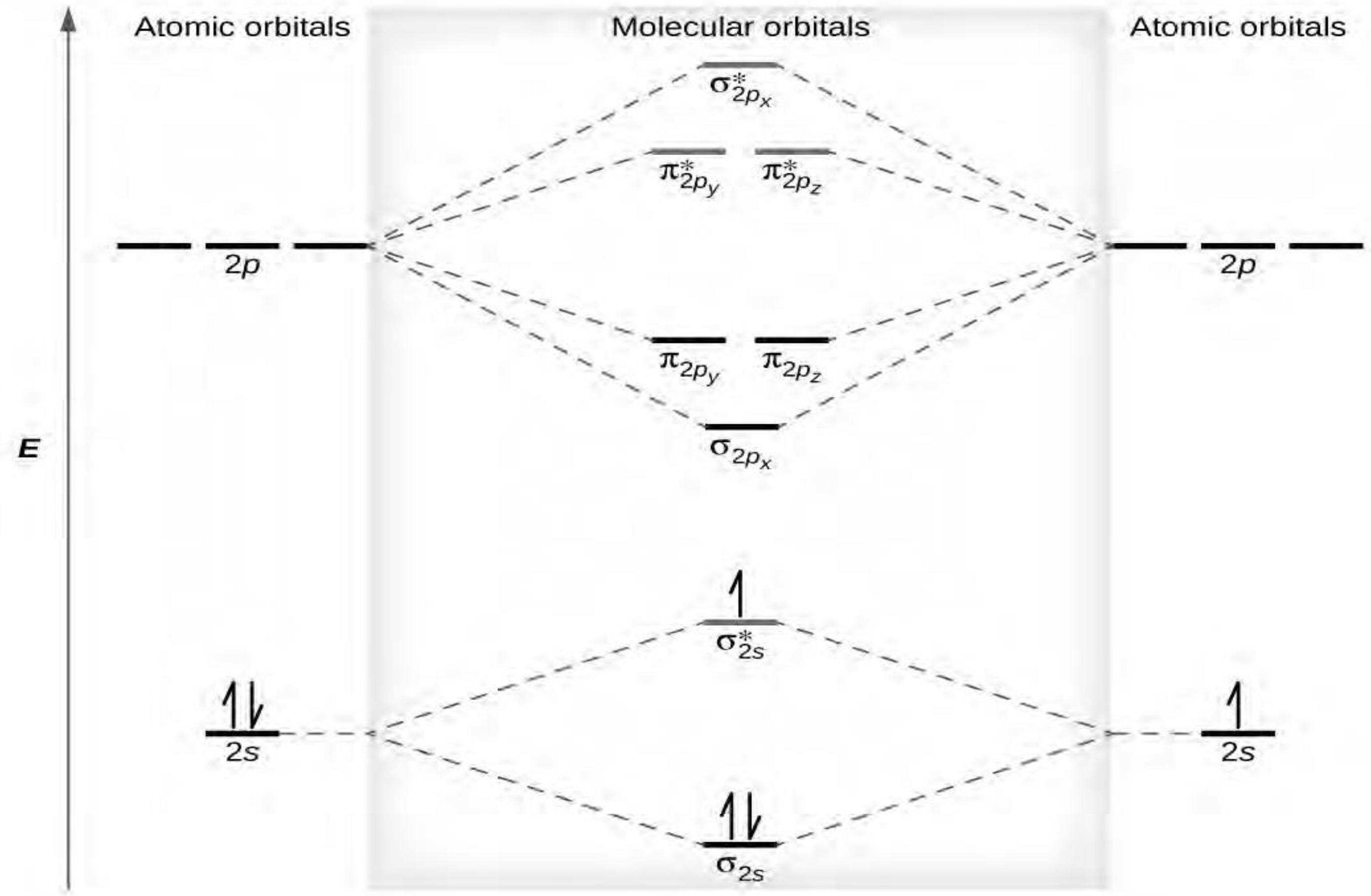
The MO Energy Diagram for Molecules with Multiple Bonds



The MO Energy Diagram for Molecules with Multiple Bonds

- We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins.
- Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital.
- Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be2+) would have the molecular electron configuration (σ1s)2 (σ*1s)2 (σ2s)2 (σ*2s)1. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

The MO Energy Diagram for Molecules with Multiple Bonds

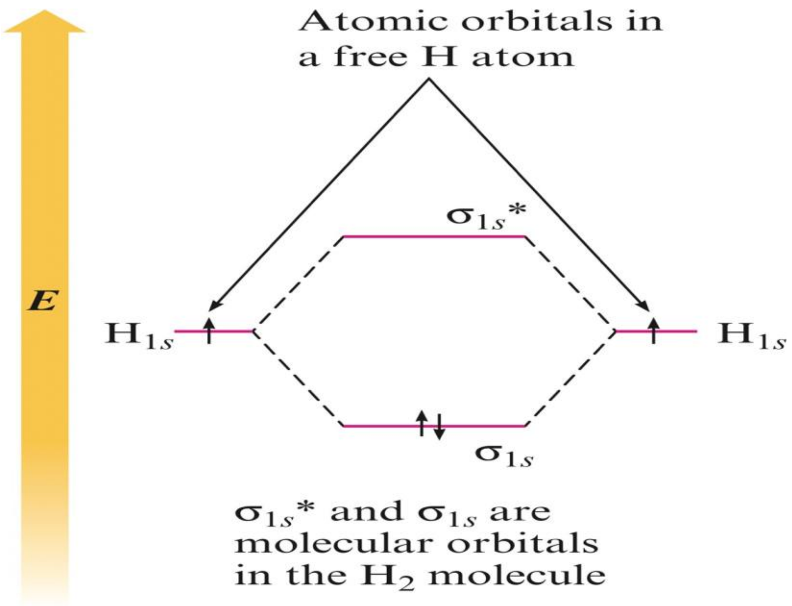


Bond Order

Larger bond order means greater bond strength.

$$\text{Bond order} = \frac{\#\text{ of bonding } e^- - \#\text{ of antibonding } e^-}{2}$$

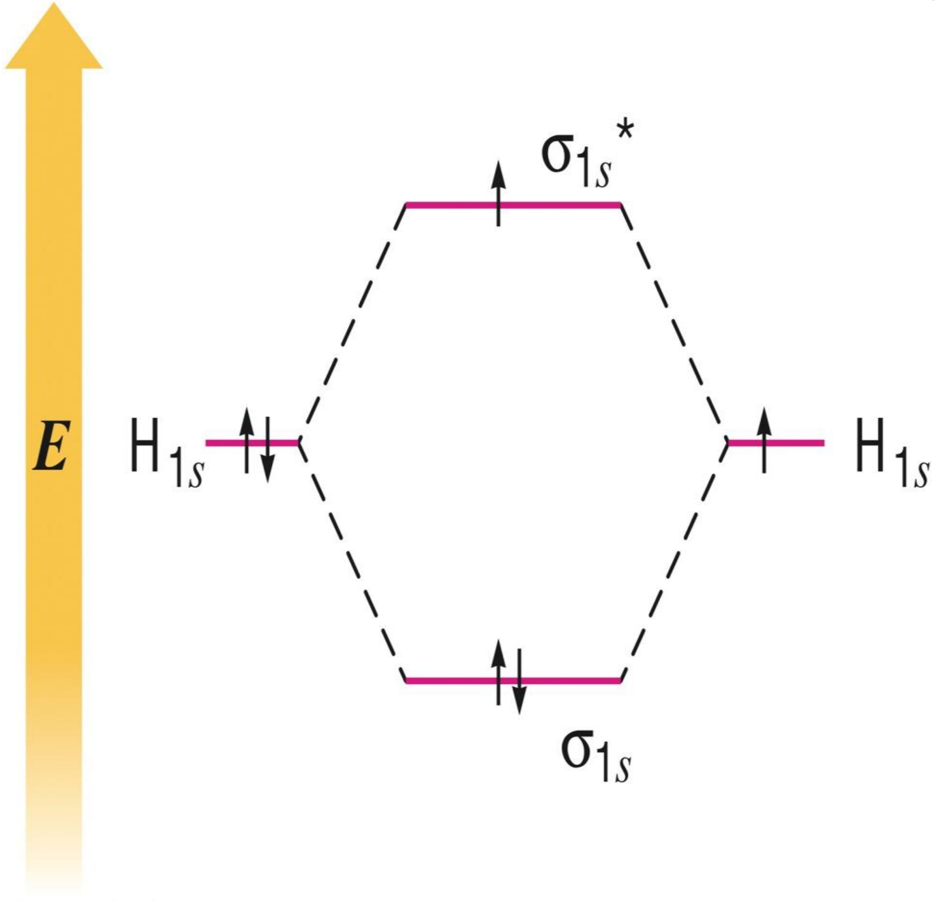
Example: H_2



$$\text{Bond order} = \frac{2 - 0}{2} = 1$$

- we define bond order as the number of bonding pairs of electrons between two atoms.
- Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same.
- The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

Example: H_2^-



$$\text{Bond order} = \frac{2 - 1}{2} = \frac{1}{2}$$

Bond-length

- The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length.
- The bond length decreases as bond order increases.

Homonuclear Diatomic Molecules

- Composed of 2 identical atoms.
- Only the valence orbitals of the atoms contribute significantly to the molecular orbitals of a particular molecule.

Paramagnetism

- Paramagnetism – substance is attracted into the inducing magnetic field.
  - ✓ The MO Contains Unpaired electrons (O_2)
- Diamagnetism – substance is repelled from the inducing magnetic field.
  - ✓ The MO Paired electrons (N_2)

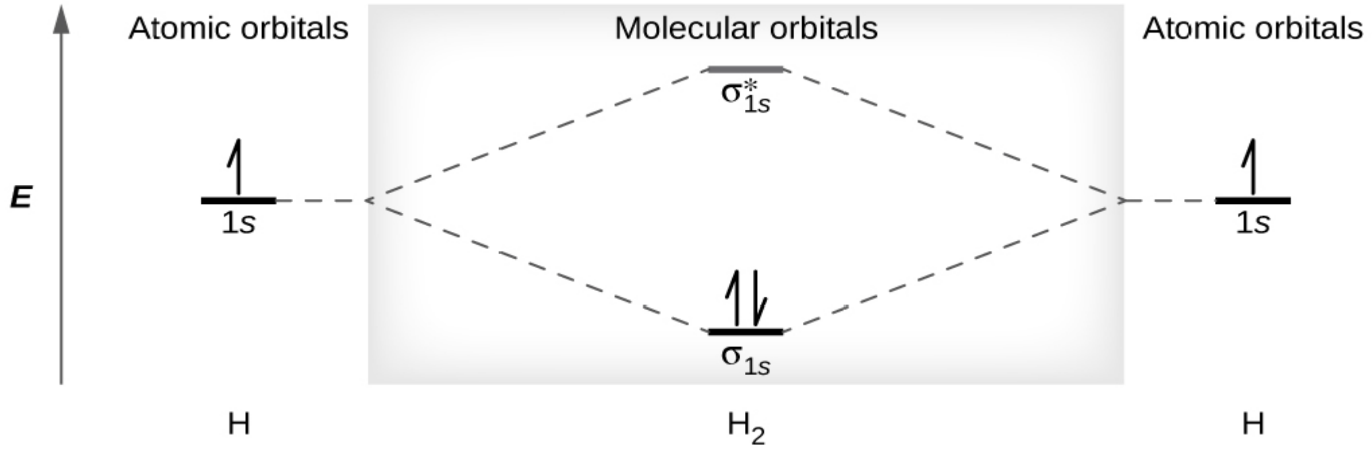
Molecular Orbital Summary of Second Row Diatomic Molecules

E (↑)	B_2	C_2	N_2
σ_{2p}^*	—	—	—
π_{2p}^*	— —	— —	— —
σ_{2p}	—	—	↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2s}^*	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic
Bond order	1	2	3
Observed bond dissociation energy (kJ/mol)	290	620	942
Observed bond length (pm)	159	131	110

E (↑)	O_2	F_2
σ_{2p}^*	—	—
π_{2p}^*	↑ ↑	↑↓ ↑↓
π_{2p}	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	↑↓	↑↓
σ_{2s}^*	↑↓	↑↓
σ_{2s}	↑↓	↑↓
Magnetism	Paramagnetic	Diamagnetic
Bond order	2	1
Observed bond dissociation energy (kJ/mol)	495	154
Observed bond length (pm)	121	143

Bonding in Diatomic Molecules

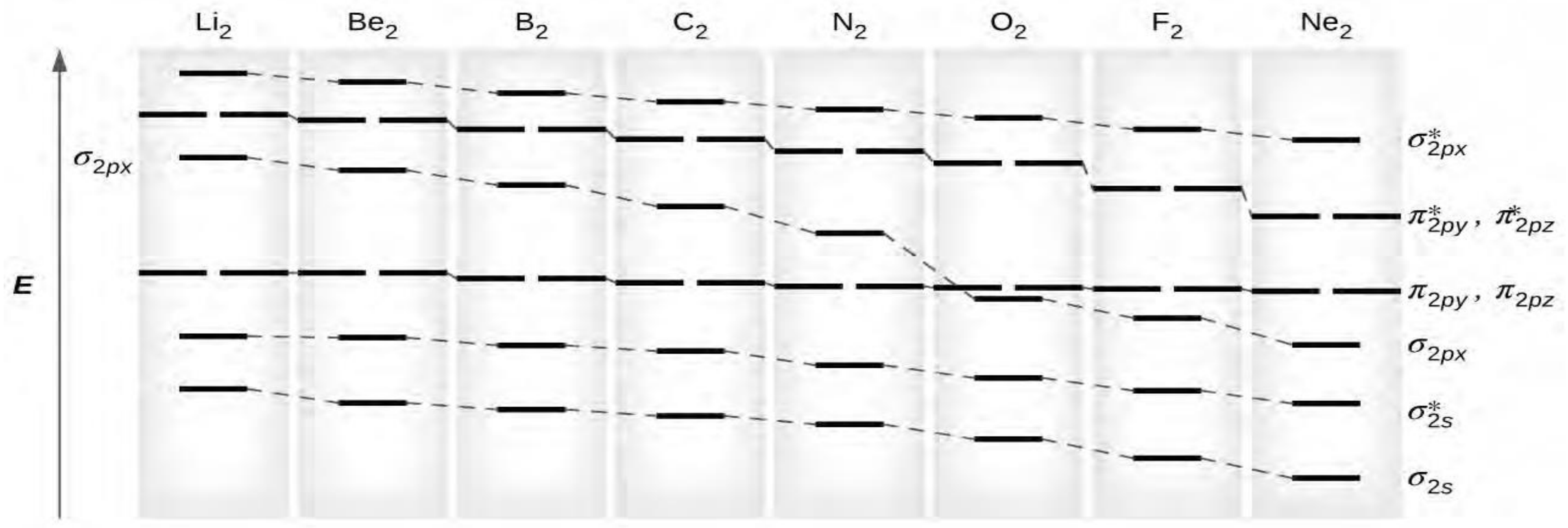
- A dihydrogen molecule (H_2) forms from two hydrogen atoms.
- When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital.
- A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms.
- The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1*s* atomic orbitals.
- A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$.



The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons

The Diatomic Molecules of the Second Period

- This shows the MO diagrams for each homonuclear diatomic molecule in the second period.
- The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases.
- Between N_2 and O_2, the order of the orbitals changes.



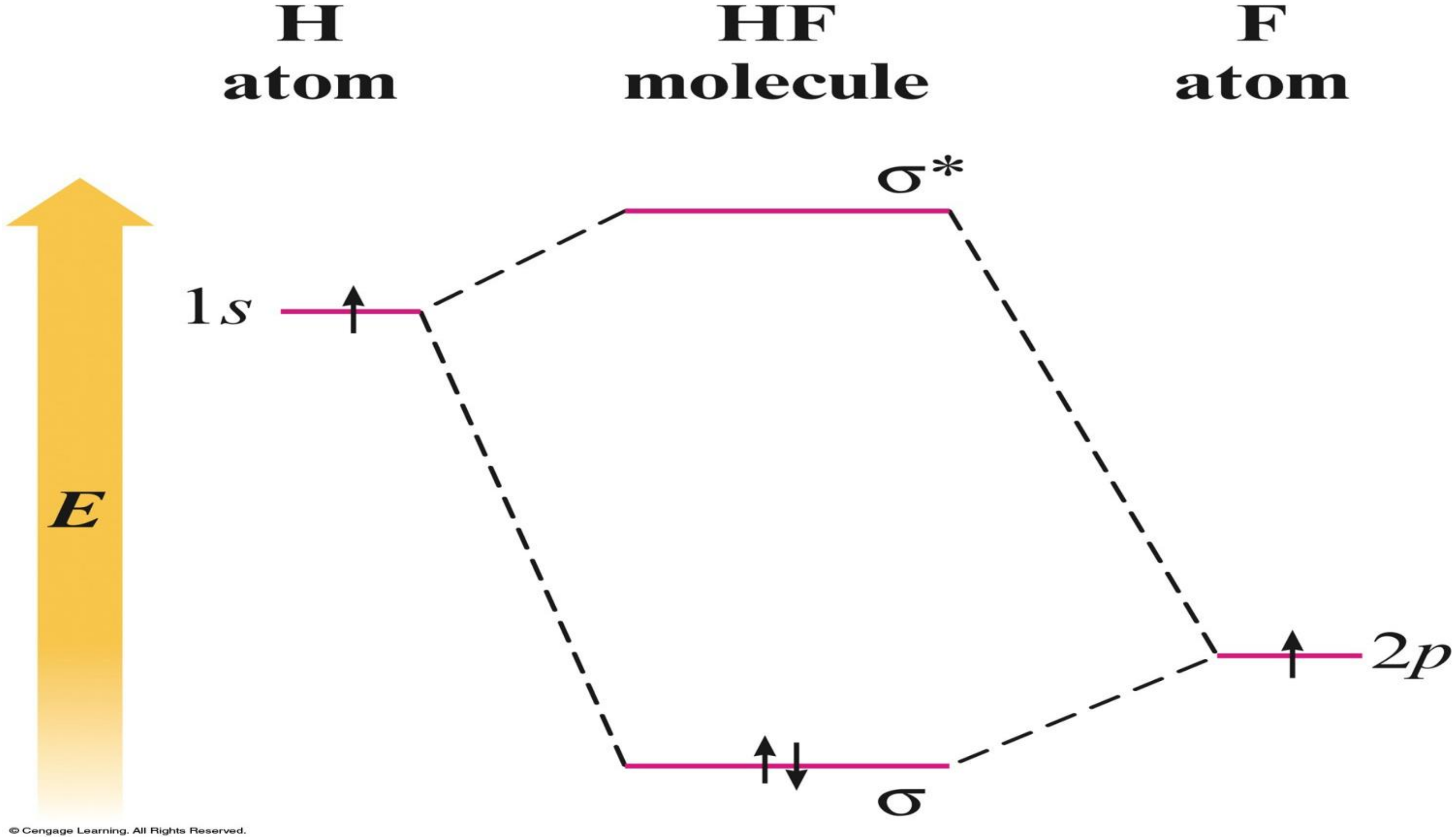
Heteronuclear Diatomic Molecules

- Composed of 2 different atoms.

For Example the Heteronuclear Diatomic Molecule: HF

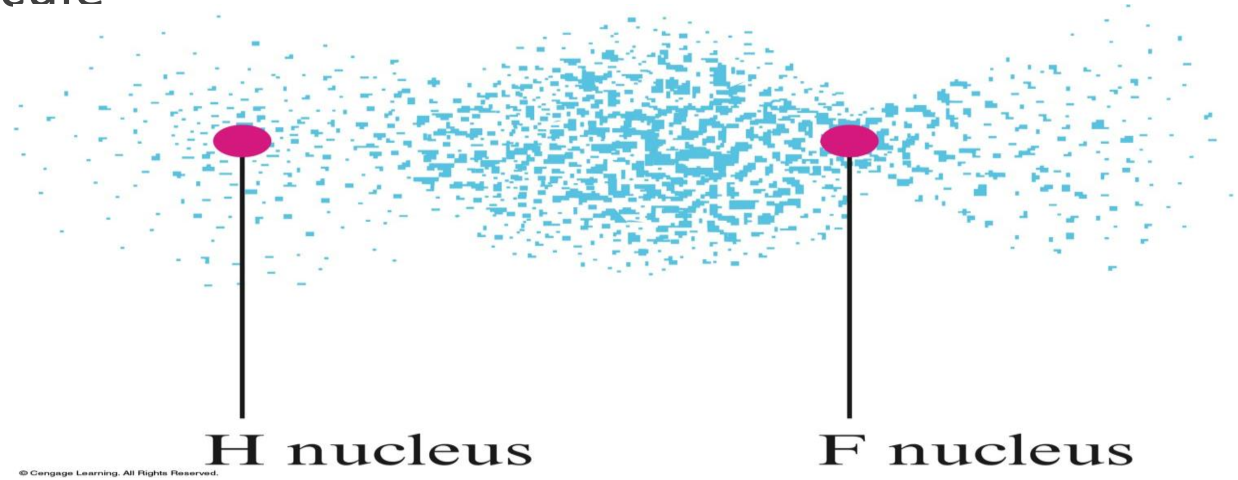
- The 2*p* orbital of fluorine is at a lower energy than the 1*s* orbital of hydrogen because fluorine binds its valence electrons more tightly.
  - ✓ Electrons prefer to be closer to the fluorine atom.
- Thus the 2*p* electron on a free fluorine atom is at a lower energy than the 1*s* electron on a free hydrogen atom.

Orbital Energy-Level Diagram for the HF Molecule



Heteronuclear Diatomic Molecule: HF

- The diagram predicts that the HF molecule should be stable because both electrons are lowered in energy relative to their energy in the free hydrogen and fluorine atoms, which is the driving force for bond formation.
- The Electron Probability Distribution in the Bonding Molecular Orbital of the HF Molecule



Heteronuclear Diatomic Molecule: HF

- The σ molecular orbital containing the bonding electron pair shows greater electron probability close to the fluorine.
- The electron pair is not shared equally.
- This causes the fluorine atom to have a slight excess of negative charge and leaves the hydrogen atom partially positive.
- This is exactly the bond polarity observed for HF.

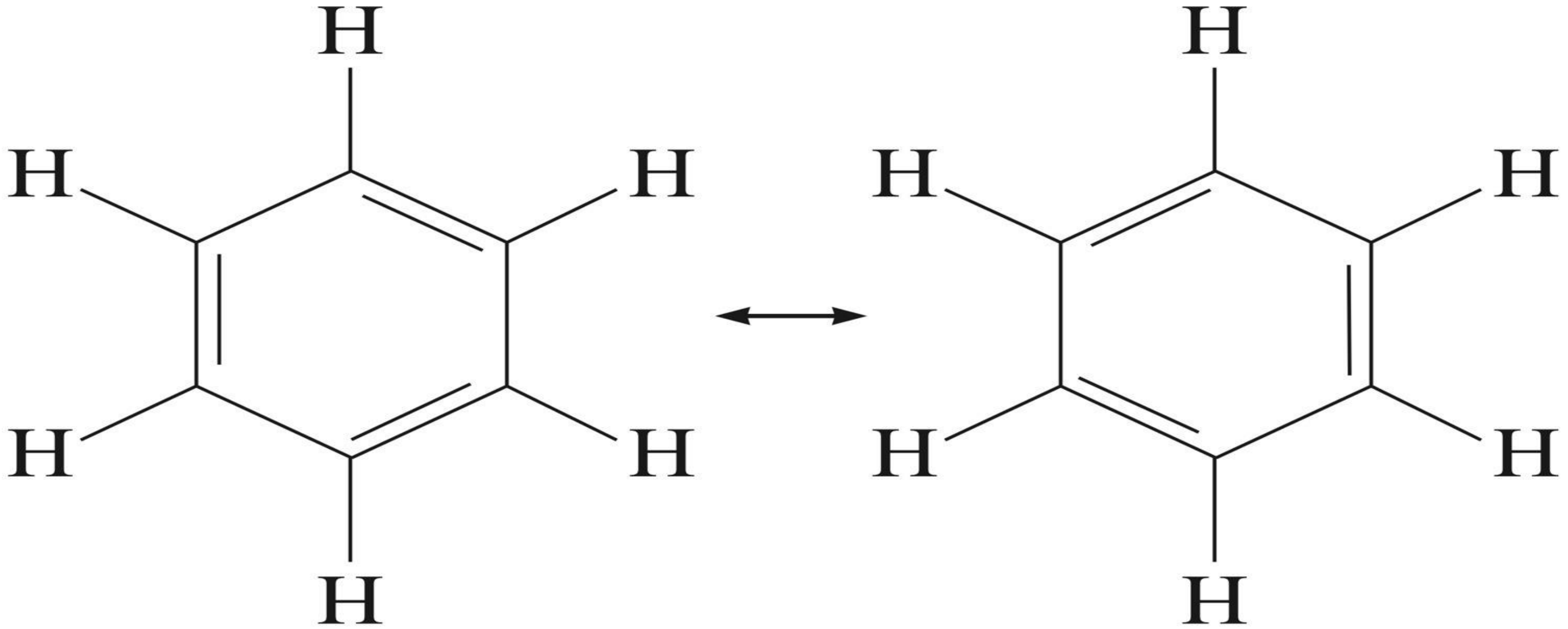
Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

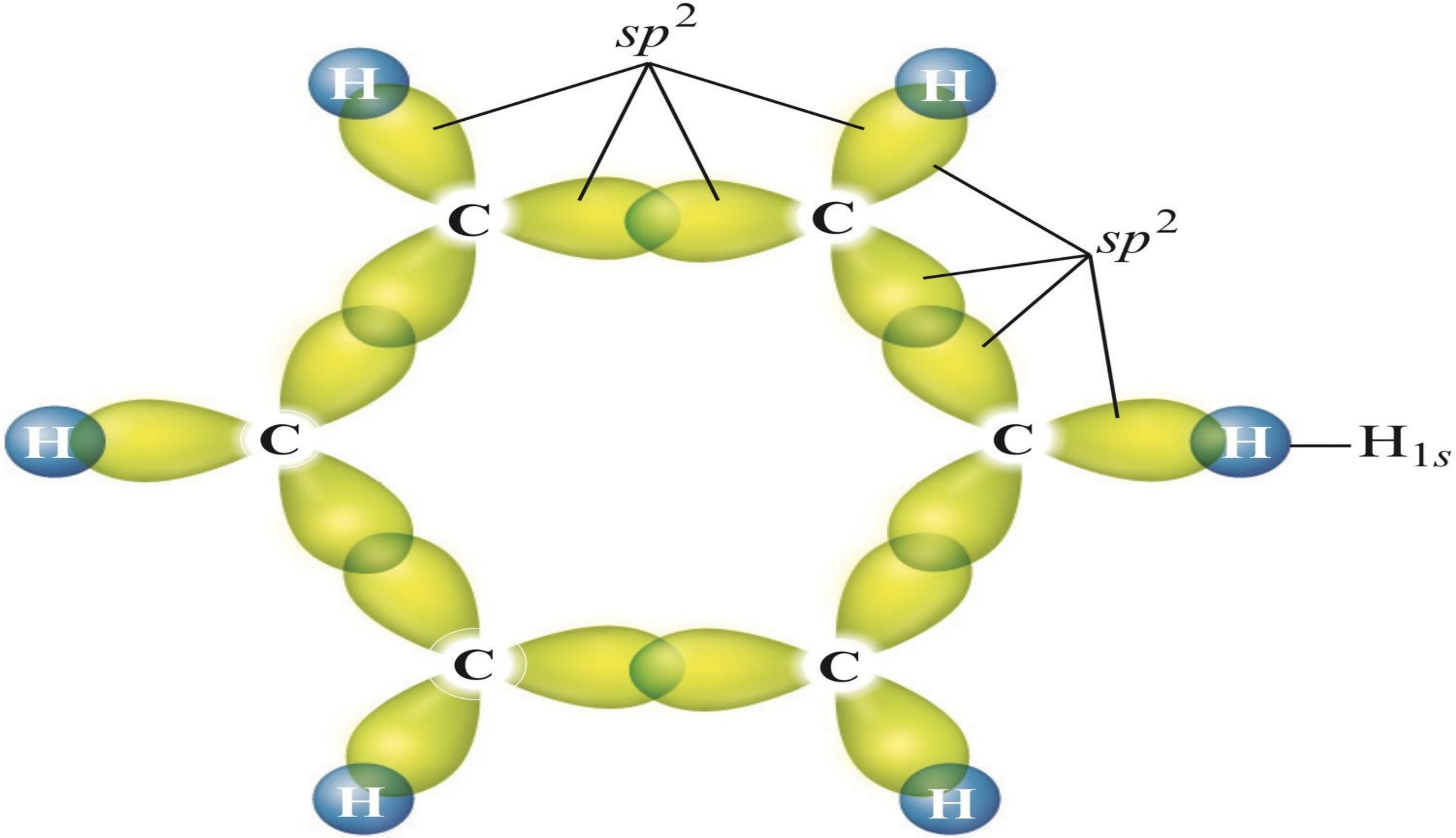
Delocalization

- Describes molecules that require resonance.
- In molecules that require resonance, it is the π bonding that is most clearly delocalized, the σ bonds are localized.
- *p* orbitals perpendicular to the plane of the molecule are used to form π molecular orbitals.
- The electrons in the π molecular orbitals are delocalized above and below the plane of the molecule.

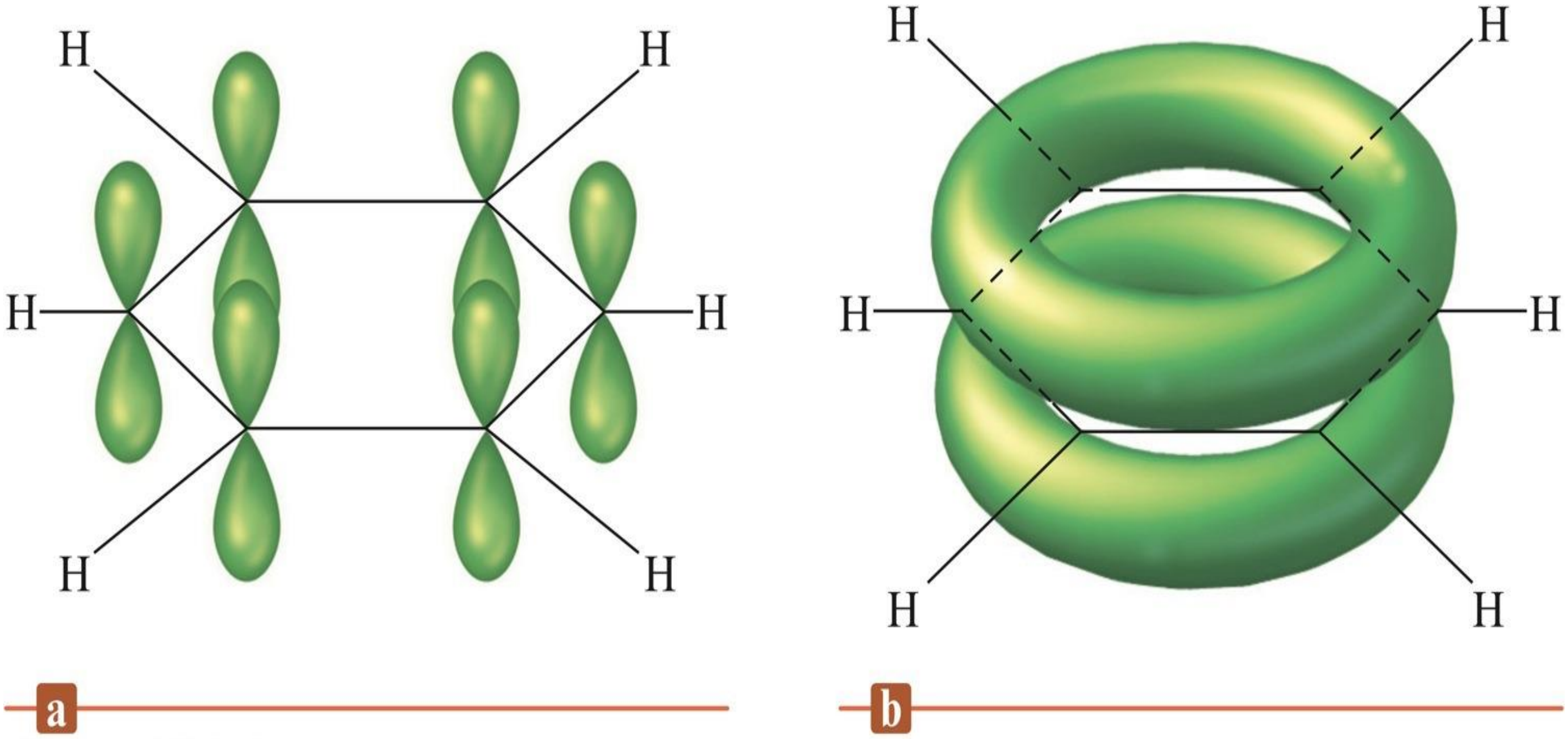
Resonance in Benzene



The Sigma System for Benzene



The Pi System for Benzene



Chapter 36

Electrochemistry

36.1 Oxidation-Reduction Reactions

- Back in general chemistry I and the beginning of this semester we covered the **half-reaction method** for balancing oxidation-reduction reactions.
  - Oxidation-reduction reactions always involve a **transfer of electrons** from one species to another.
  - **oxidation** - lose electron - higher ox state

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$$

  - **reduction -** gain electrons - lower ox state

$$Fe^{3+} + 1e^- \rightarrow Fe^{2+}$$

Oxidation-Reduction Reactions

- An **oxidizing agent** is a species that oxidizes another species; **it is itself reduced**.
- A **reducing agent** is a species that reduces another species; **it is itself oxidized**.

Loss of 2 e^-1^ oxidation

reducing agent

$$Fe_{(s)} + Cu^{+2}{}_{(aq)} \rightarrow Fe^{+2}{}_{(aq)} + Cu_{(s)}$$

oxidizing agent

Gain of 2 e^-1^ reduction

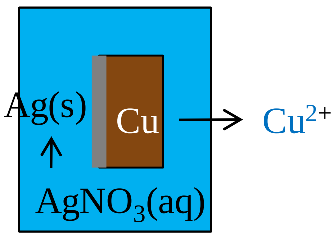
$$red: Cu^{+2}{}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$$

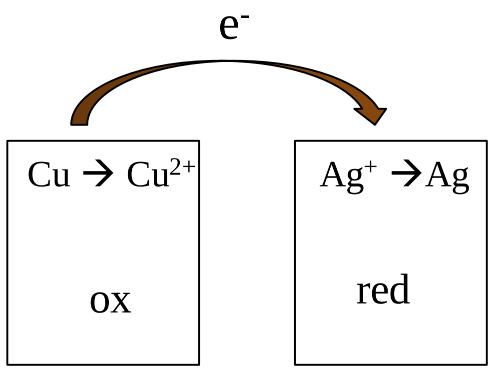
$$ox: Fe_{(s)} \rightarrow Fe^{+2}{}_{(aq)} + 2e^{-}$$

$$Fe_{(s)} + Cu^{+2}{}_{(aq)} \rightarrow Fe^{+2}{}_{(aq)} + Cu_{(s)}$$

Oxidation-Reduction Reactions

- In this chapter we will show how a cell is constructed to **physically separate** an oxidation-reduction reaction into two **half-reactions.**





electrochemical cell

$$red : (Ag^{+}{}_{(aq)} + 1e^{-} \rightarrow Ag_{(s)})2$$

$$ox : Cu_{(s)} \rightarrow Cu^{+2}{}_{(aq)} + 2e^{-}$$

$$Cu_{(s)} + 2Ag^{+}{}_{(aq)} \rightarrow Cu^{+2}{}_{(aq)} + 2Ag_{(s)}$$

  - The force with which electrons travel from the oxidation half-reaction to the reduction half-reaction is measured as **voltage (actually produces electricity)**.

Electrochemistry

- An **electrochemical cell** is a system consisting of electrodes that dip into an electrolyte in which a chemical reaction either uses or generates an electric current.
  - A **voltaic**, or **galvanic**, cell is an electrochemical cell in which a **spontaneous** reaction generates an electric current (+V, rxn occurs on own).
  - An **electrolytic cell** is an electrochemical cell in which an electric current drives an otherwise **nonspontaneous** reaction (-V, rxn does not occur on own, need outside source).

Voltaic Cells

- A **voltaic cell** consists of two half-cells that are electrically connected.
  - Each **half-cell** is a portion of the electrochemical cell in which a half-reaction takes place. No reaction between species involved just a transfer of electrons.
  - A simple half-cell can be made from a metal strip dipped into a solution of its metal ion.
  - For example, the silver-silver ion half cell consists of a silver strip dipped into a solution of a silver salt.

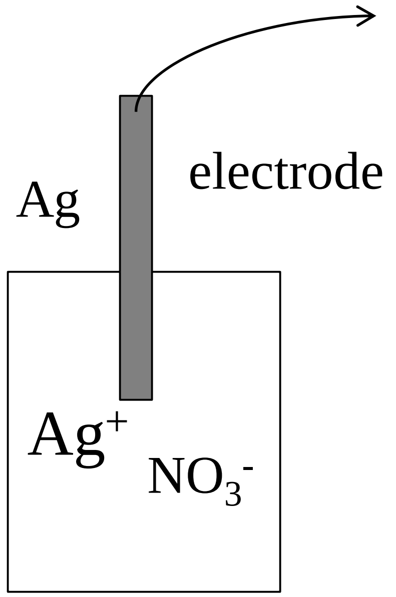
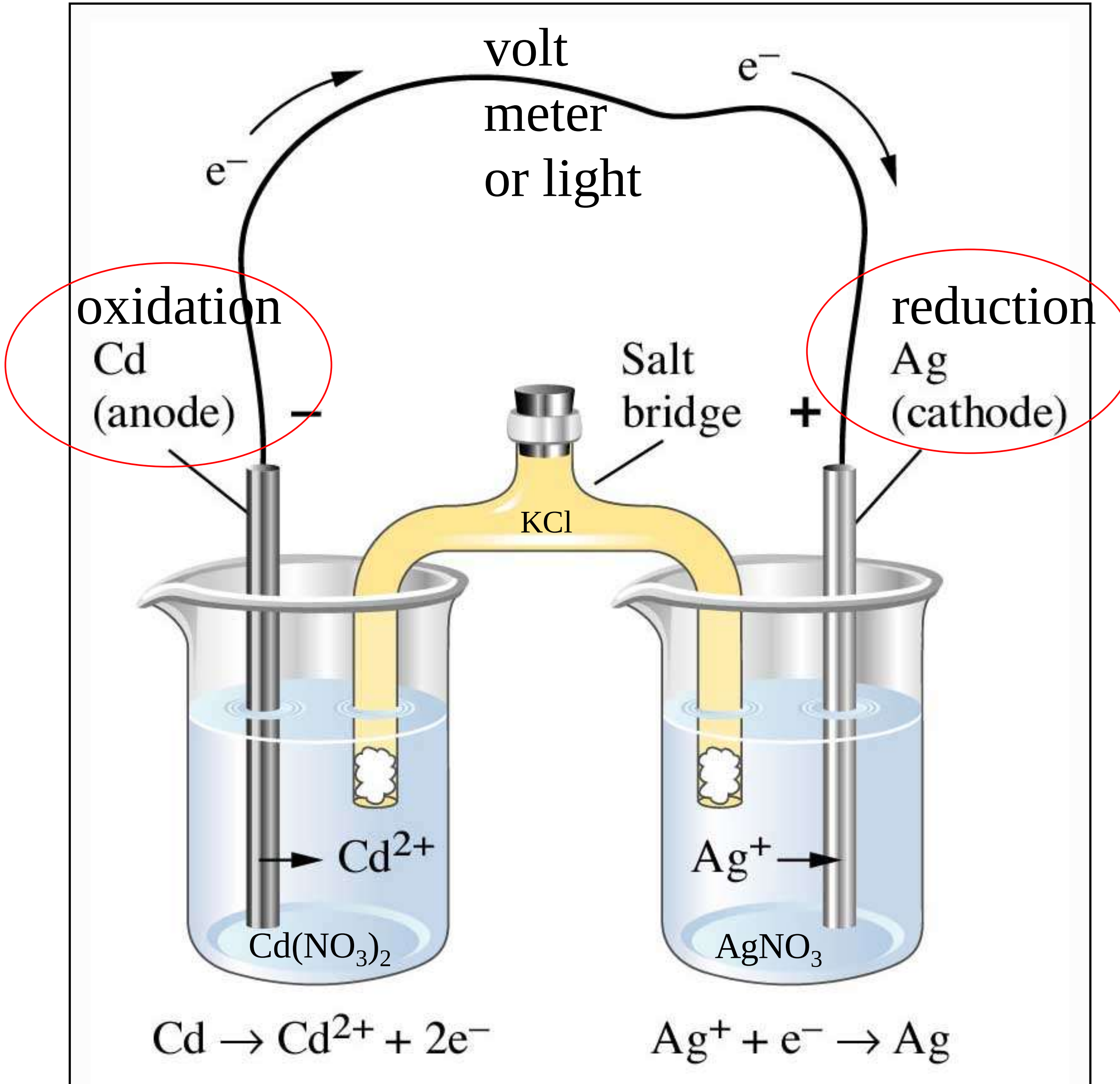


Figure : Voltaic cell consisting of cadmium and silver electrodes.



Voltaic Cells

- In a voltaic cell, two half-cells are connected in such a way that **electrons flow from one metal electrode to the other through an external circuit**.
- This cell has Ag reduced and Cd oxidized.
- Cathode red: **[Ag^+ + 1e^- → Ag (s)] 2** (must happen twice)
- Anode ox: **<u>Cd (s) → Cd^{2+} + 2 e^-</u>**

  overall: **2Ag^+ + Cd (s) → 2 Ag (s) + Cd^{2+}**

  is the <u>net reaction</u> that occurs in the voltaic cell; it is called the **cell reaction**

- Note that electrons are <u>given up</u> at the anode (-) and thus **flow from it** to the cathode (+) where reduction occurs.

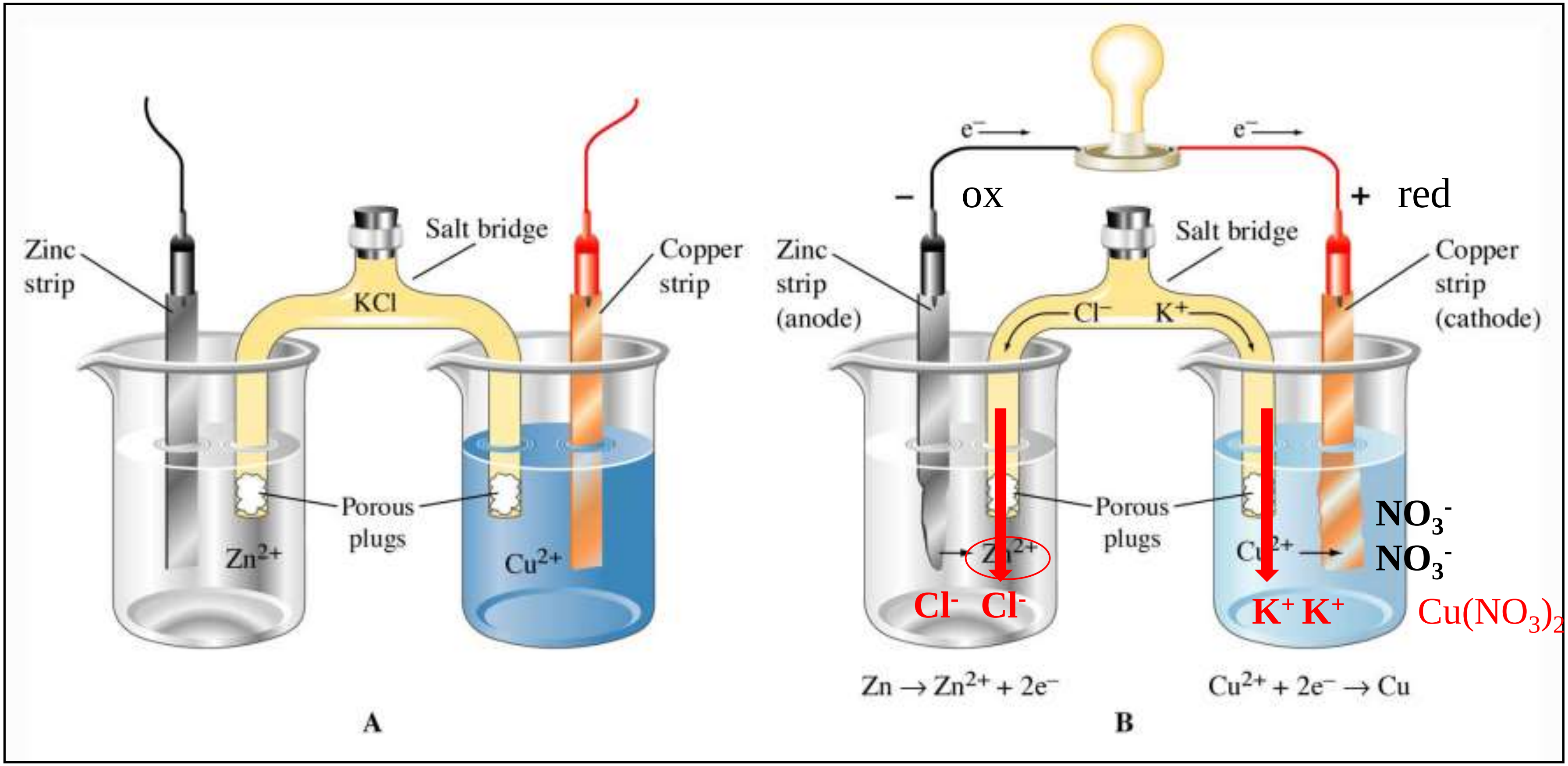
Voltaic Cells

- **As long as there is an external circuit, electrons can flow** through it from one electrode to the other.
  - Because **cadmium has a greater tendency to lose electrons than silver**, cadmium atoms in the cadmium electrode lose electrons to form cadmium ions.
  - The electrons flow through the external circuit to the silver electrode where silver ions gain the electrons to become silver metal.28
  - The anode (oxidation) in a voltaic cell has a **negative** sign because electrons flow from it.
  - The cathode (reduction) in a voltaic cell has a **positive** sign

Voltaic Cells

- The two half-cells **must also be connected internally** to allow ions to flow between them and complete the circuit.
  - Without this internal connection (salt bridge), too much positive charge builds up in the cadmium half-cell (and too much negative charge in the silver half-cell) causing the reaction to stop (must have counter ion to balance charges).
  - KCl salt bridge is present for this purpose.

Figure : Two electrodes are connected by an external circuit.



Ebbing, D. D.; Gammon, S. D. *General Chemistry*, 8th ed., Houghton Mifflin, New York, NY, 2005.

Voltaic Cells

- A **salt bridge** is a tube of an electrolyte in a gel that is connected to the two half-cells of a cell.

  - The salt bridge allows the flow of ions but **prevents the mixing of the different solutions that would allow direct reaction** of the cell reactants.
  - completes circuit
  - keeps electrostatic neutral

- The voltage produced is from the potential difference between the two metals at any instant.
- It is a measure of the tendency of the cell reaction to proceed toward equilibrium.
- Equil is driving force of reaction. As reaction proceeds, potential difference decreases continuously and approaches zero as equil is approached.
- Not infinite amount of electricity. When reach equil have 0V. The conc . of species has effect on equil and the amount of voltage.
- Further away from equil, the higher the potential difference.

Electrochemical Cell Notation

- It is convenient to have a **shorthand** way of designating particular cells.
  - The cell consisting of the cadmium-cadmium ion half-cell and the silver-silver ion half-cell, is written

$$Cd(s)\,|\,Cd^{2+}(aq)\,||\,Ag^{+}(aq)\,|\,Ag(s)$$

anode (ox) **salt bridge** **cathode red**

  - The anode (oxidation half-cell) is written on the left. The cathode (reduction half-cell) is written on the right.
  - Double line indicates salt bridge is present but not always present; both half reactions can be in same container.

$$\mathrm{Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)}$$

anode **salt bridge** **cathode**

- The cell **terminals** are at the extreme ends in the cell notation (electrode metal).
- A single vertical bar indicates a phase boundary, such as between a solid terminal and the electrode solution (states usually omitted).

$$red: Cu^{2+}{}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$$

$$ox: Zn_{(s)} \rightarrow Zn^{+2}{}_{(aq)} + 2e^{-}$$

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}{}_{(aq)}$$

Notation for Cells

- When the **half-reaction involves a gas**, an inert material such as platinum or carbon serves as a terminal and the electrode surface on which the reaction occurs.

– Example is the **hydrogen electrode**; hydrogen bubbles over a platinum plate immersed in an acidic solution.

– The cathode half-reaction is

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

Notation for Cells

– The notation for the hydrogen electrode, written as a cathode, is

anode $\| H^+(aq) | H_2(g) | Pt$ Sometimes written as SHE (1atm, 1M)

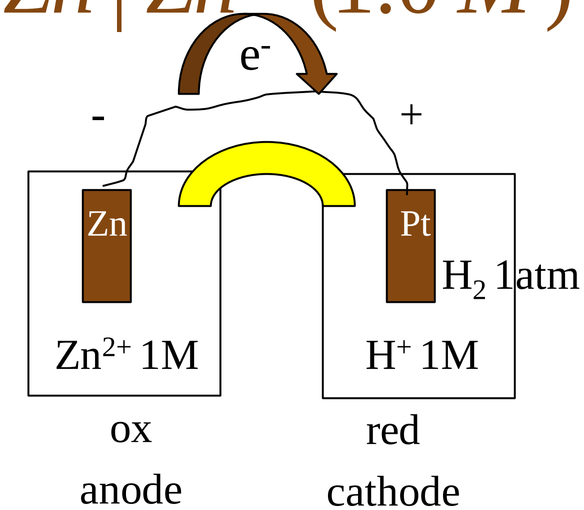
– To write such an electrode as an anode, you simply reverse the notation; want terminal as extreme end.

$Pt | H_2(g) | H^+(aq) \|$ cathode

Notation for Cells

- To fully specify a cell, it is necessary to give the **concentrations of solutions** and the **pressure of gases**.
  - In the cell notation, these are written in parentheses. For example,

$$Zn\,|\,Zn^{2+}(1.0\,M)\,\|\,H^{+}(1.0M)\,|\,H_2(1.0\,atm)\,|\,Pt$$



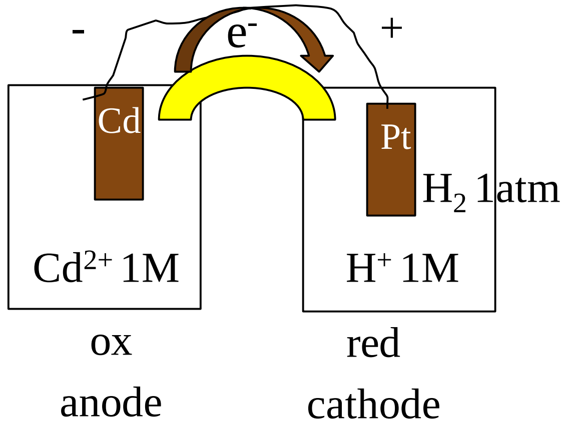
ox: $Zn \rightarrow Zn^{2+} + 2e^{-}$ E^o

red: $2H^{+} + 2e^{-} \rightarrow H_2$ E^o

$2H^{+} + Zn \rightarrow Zn^{2+} + H_2$ E^o_{cell}

note: spectator ions are not usually present in short notation.

This is an example of a standard cell: 1M, 1atm, 25^{o}C (298K)



- Draw cell and write the overall cell reaction for the given cell

$$Cd(s)\,|\,Cd^{2+}(1.0\,M)\,\|\,H^{+}(1.0M)\,|\,H_2(1.0\,atm)\,|\,Pt$$

  - The half-cell reactions are

anode ox: $$\mathbf{Cd(s) \rightarrow Cd^{2+}(aq) + \cancel{2e^-}}$$ E°

cath red: $$\mathbf{2H^+(aq) + \cancel{2e^-} \rightarrow H_2(g)}$$ E°

$$\mathbf{Cd(s) + 2H^+(aq) \rightarrow Cd^{2+}(aq) + H_2(g)}$$ E^o_{cell}

Electromotive Force

- **Potential difference, E_{cell},** is the difference in electric potential (electrical pressure) between two points.
  - You measure this quantity in volts.
  - The **volt, V,** is the SI unit of potential difference equivalent to 1 joule of energy per coulomb of charge.

$$\mathbf{1\ volt = 1\ J / C}$$

Electromotive Force

- The **Faraday constant, F**, is the magnitude of charge on one mole of electrons; **it equals 96,500 coulombs (9.65 x 10^4 C).**

$$1\text{ F} = 96{,}500\text{ C} = \text{charge of 1 mole } e^-$$

  - In moving 1 mol of electrons through a circuit, the numerical value of the **work done by a cell** is the product of the Faraday constant (F) times the potential difference between the electrodes.

$$\text{work(J)} = -\text{F(coulombs)} \times \text{volts(J/coulomb)}$$

work done by the system (refers to the minus sign)

Electromotive Force

- In the normal operation of a voltaic cell, the potential difference (**voltage**) across the electrodes is **less than the maximum** possible voltage of the cell.

- The actual flow of electrons reduces the electrical pressure; therefore, slightly lower voltage obtained.

Electromotive Force

- **electromotive force (emf)** of the cell, or $\mathbf{E_{cell}}$ - the maximum potential difference between the electrodes of a cell.
  - It can be measured by an electronic digital voltmeter.

Standard Cell emf's and Standard Electrode Potentials

- A **cell emf** is a measure of the driving force of the cell reaction.
  - The reaction at the anode has a definite **oxidation potential**, while the reaction at the cathode has a definite **reduction potential**.
  - Thus, the overall cell emf is a combination of these two potentials.

E_{cell} = reduction potential, E_{red} + oxidation potential, E_{ox}

Standard Cell emf's and Standard Electrode Potentials

- A **reduction potential, E_{red},** is a measure of the tendency to gain electrons in the reduction half-reaction.

$$E_{red} \qquad A^{+} + 1e^{-} \rightarrow A\,(s) \qquad E = x\ V$$

  - You can look at the oxidation half-reaction as the reverse of a corresponding reduction reaction.

- The **oxidation potential, E_{ox},** for an oxidation half-reaction is the negative of the reduction potential for the reverse reaction.

$$E_{ox} \qquad A\,(s) \rightarrow A^{+} + 1e^{-} \qquad E = -x\ V$$

36.3 Standard Electrode Potentials

- By convention, the **Table of Standard (1M, 1atm, 25°C) Electrode Potentials** are tabulated as reduction potentials (all).
  - Consider the zinc-copper cell described earlier, calculate the E^o_{cell}.

$$Zn(s)\,|\,Zn^{2+}(1M)\,\|\,Cu^{2+}(1M)\,|\,Cu(s)$$

- The two half-reactions are

$$ox: Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E^o = 0.76V \text{ (changed sign from table)}$$

$$red: Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^o = 0.34V$$

$$Zn + Cu^{2+} \text{ --> } Zn^{2+} + Cu \qquad E^o_{cell} = 1.10\text{ V voltaic, spon}$$

This voltage for standard cell: 1M otherwise need to correct from std conc of 1M.
Note table is electrode potentials for standard (superscript ^{o}: 1M, 1atm, 298K)

TABLE 20.1
Standard Electrode (Reduction) Potentials in Aqueous Solution at 25°C*

Cathode (Reduction) Half-Reaction	Standard Potential, $E°$(V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.04
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.38
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.41
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.23
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	−0.04
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.16
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.34
$IO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.78
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	2.01
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	2.87

*See Appendix I for a more extensive table.

reducing agent

oxidized

reduced

oxidizing agent

All are reductions;
Flip and change sign
for oxidation

Std: 1M, 1atm, 25°C

H: reference electrode

$Cu \rightarrow Cu^{2+}$

$Ag^+ \rightarrow Ag$ spon

Slide 26

Slide 33

Ebbing, D. D.; Gammon, S. D. *General Chemist*
8th ed., Houghton Mifflin, New York, NY, 2005.

Standard Cell emf's and Standard Electrode Potentials

– The electrode potential is an **intensive property** whose **value is independent of the amount** of species in the reaction.

Standard Cell emf's and Standard Electrode Potentials

– Thus, the electrode potential for the half-reaction

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \qquad E^{o} = 0.34V$$

is the same as for

$$2Cu^{2+}(aq) + 4e^{-} \rightarrow 2Cu(s) \qquad E^{o} = 0.34V$$

Recall:	K	flip	$1/K$
		n factor	K^n
	ΔH	flip	$-\Delta H$
		n factor	$n\,\Delta H$
	E^o	flip	$-E^o$
		n factor	E^o

36.3.1 Standard Cell Electrode Potentials

- The **standard emf (theoretical potential), $E°_{cell}$**, is the emf of a cell operating under standard conditions of concentration (1 M), pressure (1 atm), and temperature (25°C).
  - Note that individual electrode potentials require that we choose a **reference electrode**.
  - arbitrarily assign this reference electrode a potential of zero and obtain the potentials of the other electrodes by measuring the emf's. These are relative values not absolute.

Tabulating Standard Electrode Potentials

- By convention, the reference chosen for comparing electrode potentials is the **standard hydrogen electrode (SHE).**
- **Standard electrode potentials** are measured relative to this hydrogen reference as the anode.
- For example, when measure the emf of a cell composed of a **zinc electrode connected to a hydrogen electrode**, you obtain 0.76 V with hydrogen being cathode and zinc as anode for the spon rxn. By definition, we want the comparison of hydrogen to other species to be hydrogen as anode and the other species as cathode; Since hydrogen is given zero value all voltage measured is given to zinc but we must change sign for reduction value of zinc as defined in table.
- Since zinc acts as the anode (oxidation) in this spon cell, its reduction potential is listed as –0.76 V. This means that zinc has a potential that is 0.76 less than hydrogen (relative not abs)

36.4 Predicting the Spontaneous Direction of a Redox Reaction

- Standard electrode potentials are useful in determining the strengths of **oxidizing and reducing agents** under standard-state conditions.

  – the **strongest oxidizing agents (species undergoes reduction)** in a table of standard electrode potentials are the **species** corresponding to the half-reactions **with the largest (most positive) Eº values**. (For example F_2(g) highest E in the table and <u>strongest ox agent</u> in the table -- prefers to be reduced compared to any other species in table. Will always be reduced in spon rxn. with any of species in table.)

  – Bottom line: Larger Eº, stronger oxidizing agent, more tendency to undergo reduction with other species.

Strengths of Oxidizing and Reducing Agents

- Consequently, the **strongest reducing agents (species undergoes oxidation)** in a table of standard electrode potentials are the **species** corresponding to the half-reactions **with the smallest (most negative) E^o values**. (for example, Li smallest E in the table; therefore, Li (s) strongest red agent in the table [note: must flip for oxidation] -- prefers to be oxidized compared to any other species in table. Will always be oxidized in spon rxn. with any of species in table.)
- Bottom line: Smaller E^o, stronger reducing agent, more tendency to undergo oxidation with other species.

Slide 27

Calculating Cell emf's from Standard Potentials

- What would be the spon rxn between Cd and Ag? Calculate E^o_{cell} for spon rxn at 25^{o}C and 1 M (std cell)
  - Consider a cell constructed of the following two half-reactions (given from table)

$$\mathbf{Cd^{2+}(aq) + 2e^- \rightarrow Cd(s);\ E^o = -0.40\ V}$$

Reducing agent

$$\mathbf{Ag^{+}(aq) + 1e^- \rightarrow Ag(s);\ E^o = 0.80\ V}$$

Oxidizing agent

Ag^+ higher E therefore expect to be reduced (ox agent) and

Cd (s) oxidized (red agent) in spon rxn.

Calculating Cell emf's from Standard Potentials

– Therefore, you reverse the half-reaction and change the sign of the half-cell potential of cadmium.

$$ox: Cd(s) \rightarrow Cd^{2+}(aq) + 2e^{-};\ \mathrm{E^{o}} = 0.40\ \mathrm{V}$$

$$red: Ag^{+}(aq) + 1e^{-} \rightarrow Ag(s);\ \mathrm{E^{o}} = 0.80\ \mathrm{V}$$

– We must double the silver half-reaction so that when the reactions are added, the electrons cancel.

– This does not affect the half-cell potentials, which do not depend on the amount of substance.

Calculating Cell emf's from Standard Potentials

- Now we can add the two half-reactions to obtain the overall cell reaction and cell emf.

- note: positive voltage meaning spon reaction for standard cell. If not std cell must correct and will discuss later.

$$ox: Cd(s) \rightarrow Cd^{2+}(aq) + \cancel{2e^-}; \qquad E^o = 0.40\ V$$

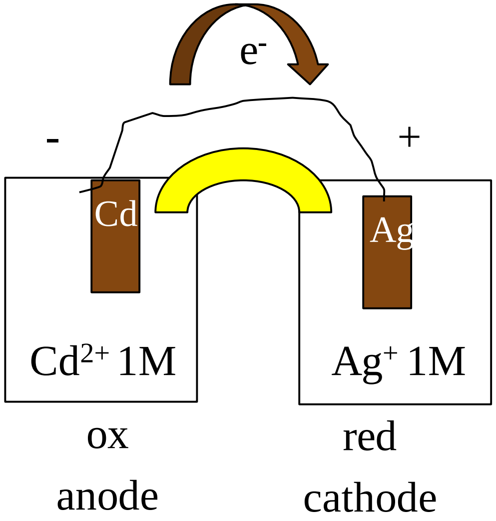
$$red: 2Ag^+(aq) + \cancel{2e^-} \rightarrow 2Ag(s); \qquad E^o = 0.80\ V$$

$$\mathbf{Cd(s) + 2Ag^+(aq) \rightarrow Cd^{2+}(aq) + 2Ag(s);\ E^o_{cell} = 1.20\ V}$$

Calculating Cell emf's from Standard Potentials

– How would we write and draw the cell we just did in short notation?

$$Cd(s)\,|\,Cd^{2+}(1M)\,||\,Ag^{+}(1M)\,|\,Ag(s)$$



A Problem To Consider

- Calculate the standard emf, E^o_{cell}, for the following cell at 25°C.

$$Al(s)\,|\,Al^{3+}(1M)\,||\,Fe^{2+}(1M)\,|\,Fe(s)$$

ox red

  - The reduction half-reactions and standard potentials are (given)

$$\mathbf{Al^{3+}(aq) + 3e^- \rightarrow Al(s);\ E^o = -1.66\ V}$$

$$\mathbf{Fe^{2+}(aq) + 2e^- \rightarrow Fe(s);\ E^o = -0.41\ V}$$

A Problem To Consider

Given

$$\mathbf{Al^{3+}(aq) + 3e^- \rightarrow Al(s);\ E^o = -1.66\ V}$$

$$\mathbf{Fe^{2+}(aq) + 2e^- \rightarrow Fe(s);\ E^o = -0.41\ V}$$

$$Al(s)\,|\,Al^{3+}(1M)\,\|\,Fe^{2+}(1M)\,|\,Fe(s)$$

– You reverse the first half-reaction and its half-cell potential to obtain

$$ox: Al(s) \rightarrow Al^{3+}(aq) + 3e^-;\ \mathrm{E^o} = 1.66\ \mathrm{V}$$

$$red: Fe^{2+}(aq) + 2e^- \rightarrow Fe(s);\ \mathrm{E^o} = -0.41\ \mathrm{V}$$

A Problem To Consider

$$Al(s)\,|\,Al^{3+}(1M)\,\|\,Fe^{2+}(1M)\,|\,Fe(s)$$

2X $ox: Al(s) \rightarrow Al^{3+}(aq) + 3e^{-};\ \mathrm{E^{o}} = 1.66\ \mathrm{V}$

3X $red: Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s);\ \mathrm{E^{o}} = -0.41\ \mathrm{V}$

– To obtain the overall reaction we must balance the electrons.

$$\mathbf{2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^{-};\ E^{o} = 1.66\ V}$$

$$\mathbf{3Fe^{2+}(aq) + 6e^{-} \rightarrow 3Fe(s);\ E^{o} = -0.41\ V}$$

note: no multiply by factor to E

A Problem To Consider

– Now we add the reactions to get the overall cell reaction and cell emf.

$$2Al(s) \rightarrow 2Al^{3+}(aq) + \cancel{6e^-};\ E^o = 1.66\ V$$

$$3Fe^{2+}(aq) + \cancel{6e^-} \rightarrow 3Fe(s);\ E^o = -0.41\ V$$

$$2Al(s) + 3Fe^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Fe(s);\ E^o = 1.25\ V$$

reducing agent   oxidizing agent

Spon - +V obtained for std cell

HW 49

code: seven

36.5 Equilibrium Constant, K, and E^o_{cell}

- Some of the most important results from electrochemistry are the relationships among **$E°_{cell}$, Gibbs free energy, and equilibrium constant.**
  - The measurement of cell emf's gives you yet another way of calculating equilibrium constants. Combining several equations we obtain

$$E^o_{cell} = \frac{2.303RT}{nF} \log K$$

Equilibrium Constants from emf's

– Substituting values for the constants R and F at 25°C gives the equation

$$E^{o}_{cell} = \frac{0.0592}{n} \log K \quad \text{(value in volts at 25 °C)}$$

0.0592 combination of constants including temp at 298 K

n = number of electrons transferred in balanced eq.

K is equil constant or setup for calc - prod/reactants
example aA +bB ⇄ cC + dD

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

- Previously we determined the standard emf for the following cell is 1.10 V Slide 26 .

$$Zn(s)\,|\,Zn^{2+}(1M)\,\|\,Cu^{2+}(1M)\,|\,Cu(s)$$

$$\mathbf{Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)} \qquad E^{o}_{cell} = 1.10V$$

Calculate the equilibrium constant K_c for the reaction

$$E^{o}_{cell} = \frac{0.0592}{n}\log K$$

- Note that n=2. Substituting into the equation relating E^{o}_{cell} and K gives

$$\mathbf{1.10\ V = \frac{0.0592}{2}\log K}$$

A Problem To Consider

– Solving for log K_c, you find

$$\log K = \frac{(1.10)(2)}{0.0592} = 37.2$$

– Now take the antilog of both sides:

$$K_c = anti\log(37.2) = 10^{37.2} = 1.6\times10^{37}$$

– The number of significant figures in the answer equals the number of decimal places in 37.2 (one). Thus

$$\mathbf{K_c = 2\times10^{37}}$$

Dependence of emf on Concentration

- Recall that everything we have done so far has been with a standard cell.
- If an electrode is a measure of the extent to which concentration in a half cell differs from an equil value; then concentration will affect equil and vary electrode potential.
- Electrode potential is dependent on concentration. Further from equil, greater potential (higher voltage).
- Remember E for table is for standard conditions. If concentrations are not std concentrations, then the cell potential must be corrected.
- Basically, the potential for non std cell will be equal to the std cell potential with a correcting factor for nonstd concentrations. The basic equation is as follows:

36.6 Nernst Equation

- The Nernst equation is an equation relating the cell emf to its standard emf and the reaction quotient.

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF}\log Q$$

$$\mathbf{E_{cell} = E^{o}_{cell} - \frac{0.0592}{n}\log Q} \quad \text{at } 25^{o}\text{C}$$

Dependence of emf on Concentration

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n}\log Q$$

- Basically, second half of equation is correcting factor for not being std conc. If at std conc (1M each), Q=1 and log 1 = 0. Could use even at std and get correct answer.

- What is the emf, E_{cell}, of the following cell at 25°C?

$$Zn(s)\,|\,Zn^{2+}(1.0\times10^{-5}M)\,\|\,Cu^{2+}(0.100M)\,|\,Cu(s)$$

note: not std cell

$$Zn(s)\,|\,Zn^{2+}(1.0\times10^{-5}M)\,||\,Cu^{2+}(0.100M)\,|\,Cu(s)$$

Given:

$$Zn^{2+}(aq)+2e^{-}\rightarrow Zn(s) \qquad E^{o} = -0.76V$$

$$Cu^{2+}(aq)+2e^{-}\rightarrow Cu(s) \qquad E^{o} = 0.34V$$

– The two half-reactions are

$$ox: Zn(s)\rightarrow Zn^{2+}(aq)+2e^{-} \qquad E^{o} = 0.76V$$ (changed sign from table)

$$red: Cu^{2+}(aq)+2e^{-}\rightarrow Cu(s) \qquad E^{o} = 0.34V$$

– The cell reaction is

$$\mathbf{Zn(s)+Cu^{2+}(aq)} \rightleftharpoons \mathbf{Zn^{2+}(aq)+Cu(s)} \qquad E^{o}_{cell} = 1.10V$$

for std cell but not a std cell

$$\mathbf{Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)}$$

E^o_{cell} = 1.10V

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q$$

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10\,V - \frac{0.0592}{2} \log \frac{1.0 \times 10^{-5}}{0.100}$$

$$\mathbf{E_{cell} = 1.10\ V - (-0.12) = 1.22\ V}$$

voltaic, spon

36.7 Electrolytic Cells

- An electrolytic cell is an electrochemical cell in which an electric current drives an otherwise nonspontaneous reaction.
  - The process of producing a chemical change in an electrolytic cell is called **electrolysis.**
  - Many important substances, such as aluminum metal and chlorine gas are produced commercially by electrolysis.

example : Calculate E_{cell}

$$Ag(s)\,|\,Ag^{+}(1.00\times10^{-2}M)\,\|\,Cu^{2+}(1.50M)\,|\,Cu(s)$$

Given: ox red

$$Ag^{+}(aq)+1e^{-}\rightarrow Ag(s)$$ $E^o = 0.80V$

$$Cu^{2+}(aq)+2e^{-}\rightarrow Cu(s)$$ $E^o = 0.34V$

– The two half-reactions are

$$ox:[Ag(s)\rightarrow Ag^{+}(aq)+1e^{-}]2$$ $E^o = -0.80V$ (changed sign from table)

$$red:Cu^{2+}(aq)+2e^{-}\rightarrow Cu(s)$$ $E^o = 0.34V$

$$2Ag(s)+Cu^{2+}(aq)\rightleftharpoons 2Ag^{+}(aq)+Cu(s)$$ $E^o_{cell} = -0.46V$

for std cell but not a std cell

continue

$$2Ag(s) + Cu^{2+}(aq) \rightleftharpoons 2Ag^{+}(aq) + Cu(s)$$ E^{o}_{cell} = -0.46V

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n}\log Q$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n}\log \frac{[Ag^{+}]^2}{[Cu^{2+}]}$$

$$E_{cell} = -0.46\,V - \frac{0.0592}{2}\log \frac{(1.00\times 10^{-2})^2}{1.50}$$

$$E_{cell} = -0.46\,V - (-0.124V) = -0.34\,V$$

electrolytic, nonspon

Calculate E^o_{cell} What if source of H^+ is HCl? SA, problem works the same.

Pt | U^{4+} (0.200M), UO_2^{2+} (0.0150M), H^+ (0.0300M) || Fe^{3+} (0.0250M), Fe^{2+} (0.0100M) | Pt

ox red

Given: $Fe^{3+} + 1e^- \rightarrow Fe^{2+}$ $E^o = 0.771V$

$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$ $E^o = 0.334V$

Red: $2(Fe^{3+} + 1e^- \rightarrow Fe^{2+})$ $E^o = 0.771V$

Ox: $U^{4+} + 2H_2O \rightarrow UO_2^{2+} + 4H^+ + 2e^-$ $E^o = -0.334V$

$2Fe^{3+} + U^{4+} + 2H_2O \rightarrow UO_2^{2+} + 4H^+ + 2Fe^{2+}$ $E^o = 0.437V$

$$E = E^o_{cell} - \frac{0.0592}{n} log \frac{[UO_2^{2+}][H^+]^4[Fe^{2+}]^2}{[Fe^{3+}]^2[U^{4+}]}$$

$$E = 0.437V - \frac{0.0592}{2} log \frac{[0.0150][0.0300]^4[0.0100]^2}{[0.0250]^2[0.200]}$$

$$= 0.437 + 0.237 = 0.674V$$

Calculate E^o_{cell} What if source of H^+ is HCN, weak acid?

Pt | U^{4+} (0.200M), UO_2^{2+} (0.0150M), HCN (0.0300M, $K_a = 6.2 \times 10^{-10}$) || Fe^{3+} (0.0250M), Fe^{2+} (0.0100M) | Pt

$$HCN\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CN^-\,(aq)$$

	[HCN]	$[H_3O^+]$	$[CN^-]$
Initial, $[\ ]_o$	0.0300	~ 0	0
Change, $\Delta[\ ]$	$-x$	$+x$	$+x$
Equilibrium, $[\ ]_{eq}$	$0.0300 - x$	x	x

$$K_a = \frac{[H_3O^+]_{eq}[CN^-]_{eq}}{[HCN]_{eq}} = \frac{(x)(x)}{(0.0300 - x)} = \frac{x^2}{0.0300 - x} = 6.2 \times 10^{-10}$$

$$\sqrt{x^2} = \sqrt{(6.2 \times 10^{-10})(0.0300)}$$

$$x = 4.3 \times 10^{-6}\,M = [H_3O^+]_{eq}$$

H^+

$$E = 0.437 - \frac{0.0592}{2} log \frac{[0.0150][4.3 \times 10^{-6}]^4[0.0100]^2}{[0.0250]^2[0.200]}$$

$$= 0.437 + 0.692 = 1.129V$$

Calculate E^o_{cell}

ox red

Ag | AgCl (sat'd, K_{sp} = 1.82 x 10^{-10}), NaCl (0.0200 M) || HBr (0.0200 M) | H_2 (0.800 atm) | Pt

Given: $Ag^+ + 1e^- \rightarrow Ag$ $E^o = 0.799V$

$2H^+ + 2e^- \rightarrow H_2$ $E^o = 0.000V$

ox: $2(Ag \rightarrow Ag^+ + 1e^-)$ $E^o = -0.799V$

red: $2H^+ + 2e^- \rightarrow H_2$ $E^o = 0.000V$

$2Ag + 2H^+ \rightarrow 2Ag^+ + H_2$ $E^o = -0.799V$

?

$$E = E^o_{cell} - \frac{0.0592}{n} \log \frac{[Ag^+]^2[P_{H_2}]}{[H^+]^2}$$

$NaCl (s) \rightarrow Na^+ (aq) + Cl^- (aq)$

0.0200 M 0.0200 M

$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$

		$[Ag^+]$	$[Cl^-]$
Initial, $[\ ]_o$		0	0.0200
Change, $\Delta[\ ]$		$+s$	$+s$
Equilibrium, $[\ ]_{eq}$		s	$0.0200 + s$

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

		$[Ag^+]$	$[Cl^-]$
Initial, $[\ ]_o$		0	0.0200
Change, $\Delta[\ ]$		$+s$	$+s$
Equilibrium, $[\ ]_{eq}$		s	$0.0200 + s$

$$K_{sp} = 1.82 \times 10^{-10} = [Ag^+][Cl^-] = (s)(0.0200 + s) = 0.0200\,s$$

$$s = \frac{1.82 \times 10^{-10}}{0.0200} = 9.10 \times 10^{-9} = [Ag^+] = [AgCl]$$

$$E = E^o_{cell} - \frac{0.0592}{n}\,log\,\frac{[Ag^+]^2[P_{H_2}]}{[H^+]^2}$$

$$E = -0.799 - \frac{0.0592}{2}\,log\,\frac{[9.10 \times 10^{-9}]^2[0.800]}{[0.0200]^2}$$

$$= -0.799 + 0.378 = -0.421V$$

36.8 Stoichiometry of Electrolysis

- What is new in this type of stoichiometric problem is the measurement of numbers of electrons.
  - You do not weigh them as you do substances.
  - Rather, you measure the **quantity of electric charge** that has passed through a circuit.
  - To determine this **we must know the current and the length of time** it has been flowing.

Stoichiometry of Electrolysis

- Electric current is measured in amperes.
- An **ampere (A)** is the base SI unit of current equivalent to **1 coulomb/second**. 1 A = 1 C/s
- The quantity of electric charge passing through a circuit in a given amount of time is given by

Electric charge(coul) = electric current (A or coul/sec) × time lapse(sec)

note: A = C/s

A Problem To Consider

- When an aqueous solution of potassium iodide is electrolyzed using platinum electrodes, the half-reactions are

$$ox: 2I^-(aq) \rightarrow I_2(s) + 2e^-$$

$$red: 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

How many grams of iodine are produced when a current of 8.52 mA flows through the cell for 10.0 min?

Electric charge(coul) = electric current (A or coul/sec) × time lapse(sec)

- When the current flows for 6.00 x 10^2 s (10.0 min), the amount of charge is

$$\text{charge} = (8.52 \times 10^{-3} C/s) \times (6.00 \times 10^2 s) = 5.11\,\text{C}$$

A=C/s

96,500 C = charge of 1 mole e^-

A Problem To Consider

$$2I^-(aq) \rightarrow I_2(s) + 2e^-$$

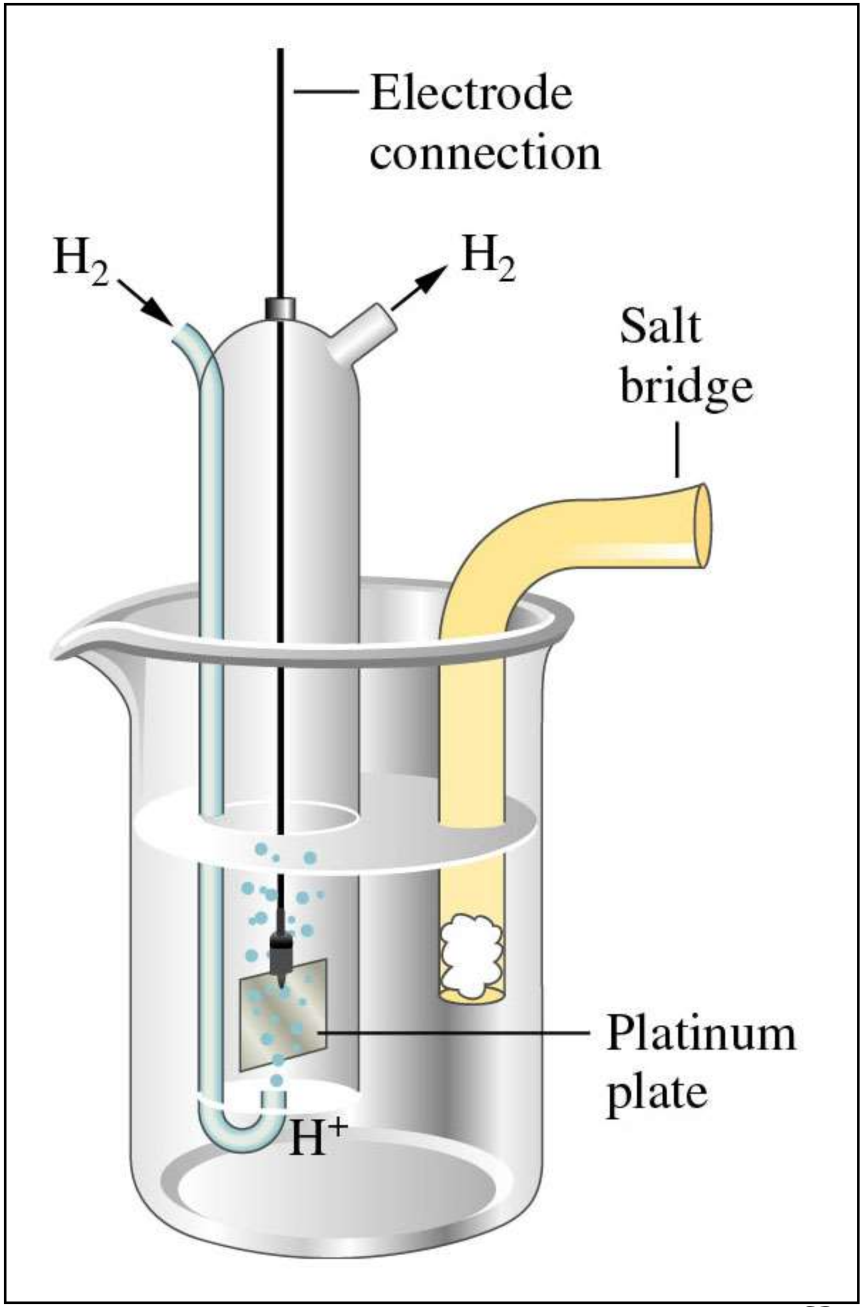
- Note that two moles of electrons are equivalent to one mole of I_2. Hence,

$$5.11\,C \times \frac{1\,mol\,e^-}{9.65\times10^4\,C} \times \frac{1\text{ mol I}_2}{2\text{ mol e}^-} \times \frac{254\text{ g I}_2}{1\text{ mol I}_2} = 6.73\times10^{-3}\text{ g I}_2$$

HW 50

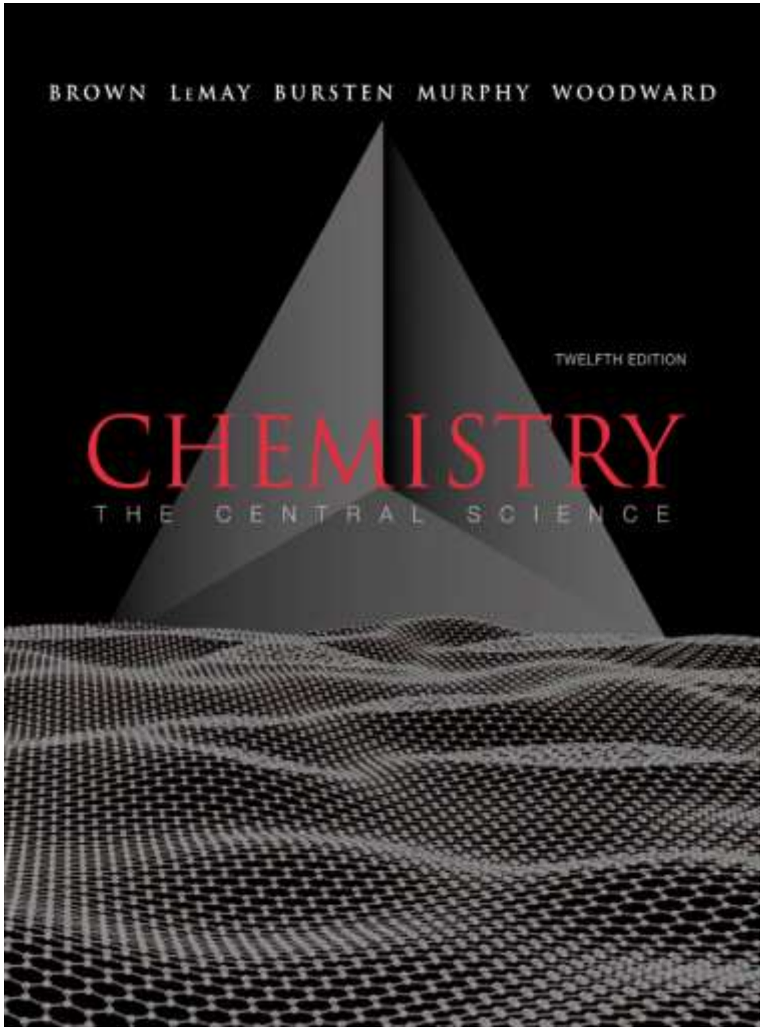
code: nernst

Figure : A hydrogen electrode.



Ebbing, D. D.; Gammon, S. D. *General Chemistry*, 8th ed., Houghton Mifflin, New York, NY, 2005.

Slide 16



Thermochemistry lecture notes

FOR

CHE 1000

UNZA

- The concept of energy is at the very heart of science.
- All physical and chemical processes are accompanied by the transfer of energy.
- Because energy cannot be created or destroyed, we must understand how to do the “accounting” of energy transfers from one body or one substance to another or from one form of energy to another.
- **In this chapter you are going to look at one of the most important areas of chemistry – the energy change in reactions, and how these energy changes reflect changes at a molecular level**

THERMODYNAMICS/ENERGETICS

- **THERMODYNAMICS** is basically concerned with the energy changes that accompanies chemical and physical process **(Greek:** *thérme-, “heat”; dy’namis, “power”).*
- *This area of study began during the Industrial Revolution* in order to develop the relationships among heat, work, and fuels in steam engines.
- Here we will examine the relationships between chemical reactions and energy changes that involve heat.

THERMODYNAMICS/ENERGETICS

- The study of this portion of thermodynamics known as ***Energetics or Thermochemistry***.
- **Energetics** / **Thermochemistry** is therefore the study of energy transfers between reacting chemicals and their surroundings.
- In chemical systems, the most common way of transferring energy is by heating.
- Remember that this means the increased jostling of molecules that causes other molecules to vibrate more.

The Nature of Chemical Energy

- We will define **ENERGY** as the *capacity to do work or to transfer heat.*
- There are **two ways** in which energy is exchanged between the system and its surroundings and these are through ***heat*** and ***work***
- Chemical reactions absorb heat, such as those that occur when during photosynthesis.
- Chemical reactions can also do work such as in the combustion reaction between gasoline and oxygen produces gases that expand and in the process do work that can be used to power an automobile.

The Nature of Chemical Energy

- **Work** is a force acting over a distance.
  - ✓ Energy = Work = force (F) × distance (d)
- One of the most important characteristics of energy is that it is conserved.
- The **law OF CONSERVATION OF ENERGY** states that *energy can be converted from one form to another but can be neither created nor destroyed.* That is, the energy of the universe is constant.

Energy, Heat, and Work

- Energy can be exchanged between objects through contact.
  - ✓ collisions
- You can think of **energy** as a quantity an object can possess.
  - ✓ or collection of objects
- You can think of **heat and work** as the two different ways that an object can exchange energy with other objects.
  - ✓ either out of it, or into it

Energy

– Chemists define work as directed energy change resulting from a process.

– Energy used to cause the temperature of an object to rise is called **heat**.

Energy

- Chemists are interested in different kind of energies:

1. Kinetic Energy
2. Radiant Energy
3. Thermal Energy
4. Chemical Energy
5. Potential Energy

Kinetic Energy, E_K

The energy associated with an object by virtue of its motion.

$$E_K = \frac{1}{2}mv^2$$

m = mass (kg)

v = velocity (m/s)

Thermal energy is a kind of kinetic energy.

Radiant Energy

- It's solar energy and comes from sun
- It's the primary Energy source for Earth
- It heats the atmosphere and surface of earth
- Vegetation through photosynthesis

Thermal Energy

- It's the energy that is associated with the random motion of atoms and molecules
- Temperature is not the measurement of the thermal energy
- It's depend on quantity: Extensive property

Heat

- **Heat** and Thermal energy are different
- **Heat** is the transfer of thermal energy between two bodies that are at the different temperatures.
- Heat flows from warmer objects to cooler objects.
- **Thermochemistry** is the study of heat changes in chemical reactions.

Chemical Energy

- It is stored within the structural units of chemical substances. (It's a kind of potential energy)
- When substances participate in chemical reactions chemical energy is released, stored, or converted to other form of energies.

Potential Energy, E_P

- The energy an object has by virtue of its position in a field of force, such as gravitaitonal, electric or magnetic field.

- Gravitational potential energy is given by the equation

$$E_P = mgh$$

m = mass (kg)

g = gravitational constant (9.80 m/s^2)

h = height (m)

- The SI unit of energy is the **joule, J**, pronounced "jewel."

$$J = \frac{kg \bullet m^2}{s^2}$$

- The calorie is a non-SI unit of energy commonly used by chemists. It was originally defined as the amount of energy required to raise the temperature of one gram of water by one degree Celsius.
- The exact definition is given by the equation:

$$1\,cal = 4.184\ J\ \ (exact)$$

?

A person weighing 75.0 kg (165 lbs) runs a course at 1.78 m/s (4.00 mph). What is the person's kinetic energy?

m = 75.0 kg

v = 1.78 m/s

$E_K = \frac{1}{2} mv^2$

$$E_K = \frac{1}{2}(75.0\text{ kg})\left(1.78\,\frac{\text{m}}{\text{s}}\right)^2$$

$$E_K = 119\,\frac{\text{kg}\bullet\text{m}^2}{\text{s}^2} = 119\text{ J}$$

(3 significant figures)

Thermodynamic System

- The substance under study in which a change occurs is called the thermodynamic system (or just system).

Thermodynamic Surroundings

- Everything else in the vicinity is called the thermodynamic surroundings (or just the surroundings).

Three Types of System

1. **Open System**: e.g. water in an open container. Can exchange mass and heat with surroundings(in the form of heat).

2. **Closed System**: e.g. water in a closed containers. Only transfer of energy, not mass.

3. **Isolated System**: e.g. water in a insulted container. No transfer of mass or energy

Endothermic and Exothermic Processes

- For some chemical reaction to take happen, they need energy for heating.
- Other reaction release energy as heat.
- Therefore, the transfer of heat to and from the system is central to our discussion.
- For this reason, we need some special terminology to indicate the direction of transfer.

Endothermic Process (*endo- means “into”).*

- This is a chemical reaction or process in which heat is absorbed by the system (*q* is positive).
- *During an endothermic process, such as the melting of ice, heat* flows *into the system from its surroundings*
- ***If we, as part of the surroundings,*** touch a container in which ice is melting, the container feels cold to us because heat has passed from our hand to the container.
- The reaction vessel will feel cool.

Exothermic Process (*exo- means “out* of”).

- This a chemical reaction or process in which heat is evolved (given out) by the system (*q* is negative).
- During an exothermic process, such as the combustion of gasoline, heat *exits or* flows *out of the system into the surroundings*
- ***If we, as part of the surroundings,*** touch a container in which the combustion of gasoline is taking place, the container feels warm to us because heat has passed from our the system to our hand.
- The reaction vessel will feel warm.

Endothermic and Exothermic Reactions

Examples:

- Chemical heat packs contain iron filings that are oxidized in an exothermic reaction. Your hands get warm because the released heat of the reaction is absorbed by your hands.
- Chemical cold packs contain NH_4NO_3 that dissolves in water in an endothermic process. Your hands get cold because they are giving away your heat to the reaction.

Endothermic and Exothermic Reactions

- Whether a reaction takes in or releases energy depends on what is happening to the chemical bonds in the reacting particles.
- Separating atoms or oppositely charged particles requires energy, while joining oppositely charged particles or atoms together releases energy
- In other words,
  - ✓ ***Bond breaking requires energy while***
  - ✓ ***Bond making releases energy***
- Bond breaking and bond making happens in any chemical reaction

Endothermic and Exothermic Reactions

- Whether the reaction is exothermic or endothermic depends on the balance between the energy required to break bonds and the energy released when new bond are formed.
- Different bond have different bond requirements for making and breaking.
- In an exothermic reaction the energy released by bond formation in the products is greater than the energy needed to break the bond in the reactants.
- In the exothermic reaction of the combustion of methane, heat is given out:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Energy changes in exothermic reaction

- More energy is released when the new bond are formed in the products (carbon dioxide and water) than is required to break the bonds in the reactants (methane and oxygen) and the reaction products store less chemical energy than the reactants.
- Neutralization reactions between acids and alkalis are also exothermic, and the raise in temperature produced during the reaction can easily be measured in the lab.

Energy changes in endothermic reaction

- In endothermic reactions, the energy required to break the bonds in reactants is greater than released when new bonds are formed in the products, So the difference is absorbed from the surroundings.
- Endothermic reactions are less common than exothermic reaction.
- E.g. the thermal decomposition of calcium carbonate to calcium oxide and carbon dioxide is endothermic

Summary

In an **endothermic** reaction:

- ✓ The reaction vessel cools.
- ✓ Heat is absorbed.
- ✓ Energy is added to the system.
- ✓ Heat *(q)* is positive.

In an **exothermic** reaction:

- ✓ The reaction vessel warms.
- ✓ Heat is evolved.
- ✓ Energy is subtracted from the system.
- ✓ Heat (*q*) is negative.

Exchanging Energy

- All the energy that leaves the system is transferred to the surrounding (or vice versa).
- The energy that is transferred to the surroundings is not lost to the universe
- It is dissipated, or spread throughout the surroundings
- Energy cannot be created or destroyed.
- Energy can be exchanged between objects.
- Energy can also be transformed from one form to another.
  - ✓ heat → light → sound

The First Law of Thermodynamics—Law of Conservation of Energy

- When energy is exchanged between objects or transformed into another form, all the energy is still there.
- The total amount of energy in the universe before the change has to be equal to the total amount of energy in the universe after the change.
- You can, therefore, never design a system that will continue to produce energy without some source of energy.

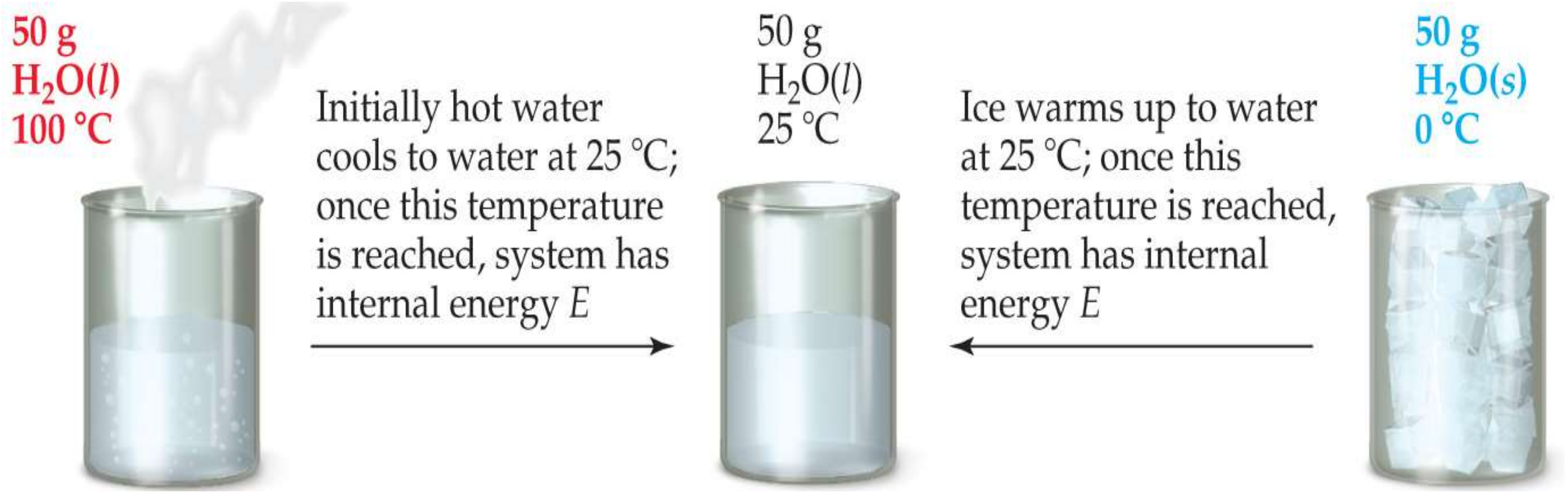
Internal Energy

- The **internal energy** is the total amount of kinetic and potential energy a system possesses.
- The change in the internal energy of a system depends only on the amount of energy in the system at the beginning and end.
  - ✓ A **state function** is a mathematical function whose result depends only on the initial and final conditions, not on the process used.
  - ✓ $\Delta E = E_{final} - E_{initial}$
  - ✓ $\Delta E_{reaction} = E_{products} - E_{reactants}$

State Functions

- **State functions** are the properties that are determined by the state of the system, regardless of how that condition was achieved.
- Energy, pressure, volume, and temperature are the examples of State functions.
- However, we do know that the internal energy of a system is independent of the path by which the system achieved that state.
- In the system depicted in the figure below, the water could have reached room temperature from either direction.

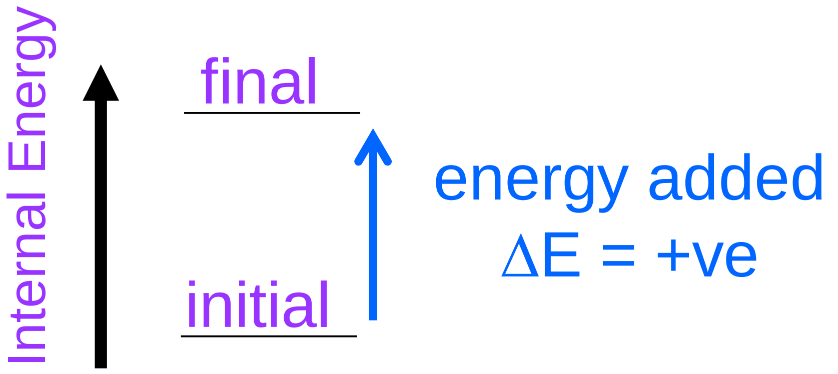
State Functions

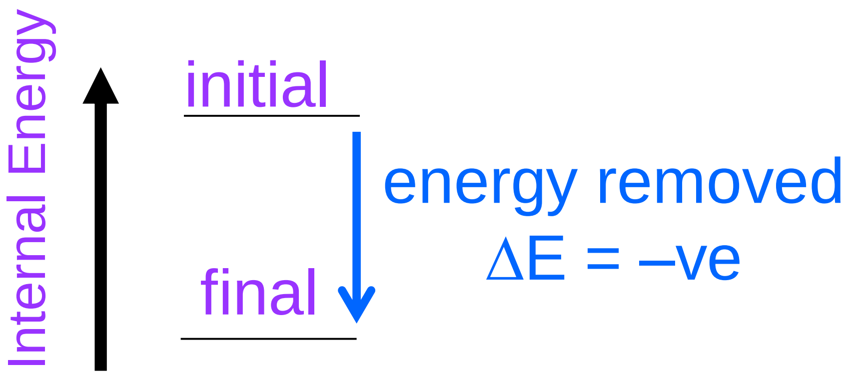


- Therefore, internal energy is a state function.
- It depends only on the present state of the system, not on the path by which the system arrived at that state.
- And so, ΔE depends only on E_{initial} and E_{final}.

Energy Diagrams

- Energy diagrams are a "graphical" way of showing the direction of energy flow during a process.
- If the final condition has a larger amount of internal energy than the initial condition, the change in the internal energy will be +ve.
- If the final condition has a smaller amount of internal energy than the initial condition, the change in the internal energy will be –ve.

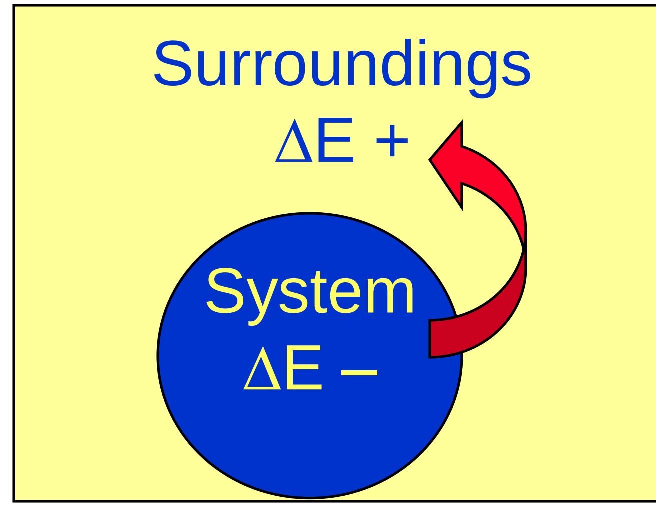


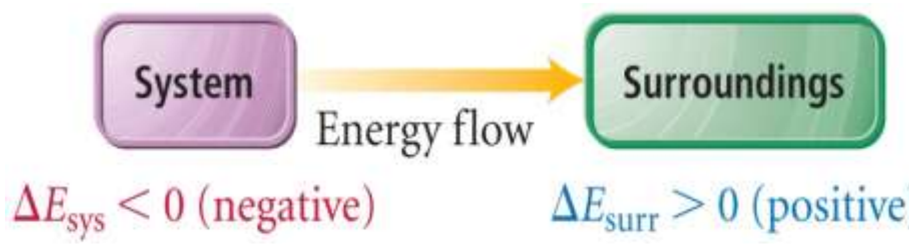


Energy Flow

- When energy flows out of a system, it must all flow into the surroundings.
- When energy flows out of a system, ΔE_{system} is –ve.
- When energy flows into the surroundings, $\Delta E_{surroundings}$ is +ve.
- Therefore:

$$-\Delta E_{system} = \Delta E_{surroundings}$$

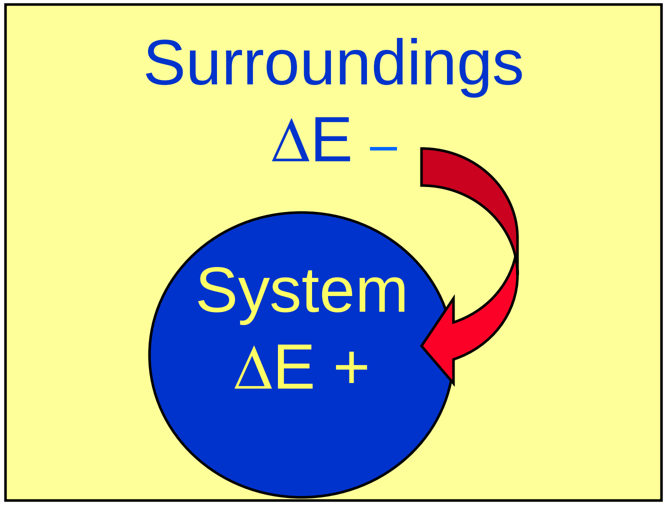


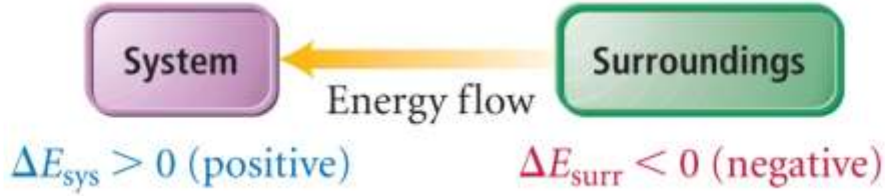


Energy Flow

- When energy flows into a system, it must all come from the surroundings.
- When energy flows into a system, ΔE_{system} is +ve.
- When energy flows out of the surroundings, $\Delta E_{surroundings}$ is –ve.
- therefore:

$$\Delta E_{system} = -\Delta E_{surroundings}$$





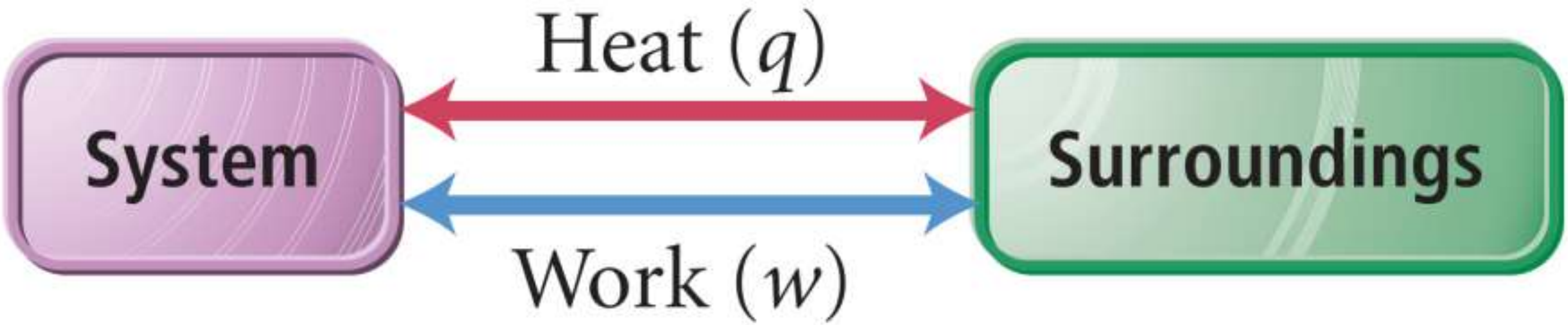
Energy Exchange

- Energy is exchanged between the system and surroundings through heat and work.
  - ✓ q = heat (thermal) energy
  - ✓ w = work energy
  - ✓ q and w are NOT state functions; their value depends on the process.

$$\Delta E = q + w$$

q (heat)	system gains heat energy +	system releases heat energy —
w (work)	system gains energy from work +	system releases energy by doing work —
ΔE	system gains internal energy +	system loses some of its internal energy —

Energy Exchange

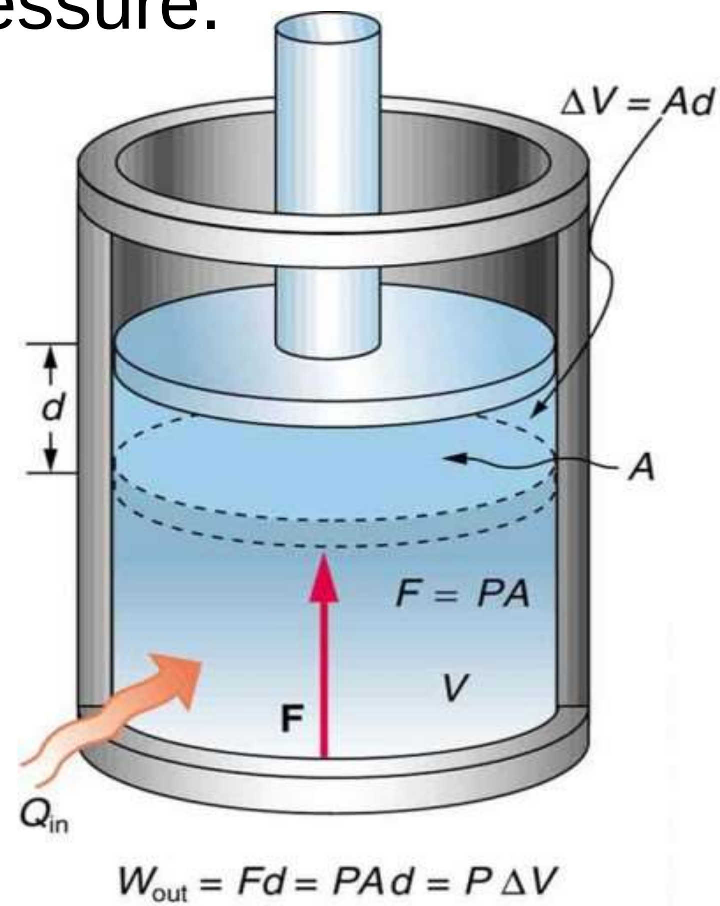


- Energy is exchanged between the system and surroundings through either heat exchange or work being done.

Pressure-Volume Work

- The PV work is work that is as a result of a volume change against an external pressure.
- When gases expand, ΔV is +ve, but the system is doing work on the surroundings, so w_{gas} is –ve.
- As long as the external pressure is kept constant,

–*work* = external pressure × change in volume



$$w = -P\,\Delta\,V$$

101.3 J = 1 atm·L.

Enthalpy

- If a process takes place at constant pressure (as the majority of processes we study do) and the only work done is this pressure – volume work, we can account for heat flow during the process by measuring the *enthalpy* of the system.
- **Enthalpy** is the internal energy plus the product of pressure and volume:

$$H = E + PV$$

Enthalpy

- When the system changes at constant pressure, the change in enthalpy, ΔH, is:

$$\Delta \boldsymbol{H} = \Delta(\boldsymbol{E} + \boldsymbol{PV})$$

- This can be written as:

$$\Delta \boldsymbol{H} = \Delta \boldsymbol{E} + \boldsymbol{P}\Delta \boldsymbol{V}$$

Enthalpy

- Since

$$\Delta E = q + w \text{ and}$$

$$w = -P\Delta V,$$

- we can substitute these into the enthalpy expression:

$$\boldsymbol{\Delta H = \Delta E + P\Delta V}$$

$$\boldsymbol{\Delta H = (q + w) - w}$$

$$\boldsymbol{\Delta H = q}$$

- So, at constant pressure, the change in enthalpy *is* the heat gained or lost.

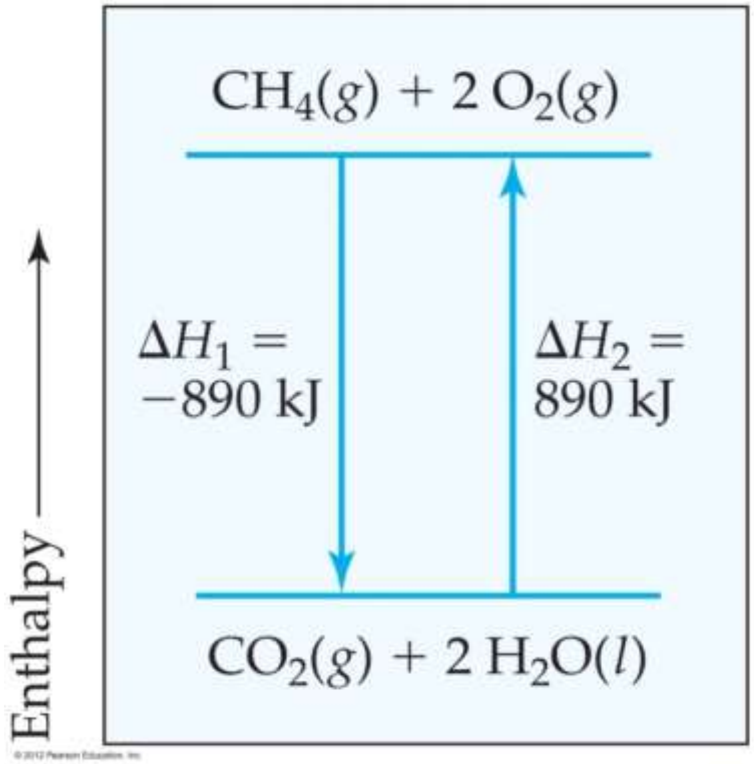
Enthalpy of Reaction

- You can't measure the enthalpy of a system but fortunately that doest matter.
- What you really want is to know the enthalpy change during a reaction.
- This is a measure of what the reaction can do for you under conditions of constant pressure.
- When a system reacts at constant pressure and gives out or takes in energy, we say that it undergoes an enthalpy change, represented, **ΔH .**
- The *change* in enthalpy, ΔH, is the enthalpy of the products minus the enthalpy of the reactants:

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

Enthalpy of Reaction

- This quantity, ΔH, is called the **enthalpy of reaction**, or the **heat of reaction**.



The Truth about Enthalpy

1. Enthalpy is an extensive property.
2. ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.
3. ΔH for a reaction depends on the state of the products and the state of the reactants.

Sample Exercise 5.3 Determining the Sign of Δ*H*

Indicate the sign of the enthalpy change, Δ*H*, in these processes carried out under atmospheric pressure and indicate whether each process is endothermic or exothermic: **(a)** An ice cube melts; **(b)** 1 g of butane (C_4H_{10}) is combusted in sufficient oxygen to give complete combustion to CO_2 and H_2O.

Solution

Analyze Our goal is to determine whether Δ*H* is positive or negative for each process. Because each process occurs at constant pressure, the enthalpy change equals the quantity of heat absorbed or released, $\Delta H = q_P$.

Plan We must predict whether heat is absorbed or released by the system in each process. Processes in which heat is absorbed are endothermic and have a positive sign for Δ*H*; those in which heat is released are exothermic and have a negative sign for Δ*H*.

Solve In (a) the water that makes up the ice cube is the system. The ice cube absorbs heat from the surroundings as it melts, so Δ*H* is positive and the process is endothermic.

In (b) the system is the 1 g of butane and the oxygen required to combust it. The combustion of butane in oxygen gives off heat, so Δ*H* is negative and the process is exothermic.

Sample Exercise 5.4 Relating ΔH to Quantities of Reactants and Products

How much heat is released when 4.50 g of methane gas is burned in a constant-pressure system? (Use the information given in Equation 5.18.)

Solution

Analyze Our goal is to use a thermochemical equation to calculate the heat produced when a specific amount of methane gas is combusted. According to Equation 5.18, 890 kJ is released by the system when 1 mol CH_4 is burned at constant pressure.

Plan Equation 5.18 provides us with a stoichiometric conversion factor: (1mol CH_4 = 890 kJ). Thus, we can convert moles of CH_4 to kJ of energy. First, however, we must convert grams of CH_4 to moles of CH_4. Thus, the conversion sequence is grams CH_4 (given) → moles CH_4 → kJ (unknown to be found).

Solve By adding the atomic weights of C and 4 H, we have 1 mol CH_4 = 16.0 CH_4. We can use the appropriate conversion factors to convert grams of CH_4 to moles of CH_4 to kilojoules:

$$\text{Heat} = (4.50\text{ g CH}_4)\left(\frac{1\text{ mol CH}_4}{16.0\text{ g CH}_4}\right)\left(\frac{-890\text{ kJ}}{1\text{ mol CH}_4}\right) = -250\text{ kJ}$$

The negative sign indicates that the system released 250 kJ into the surroundings.

Calorimetry

Since we cannot know the exact enthalpy of the reactants and products, we measure ΔH through **calorimetry**, the measurement of heat flow.

Quantity of Heat Energy Absorbed
Heat Capacity

- When a system absorbs heat, its temperature increases.
- The increase in temperature is directly proportional to the amount of heat absorbed.
- The proportionality constant is called the **heat capacity**, **C**.
  - ✓ Units of C are J/°C or J/K.

$$q = \mathbf{C} \times \Delta T$$

- The heat capacity of an object depends on its mass.
  - ✓ 200 g of water requires twice as much heat to raise its temperature by 1 °C as does 100 g of water.
- The heat capacity of an object depends on the type of material.
  - ✓ 1000 J of heat energy will raise the temperature of 100 g of sand 12 °C, but only raise the temperature of 100 g of water by 2.4 °C.

Specific Heat Capacity

- measure of a substance's ***intrinsic*** ability to absorb heat
- The **specific heat capacity** is the amount of heat energy required to raise the temperature of one gram of a substance 1 °C.
  - ✓ C_s
  - ✓ units are J/(g·°C)
- The **molar heat capacity** is the amount of heat energy required to raise the temperature of one mole of a substance 1 °C.

TABLE 6.4 Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity, C_s (J/g · °C)*
Elements	
Lead	0.128
Gold	0.128
Silver	0.235
Copper	0.385
Iron	0.449
Aluminum	0.903
Compounds	
Ethanol	2.42
Water	4.18
Materials	
Glass (Pyrex)	0.75
Granite	0.79
Sand	0.84

*At 298 K.

Quantifying Heat Energy

- The heat capacity of an object is proportional to its mass and the specific heat of the material.
- So we can calculate the quantity of heat absorbed by an object if we know the mass, the specific heat, and the temperature change of the object.

heat **= (mass) × (specific heat capacity) × (temp. change)**

$$q = (m) \times (C_s) \times (\Delta T)$$

Heat Capacity and Specific Heat

Specific heat, then, is

$$\text{Specific heat} = \frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$$

$$Cs = \frac{q}{m \times \Delta T}$$

?

A piece of zinc weighing 35.8 g was heated from 20.00° C to 28.00° C. How much heat was required? The specific heat of zinc is 0.388 J/(g° C).

m = 35.8 g

s = 0.388 J/(g° C)

Δt = 28.00° C – 20.00° C = 8.00° C

$$q = m \cdot Cs \cdot \Delta t$$

$$q = 35.8\ \text{g} \bullet \left(\frac{0.388\ \text{J}}{\text{g°C}}\right)(8.00\text{°C})$$

q = 111 J

(3 significant figures)

Sample Exercise 5.5 Relating Heat, Temperature Change, and Heat Capacity

(a) How much heat is needed to warm 250 g of water (about 1 cup) from 22 °C (about room temperature) to 98 °C (near its boiling point)? **(b)** What is the molar heat capacity of water?

Solution

Analyze In part **(a)** we must find the quantity of heat (q) needed to warm the water, given the mass of water (m), its temperature change (ΔT), and its specific heat (C_s). In part **(b)** we must calculate the molar heat capacity (heat capacity per mole, C_m) of water from its specific heat (heat capacity per gram).

Plan (a) Given C_s, m, and ΔT, we can calculate the quantity of heat, q, using Equation 5.22. **(b)** We can use the molar mass of water and dimensional analysis to convert from heat capacity per gram to heat capacity per mole.

Solve

(a) The water undergoes a temperature change of

$$\Delta T = 98\ °C - 22\ °C = 76\ °C = 76\ K$$

Using Equation 5.22, we have

$$q = C_s \times m \times \Delta T$$
$$= (4.18\ J/g\text{–}K)(250\ g)(76\ K) = 7.9 \times 10^4\ J$$

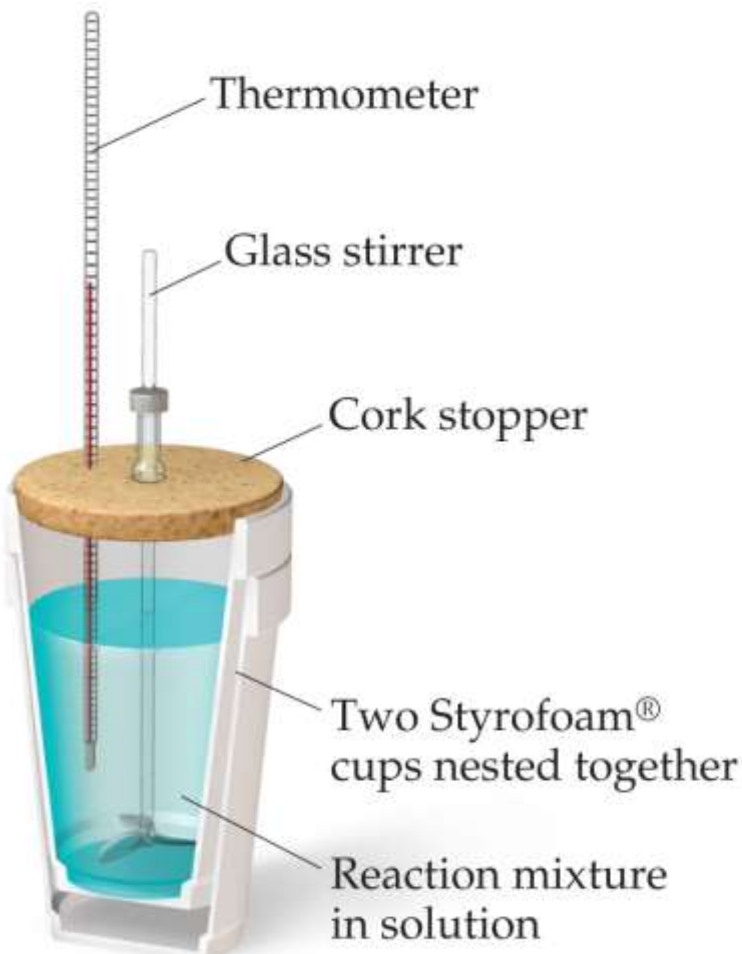
(b) The molar heat capacity is the heat capacity of one mole of substance. Using the atomic weights of hydrogen and oxygen, we have

$$1\ mol\ H_2O = 18.0\ g\ H_2O$$

From the specific heat given in part (a), we have

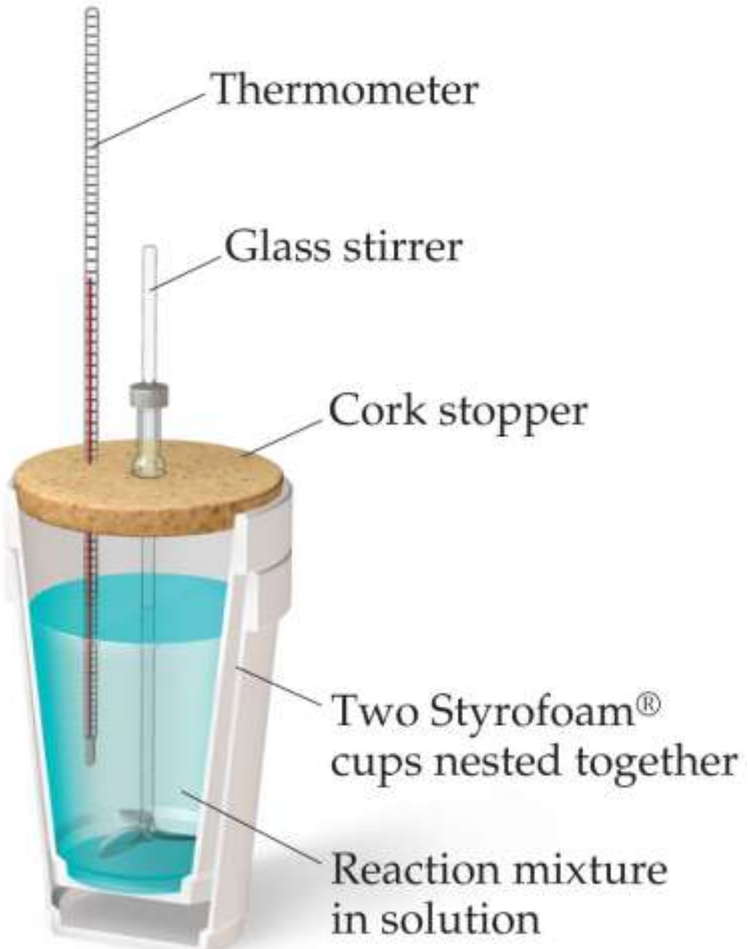
$$C_m = \left(4.18\ \frac{J}{g\text{-}K}\right)\left(\frac{18.0\ g}{1\ mol}\right) = 75.2\ J/mol\text{-}K$$

Constant Pressure Calorimetry



By carrying out a reaction in aqueous solution in a simple calorimeter such as this one, one can indirectly measure the heat change for the system by measuring the heat change for the water in the calorimeter.

Constant Pressure Calorimetry



Because the specific heat for water is well known (4.184 J/g-K), we can measure Δ*H* for the reaction with this equation:

$q = m \times Cs \times \Delta T$

Sample Exercise 5.6 Measuring ΔH Using a Coffee-Cup Calorimeter

When a student mixes 50 mL of 1.0 *M* HCl and 50 mL of 1.0 *M* NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 °C to 27.5 °C. Calculate the enthalpy change for the reaction in kj/mol HCl, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/mL, and that its specific heat is 4.18 J/g–K.

Solution

Analyze Mixing solutions of HCl and NaOH results in an acid–base reaction:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{H_2O}(l) + \mathrm{NaCl}(aq)$$

We need to calculate the heat produced per mole of HCl, given the temperature increase of the solution, the number of moles of HCl and NaOH involved, and the density and specific heat of the solution.

Plan The total heat produced can be calculated using Equation 5.23. The number of moles of HCl consumed in the reaction must be calculated from the volume and molarity of this substance, and this amount is then used to determine the heat produced per mol HCl.

Solve

Because the total volume of the solution is 100 mL, its mass is

$$(100\ \mathrm{mL})(1.0\ \mathrm{g/mL}) = 100\ \mathrm{g}$$

The temperature change is

$$\Delta T = 27.5\ °\mathrm{C} - 21.0\ °\mathrm{C} = 6.5\ °\mathrm{C} = 6.5\ \mathrm{K}$$

Using Equation 5.23, we have

$$q_{\mathrm{rxn}} = -C_s \times m \times \Delta T$$

$$= -(4.18\ \mathrm{J/g{-}K})(100\ \mathrm{g})(6.5\ \mathrm{K}) = -2.7 \times 10^3\ \mathrm{J} = -2.7\ \mathrm{kJ}$$

Sample Exercise 5.6 Measuring ΔH Using a Coffee-Cup Calorimeter

Continued

Because the process occurs at constant pressure,

$$\Delta H = q_P = -2.7 \text{ kJ}$$

To express the enthalpy change on a molar basis, we use the fact that the number of moles of HCl is given by the product of the volume (50mL = 0.050 L) and concentration (1.0 *M* = 1.0 mol/L) of the HCl solution:

$$(0.050 \text{ L})(1.0 \text{ mol/L}) = 0.050 \text{ mol}$$

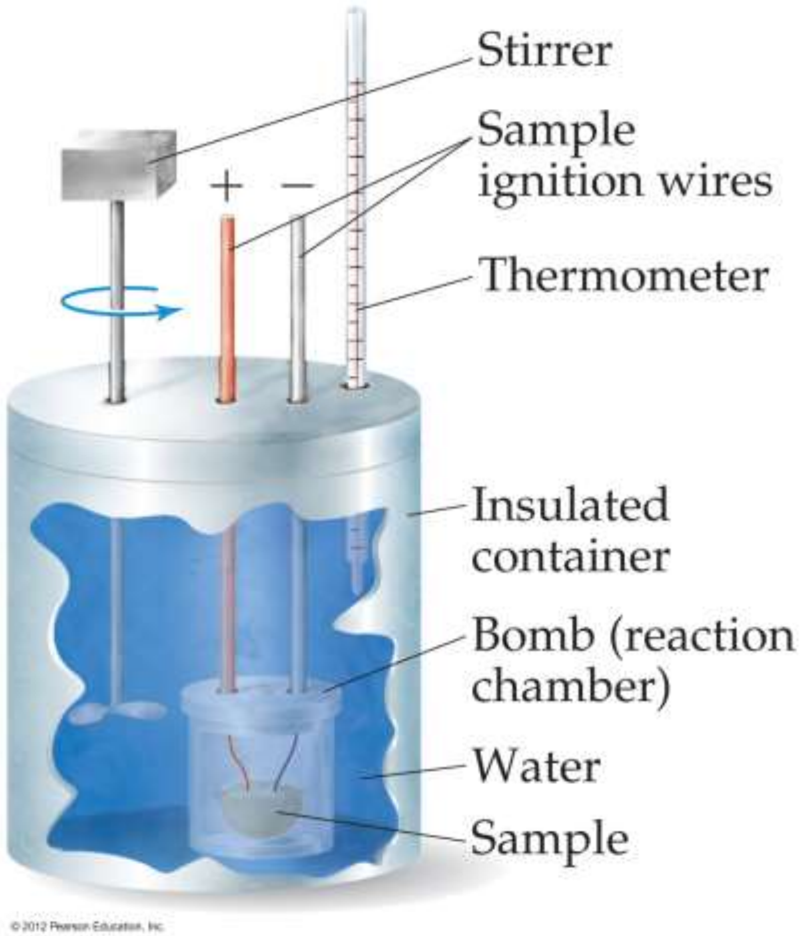
Thus, the enthalpy change per mole of HCl is

$$\Delta H = -2.7 \text{ kJ}/0.050 \text{ mol} = -54 \text{ kJ/mol}$$

Check ΔH is negative (exothermic), which is expected for the reaction of an acid with a base and evidenced by the fact that the reaction causes the temperature of the solution to increase. The magnitude of the molar enthalpy change seems reasonable.

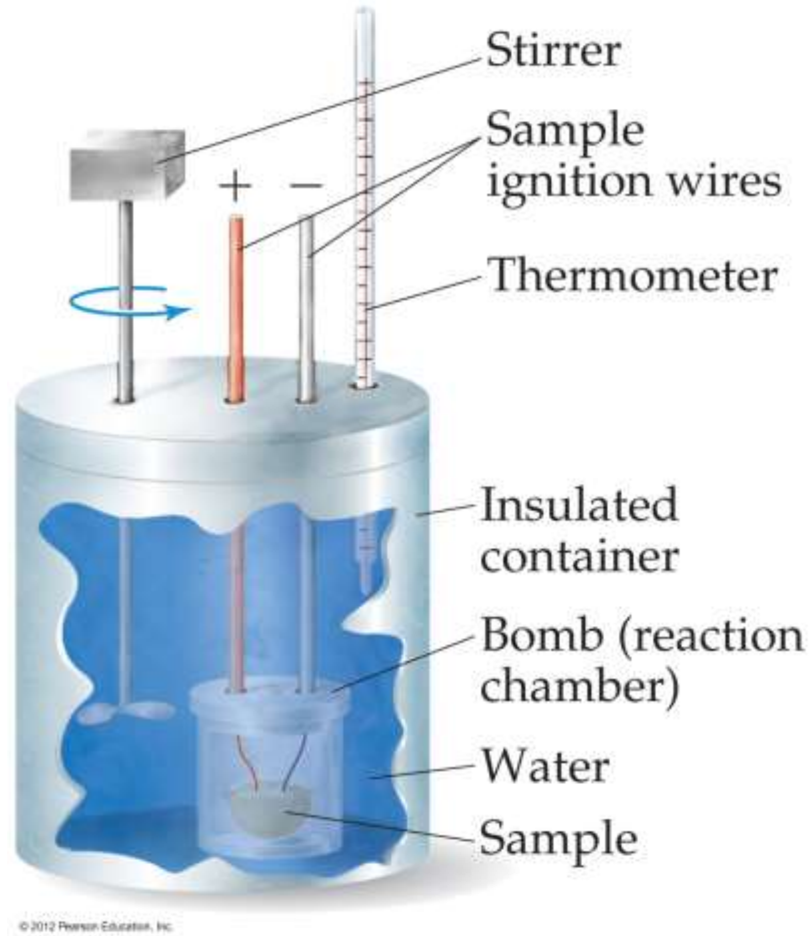
Bomb Calorimetry

- Reactions can be carried out in a sealed "bomb" such as this one.
- The heat absorbed (or released) by the water is a very good approximation of the enthalpy change for the reaction.



Bomb Calorimetry

- Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy, ΔE, not ΔH.
- For most reactions, the difference is very small.



Sample Exercise 5.7 Measuring q_{rxn} Using a Bomb Calorimeter

The combustion of methylhydrazine (CH_6N_2), a liquid rocket fuel, produces $N_2(g)$, $CO_2(g)$, and $H_2O(l)$:

$$2\ CH_6N_2(l) + 5\ O_2(g) \longrightarrow 2\ N_2(g) + 2\ CO_2(g) + 6\ H_2O(l)$$

When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 °C to 39.50 °C. In a separate experiment the heat capacity of the calorimeter is measured to be 7.794 kJ/ °C. Calculate the heat of reaction for the combustion of a mole of CH_6N_2.

Solution

Analyze We are given a temperature change and the total heat capacity of the calorimeter. We are also given the amount of reactant combusted. Our goal is to calculate the enthalpy change per mole for combustion of the reactant.

Plan We will first calculate the heat evolved for the combustion of the 4.00-g sample. We will then convert this heat to a molar quantity.

Solve

For combustion of the 4.00-g sample of methylhydrazine, the temperature change of the calorimeter is

$$\Delta T = (39.50\ °C - 25.00\ °C) = 14.50\ °C$$

We can use ΔT and the value for C_{cal} to calculate the heat of reaction (Equation 5.24):

$$q_{rxn} = -C_{cal} \times \Delta T = -(7.794\ kJ/°C)(14.50\ °C) = -113.0\ kJ$$

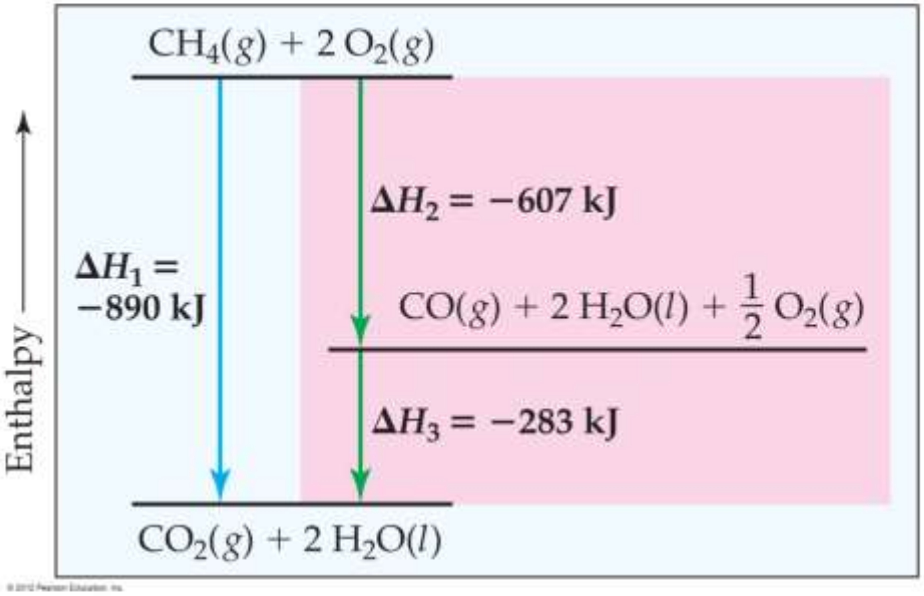
We can readily convert this value to the heat of reaction for a mole of CH_6N_2:

$$\left(\frac{-113.0\ kJ}{4.00\ g\ CH_6N_2}\right) \times \left(\frac{46.1\ g\ CH_6N_2}{1\ mol\ CH_6N_2}\right) = -1.30 \times 10^3\ kJ/mol\ CH_6N_2$$

Hess's Law

- ΔH is well known for many reactions, and it is inconvenient to measure ΔH for every reaction in which we are interested.
- However, we can estimate ΔH using published ΔH values and the properties of enthalpy.

Hess's Law



Hess's law states that "[i]f a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps."

Hess's Law

Because ΔH is a state function, the total enthalpy change depends only on the initial state of the reactants and the final state of the products.

Sample Exercise 5.8 Using Hess's Law to Calculate ΔH

The enthalpy of reaction for the combustion of C to CO_2 is –393.5 kJ/mol C, and the enthalpy for the combustion of CO to CO_2 is –283.0 kJ/mol C:

1. $$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ}$$

2. $$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -283.0 \text{ kJ}$$

Using these data, calculate the enthalpy for the combustion of C to CO:

3. $$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = ?$$

Solution

Analyze We are given two thermochemical equations, and our goal is to combine them in such a way as to obtain the third equation and its enthalpy change.

Plan We will use Hess's law. In doing so, we first note the numbers of moles of substances among the reactants and products in the target equation, (3).We then manipulate equations (1) and (2) to give the same number of moles of these substances, so that when the resulting equations are added, we obtain the target equation. At the same time, we keep track of the enthalpy changes, which we add.

Sample Exercise 5.8 Using Hess's Law to Calculate ΔH

Continued

Solve To use equations (1) and (2), we arrange them so that C(*s*) is on the reactant side and CO(*g*) is on the product side of the arrow, as in the target reaction, equation (3). Because equation (1) has C(*s*) as a reactant, we can use that equation just as it is. We need to turn equation (2) around, however, so that CO(*g*) is a product. Remember that when reactions are turned around, the sign of ΔH is reversed. We arrange the two equations so that they can be added to give the desired equation:

$$\begin{array}{lr} C(s) + O_2(g) \longrightarrow CO_2(g) & \Delta H = -393.5\ \text{kJ} \\ CO_2(g) \longrightarrow CO(g) + \tfrac{1}{2} O_2(g) & -\Delta H = 283.0\ \text{kJ} \\ \hline C(s) + \tfrac{1}{2} O_2(g) \longrightarrow CO(g) & \Delta H = -110.5\ \text{kJ} \end{array}$$

When we add the two equations, $CO_2(g)$ appears on both sides of the arrow and therefore cancels out. Likewise, ½ 0_2 (*g*) is eliminated from each side.

Sample Exercise 5.9 Using Three Equations with Hess's Law to Calculate ΔH

Calculate ΔH for the reaction

$$2\,C(s) + H_2(g) \longrightarrow C_2H_2(g)$$

given the following chemical equations and their respective enthalpy changes:

$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l) \qquad \Delta H = -1299.6\text{ kJ}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\text{ kJ}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8\text{ kJ}$$

Solution

Analyze We are given a chemical equation and asked to calculate its ΔH using three chemical equations and their associated enthalpy changes.

Plan We will use Hess's law, summing the three equations or their reverses and multiplying each by an appropriate coefficient so that they add to give the net equation for the reaction of interest. At the same time, we keep track of the ΔH values, reversing their signs if the reactions are reversed and multiplying them by whatever coefficient is employed in the equation.

Sample Exercise 5.9 Using Three Equations with Hess's Law to Calculate ΔH

Continued

Solve Because the target equation has C_2H_2 as a product, we turn the first equation around; the sign of ΔH is therefore changed. The desired equation has 2 C(*s*) as a reactant, so we multiply the second equation and its ΔH by 2. Because the target equation has H_2 as a reactant, we keep the third equation as it is. We then add the three equations and their enthalpy changes in accordance with Hess's law:

$$\begin{array}{lll}
2\,CO_2(g) + H_2O(l) \longrightarrow C_2H_2(g) + \frac{5}{2}O_2(g) & & \Delta H = 1299.6\text{ kJ} \\
2\,C(s) + 2\,O_2(g) \longrightarrow 2\,CO_2(g) & & \Delta H = -787.0\text{ kJ} \\
H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) & & \Delta H = -285.8\text{ kJ} \\
\hline
2\,C(s) + H_2(g) \longrightarrow C_2H_2(g) & & \Delta H = 226.8\text{ kJ}
\end{array}$$

When the equations are added, there are 2 CO_2, 5/2 O_2, and H_2O on both sides of the arrow. These are canceled in writing the net equation.

Enthalpies of Formation

An enthalpy of formation, ΔH_f, is defined as the enthalpy change for the reaction in which a compound is made from its constituent elements in their elemental forms.

Standard Enthalpies of Formation

Standard enthalpies of formation, ΔH_f°, are measured under standard conditions (25 °C and 1.00 atm pressure).

TABLE 5.3 • Standard Enthalpies of Formation, ΔH_f°, at 298 K

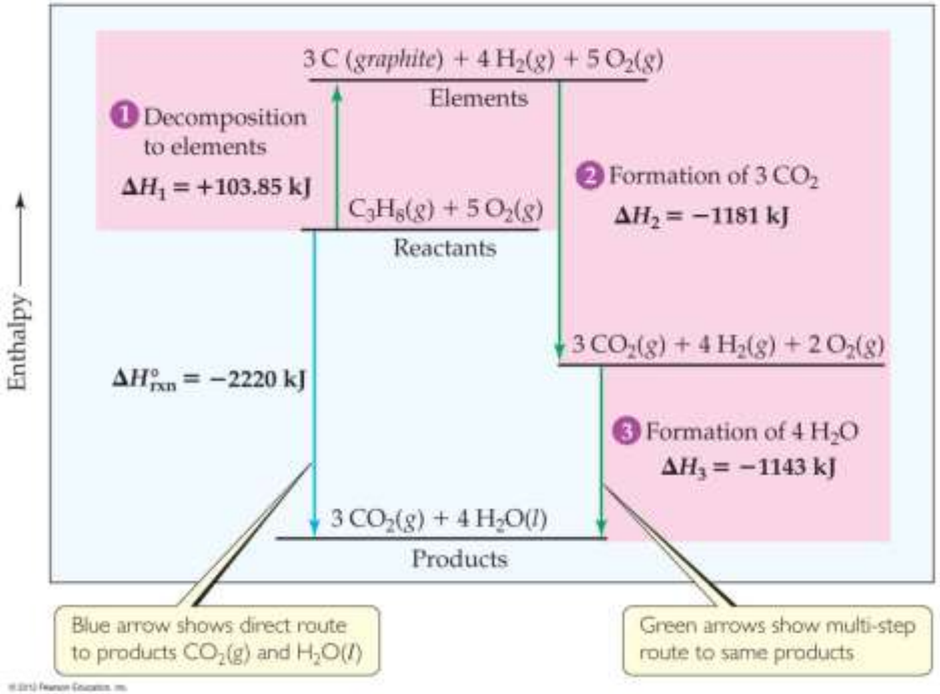
Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

Calculation of ΔH

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

- Imagine this as occurring in three steps:

$$C_3H_8(g) \longrightarrow 3C_{(graphite)} + 4H_2(g)$$

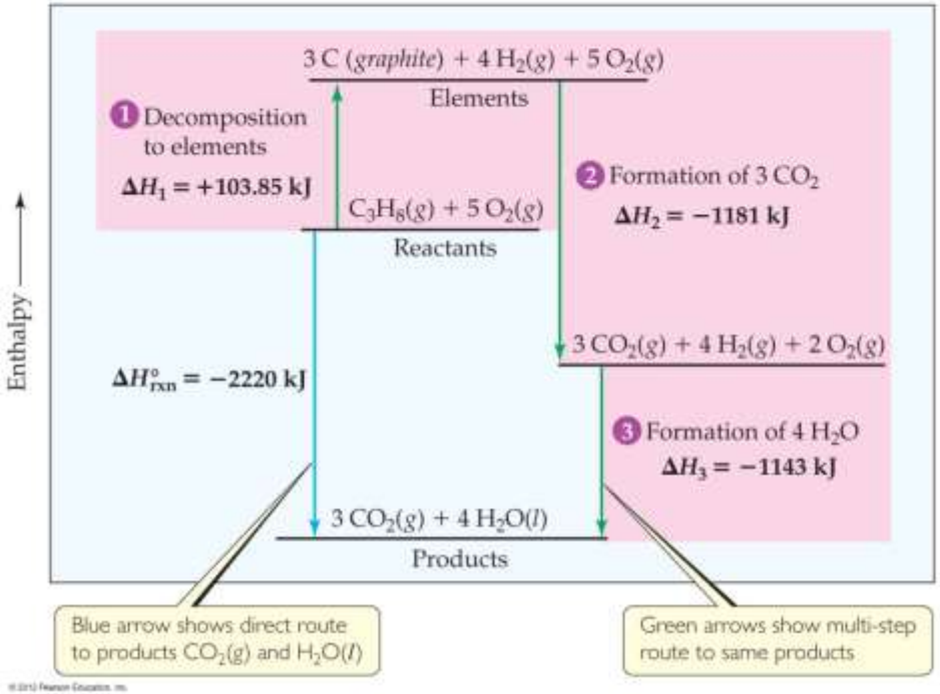


Calculation of ΔH

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

- Imagine this as occurring in three steps:

$$C_3H_8(g) \longrightarrow 3C_{(graphite)} + 4H_2(g)$$
$$3C_{(graphite)} + 3O_2(g) \longrightarrow 3CO_2(g)$$

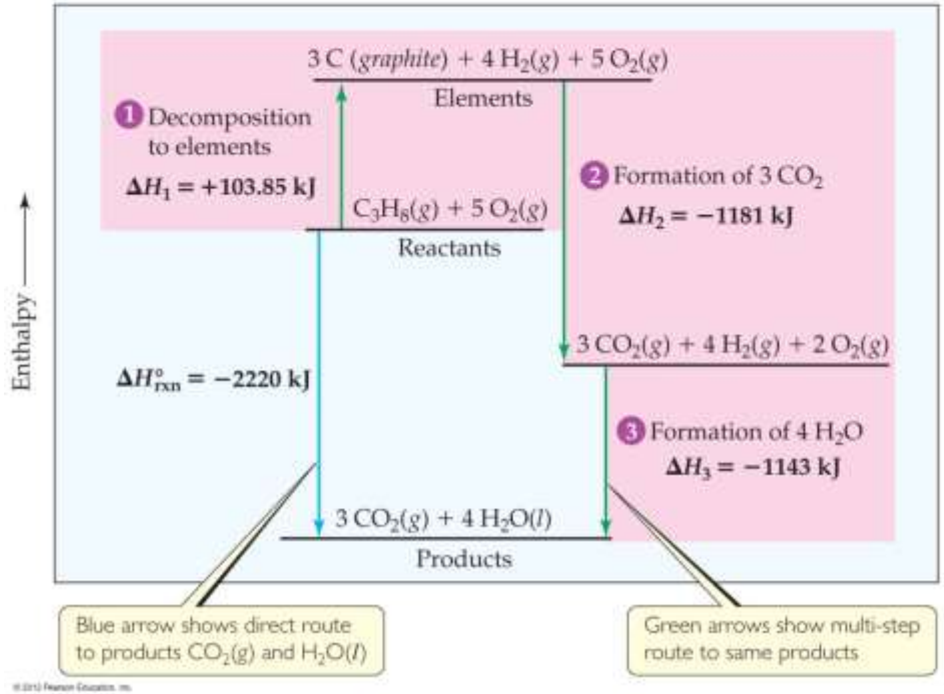


Calculation of Δ*H*

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

- Imagine this as occurring in three steps:

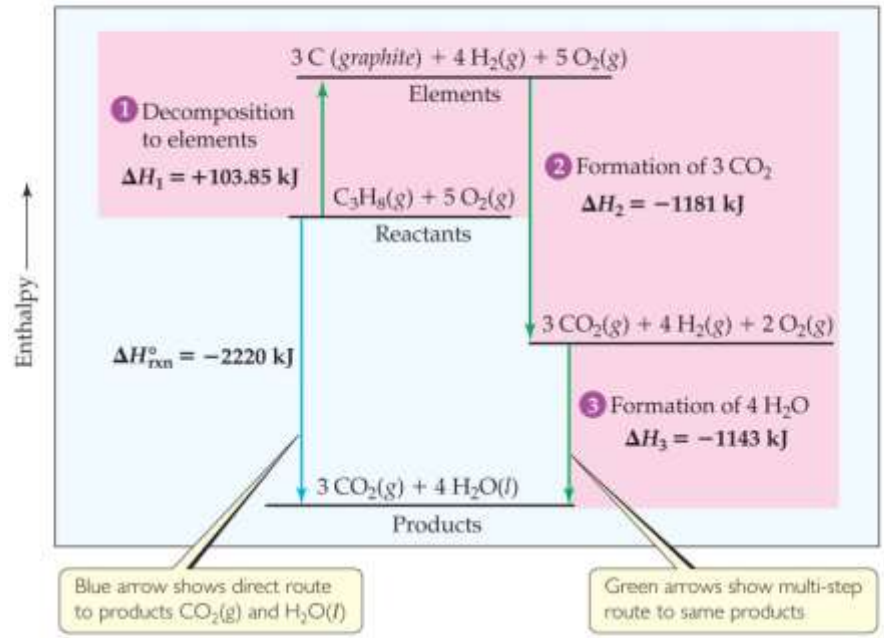
$$C_3H_8(g) \longrightarrow 3C_{(graphite)} + 4H_2(g)$$
$$3C_{(graphite)} + 3O_2(g) \longrightarrow 3CO_2(g)$$
$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l)$$



Calculation of ΔH

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

- The sum of these equations is



$$C_3H_8(g) \longrightarrow 3C_{(graphite)} + 4H_2(g)$$
$$3C_{(graphite)} + 3O_2(g) \longrightarrow 3CO_2(g)$$
$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l)$$

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

Calculation of ΔH

We can use Hess's law in this way:

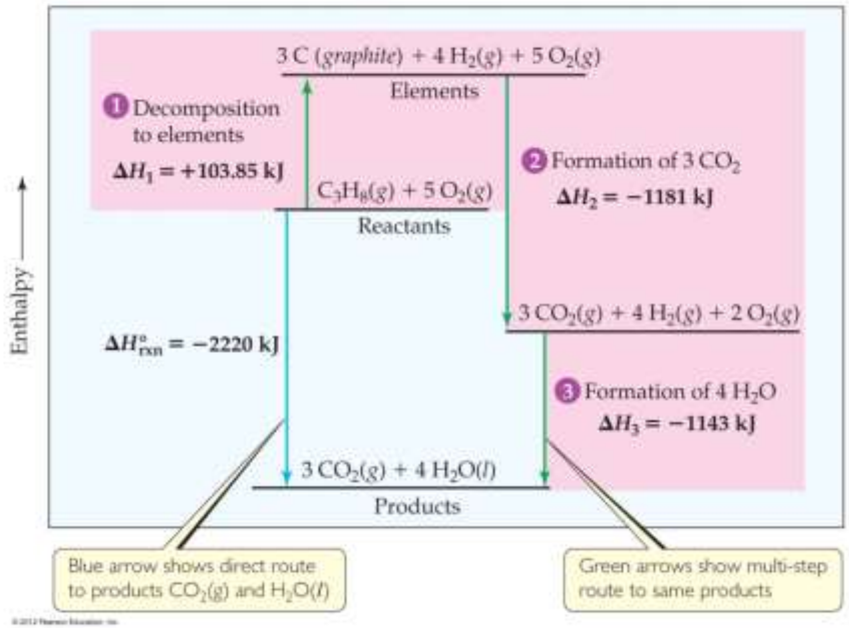
$$\Delta H = \Sigma n \Delta H_{f,\text{products}}^{\circ} - \Sigma m \Delta H_{f,\text{reactants}}^{\circ}$$

where *n* and *m* are the stoichiometric coefficients.

Calculation of ΔH

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

$$\begin{aligned}\Delta H &= [3(-393.5\text{ kJ}) + 4(-285.8\text{ kJ})] - [1(-103.85\text{ kJ}) + 5(0\text{ kJ})] \\ &= [(-1180.5\text{ kJ}) + (-1143.2\text{ kJ})] - [(-103.85\text{ kJ}) + (0\text{ kJ})] \\ &= (-2323.7\text{ kJ}) - (-103.85\text{ kJ}) \quad = \quad -2219.9\text{ kJ}\end{aligned}$$



Foods fuels three needs of the body:

- They supply substances for the growth and repair of tissue.
- They supply substances for the synthesis of compounds used in the regulation processes.
- They supply energy.

Foods do this by a combustion process.

For glucose, a carbohydrate:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l);$$
$$\Delta H_f^\circ = -2803 \text{ kJ}$$

For glycerol trimyristate, a fat:

$$C_{45}H_{86}O_6(s) + {}^{127}/_{2}O_2(g) \rightarrow 45CO_2(g) + 43H_2O(l);$$
$$\Delta H_f^\circ = -27{,}820 \text{ kJ}$$

The average value for carbohydrates is 4.0 kcal/g and for fats is 9.0 kcal/g.

Energy in Foods

Most of the fuel in the food we eat comes from carbohydrates and fats.

TABLE 5.4 • Compositions and Fuel Values of Some Common Foods

	Approximate Composition (% by mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g (Cal/g)
Carbohydrate	100	—	—	17	4
Fat	—	100	—	38	9
Protein	—	—	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer†	1.2	—	0.3	1.8	0.42
Bread	52	3	9	12	2.8
Cheese	4	37	28	20	4.7
Eggs	0.7	10	13	6.0	1.4
Fudge	81	11	2	18	4.4
Green beans	7.0	—	1.9	1.5	0.38
Hamburger	—	30	22	15	3.6
Milk (whole)	5.0	4.0	3.3	3.0	0.74
Peanuts	22	39	26	23	5.5

†Beer typically contains 3.5% ethanol, which has fuel value.

*Although fuel values represent the heat *released* in a combustion reaction, fuel values are reported as positive numbers.

Fossil fuels originated millions of years ago when aquatic plants and animals were buried and compressed by layers of sediment at the bottoms of swamps and seas.

Over time this organic matter was converted by bacterial decay and pressure to petroleum (oil), gas, and coal.

Coal, which accounts for 22.9% of total U.S. energy consumption, varies in terms of the amount of carbon it contains and so varies in terms of the amount of energy it produces in combustion.

Anthracite (hard coal) was laid down as long as 250 million years ago and can contain as much as 80% carbon. Bituminous coal, a younger variety, contains between 45% and 65% carbon.

Natural gas, which accounts for 22.7% of total U.S. energy consumption, is convenient because it is fluid and can be easily transported. Purified natural gas is primarily methane, CH_4, plus small amounts of ethane, C_2H_6; propane, C_3H_8; and butane, C_4H_{10}.

Petroleum is a mixture of compounds. Gasoline, which is obtained from petroleum, is a mixture of hydrocarbons (compounds of carbon and hydrogen).

The main issue with natural gas and petroleum is their relatively short supply. It has been estimated that petroleum deposits will be 80% depleted by 2030. Natural gas deposits may be depleted even sooner.

Coal deposits, however, are expected to last for several more centuries. This has led to the development of commercial methods for converting coal to the more easily handled liquid and gaseous fuels.

Coal gasification is one way. Steam is passed over hot coal:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

The mixture containing carbon monoxide can be converted by various methods into useful products.

The mixture of carbon monoxide and hydrogen can be converted by various methods into useful products such as methane, CH_4.

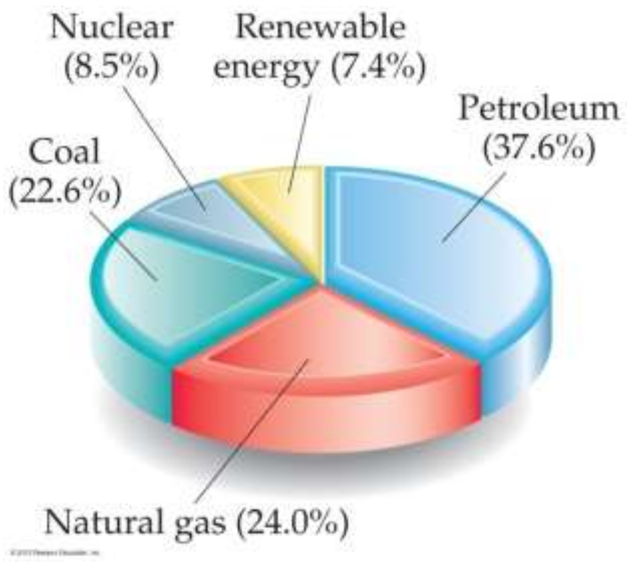
$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$$

Energy in Fuels

The vast majority of the energy consumed in this country comes from fossil fuels.

TABLE 5.5 • Fuel Values and Compositions of Some Common Fuels

	Approximate Elemental Composition (mass %)			
	C	H	O	Fuel Value (kJ/g)
Wood (pine)	50	6	44	18
Anthracite coal (Pennsylvania)	82	1	2	31
Bituminous coal (Pennsylvania)	77	5	7	32
Charcoal	100	0	0	34
Crude oil (Texas)	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49
Hydrogen	0	100	0	142



Principles and Basics

of

Organic Chemistry

10.1 Introduction

❖ **What is Organic Chemistry?**

✓ **It is a branch of chemistry that involves the study of hydrocarbons (compounds of carbon and hydrogen) and their derivatives**

❖ **Why is organic chemistry important?**

✓ **The answer lies in the fact that every aspect of life—mammalian and non-mammalian as well as plant and microscopic life—involves organic chemistry**

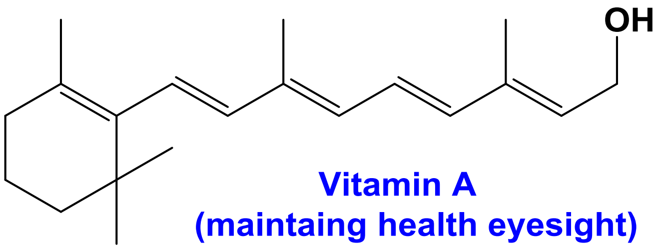
Contd……

- ✓ In addition many of the products used every day (pharmaceuticals, plastics, clothing, etc.) involve organic molecules
- ✓ Organic chemistry holds a central place in chemical studies because its fundamental principles and its applications touch virtually all other disciplines

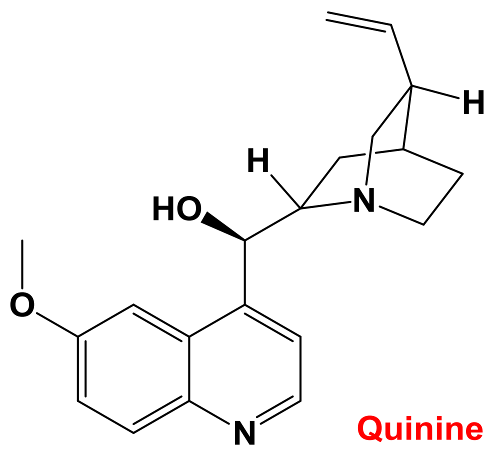
Contd……

❖ **Representative organic compounds with biological activity;**

Natural compounds

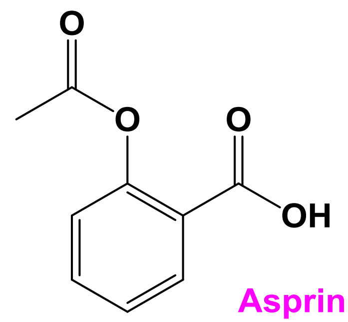


Vitamin A
(maintaing health eyesight)



Quinine
(anti-malarial drug)

Synthetic compound



Asprin
(pain killer drug)

10.2 Hybridization States of Carbon

- There are only 3 types of carbons in all known over 10,000,000 compounds of carbon, namely sp^3, sp^2 and sp carbon:

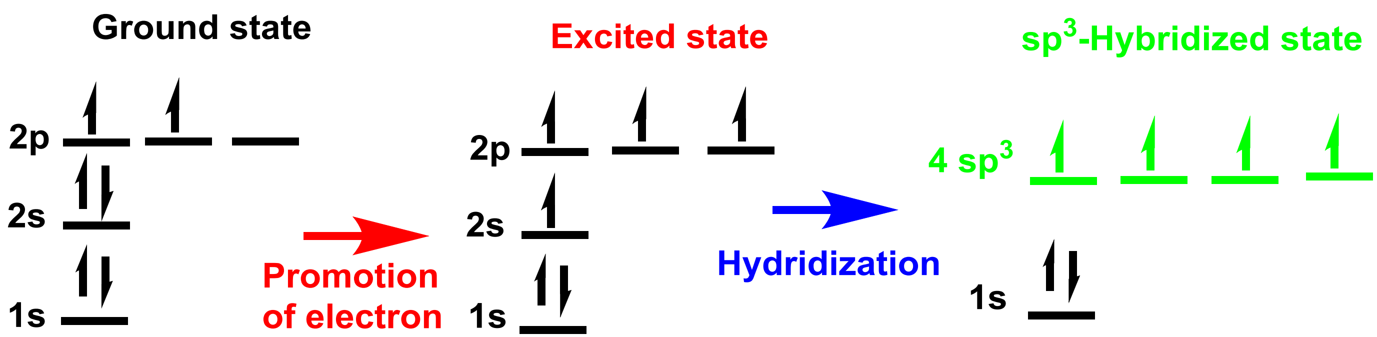
✓ (i) sp^3 Carbon: has 4 sp^3 hybrid orbitals , no pure s or p orbital

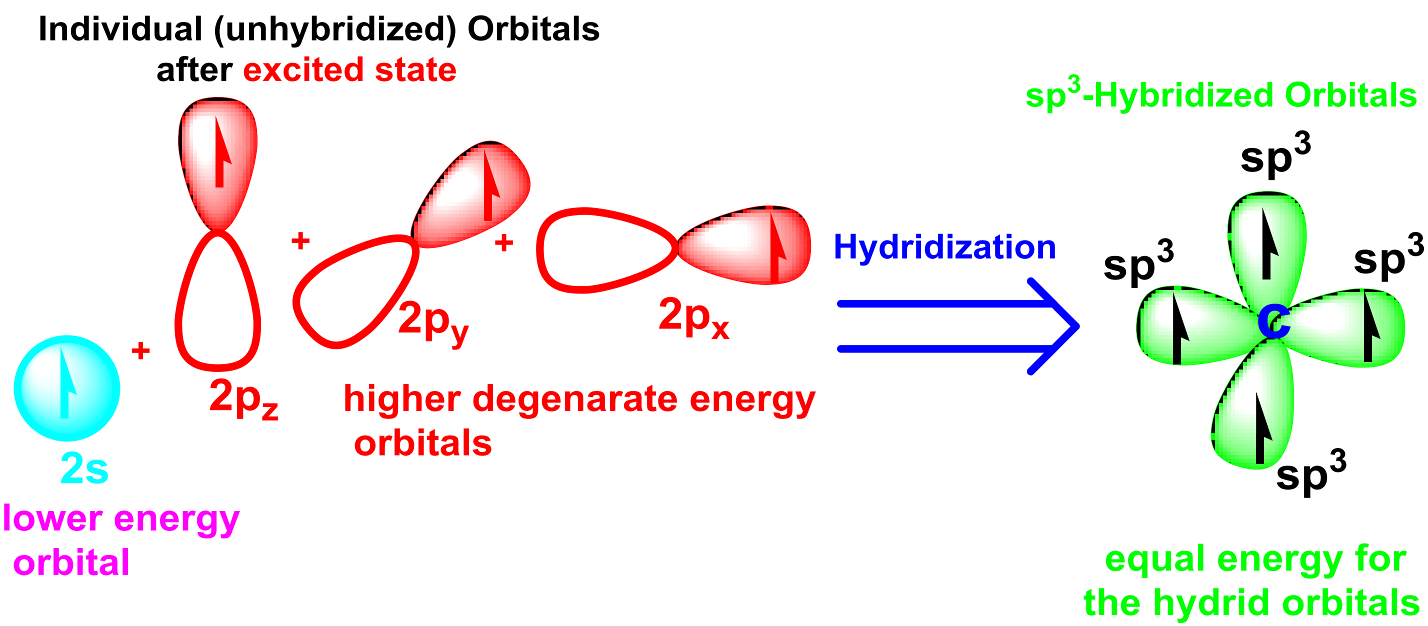
✓ (ii) sp^2 Carbon: has 3 sp^2 hybrid orbitals and 1 pure unhybridized p orbital

✓ (iii) sp Carbon: has 2 sp hybrid orbitals and 2 pure unhybridized p-orbitals

Contd……

❖ sp^3 hybridization state of carbon





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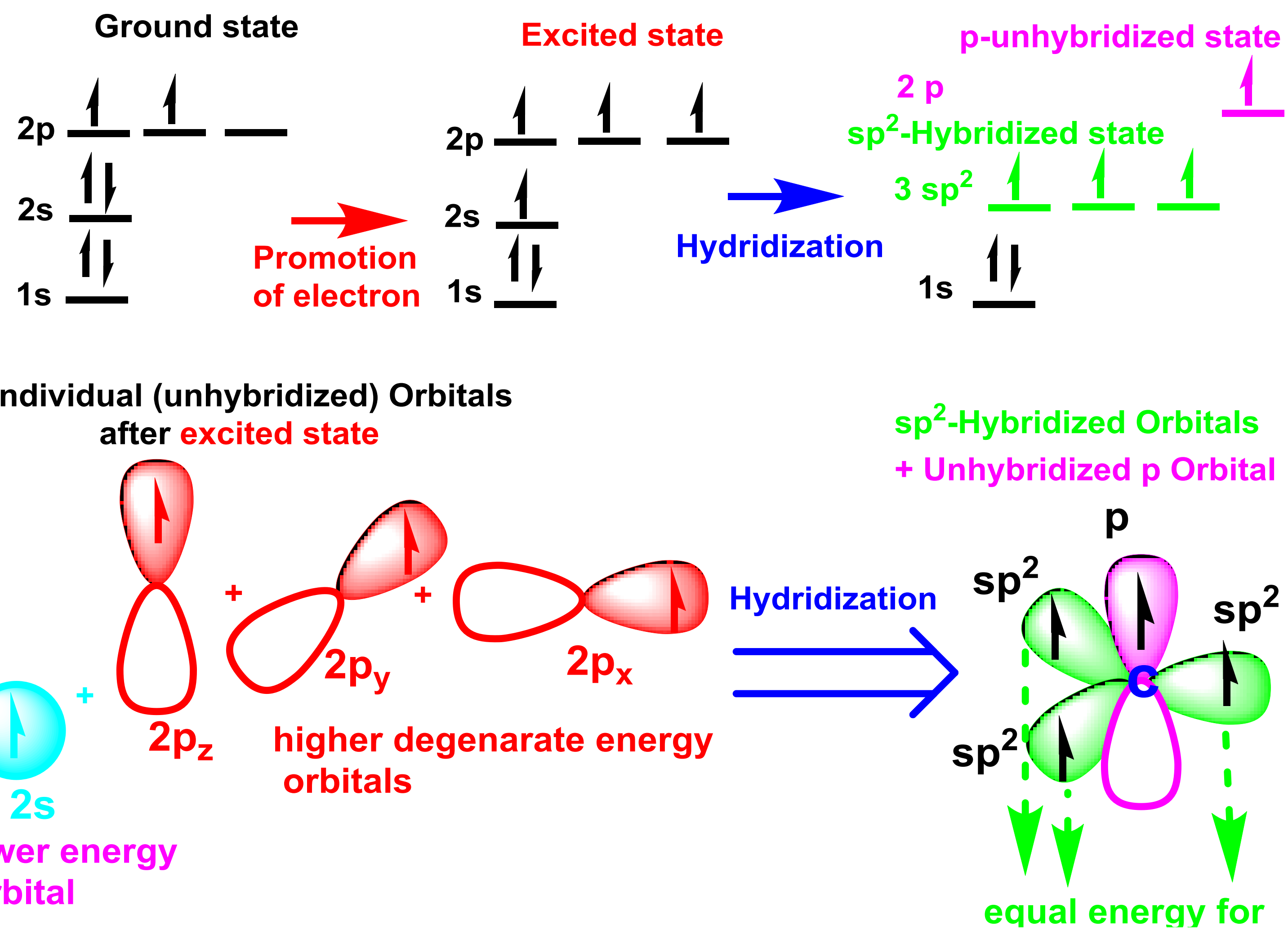
❖ sp^2 hybridization state of carbon



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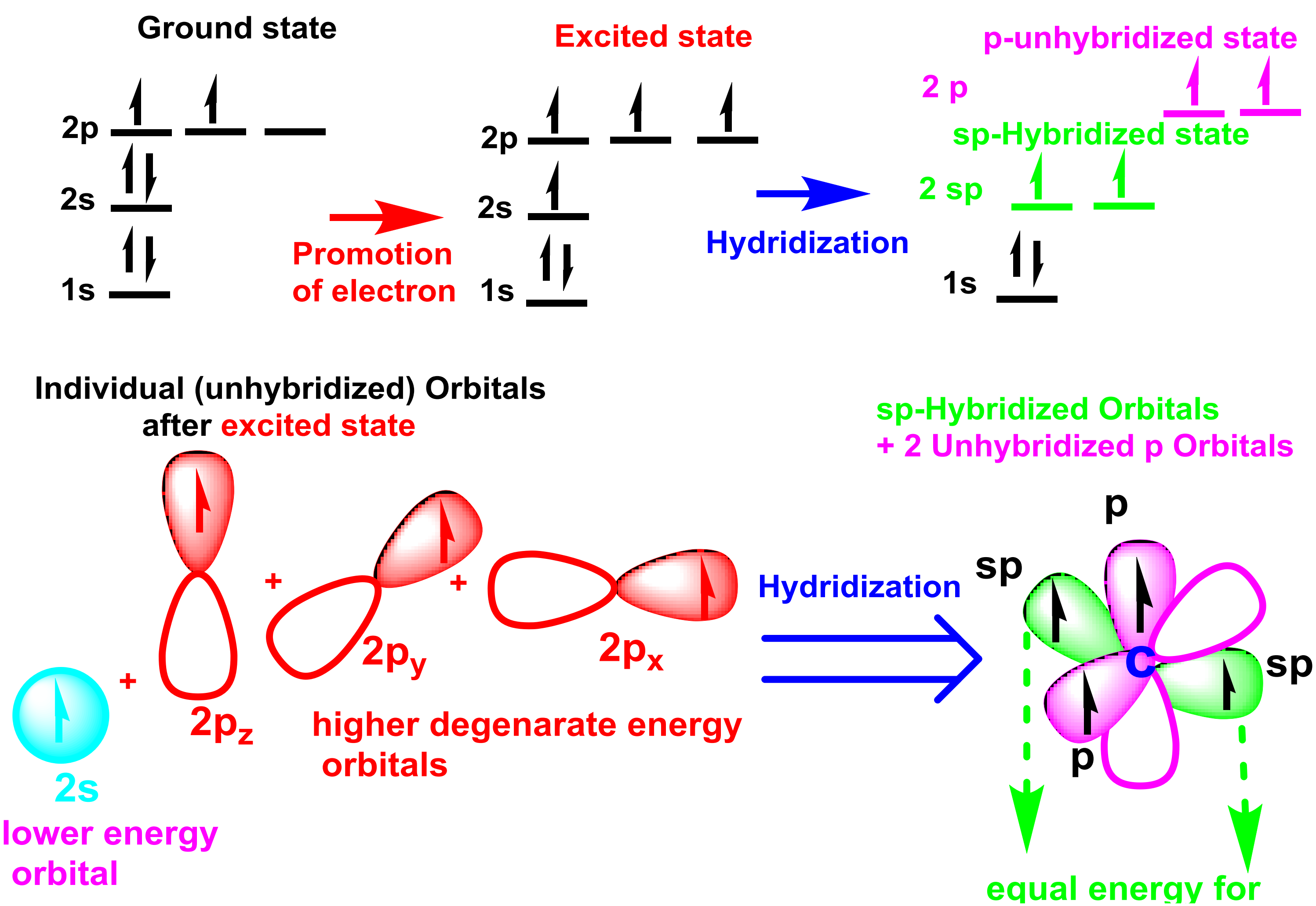
❖ **sp hybridization state of carbon**



10.21 Covalent bonding Associated with the Hybridization

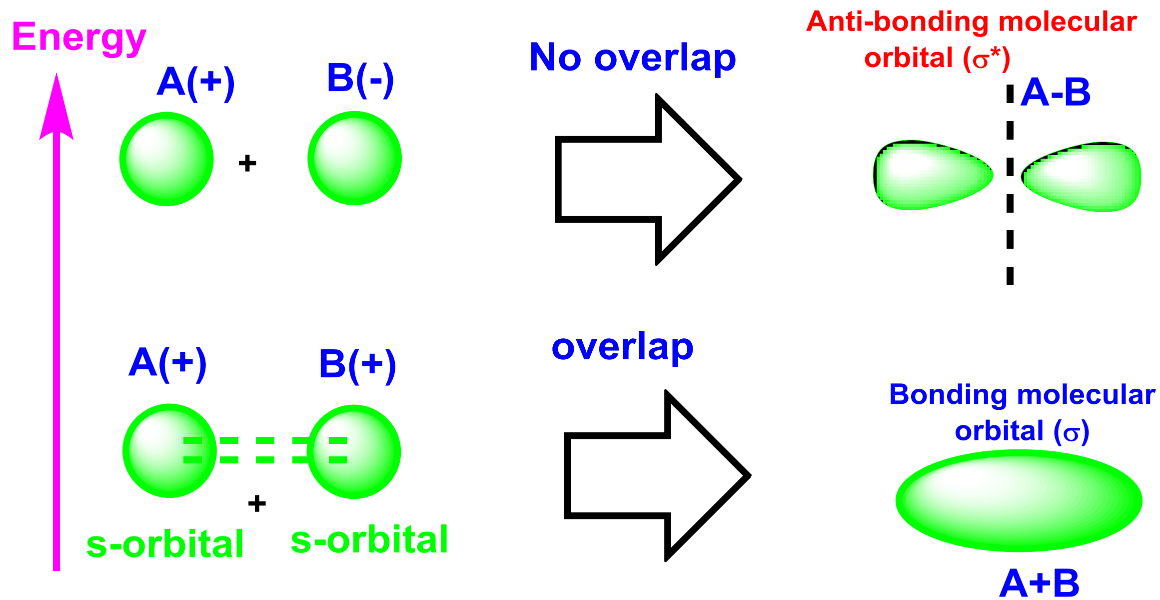
❖ **Organic compounds have mainly 2 types of covalent bonds**

✓ **1. Sigma (σ) bond and**

✓ **2. Pi (π) bond**

❖ **The Sigma (σ) Bond: Is formed in many ways:**

✓ **1. head-on overlap of two s orbitals**



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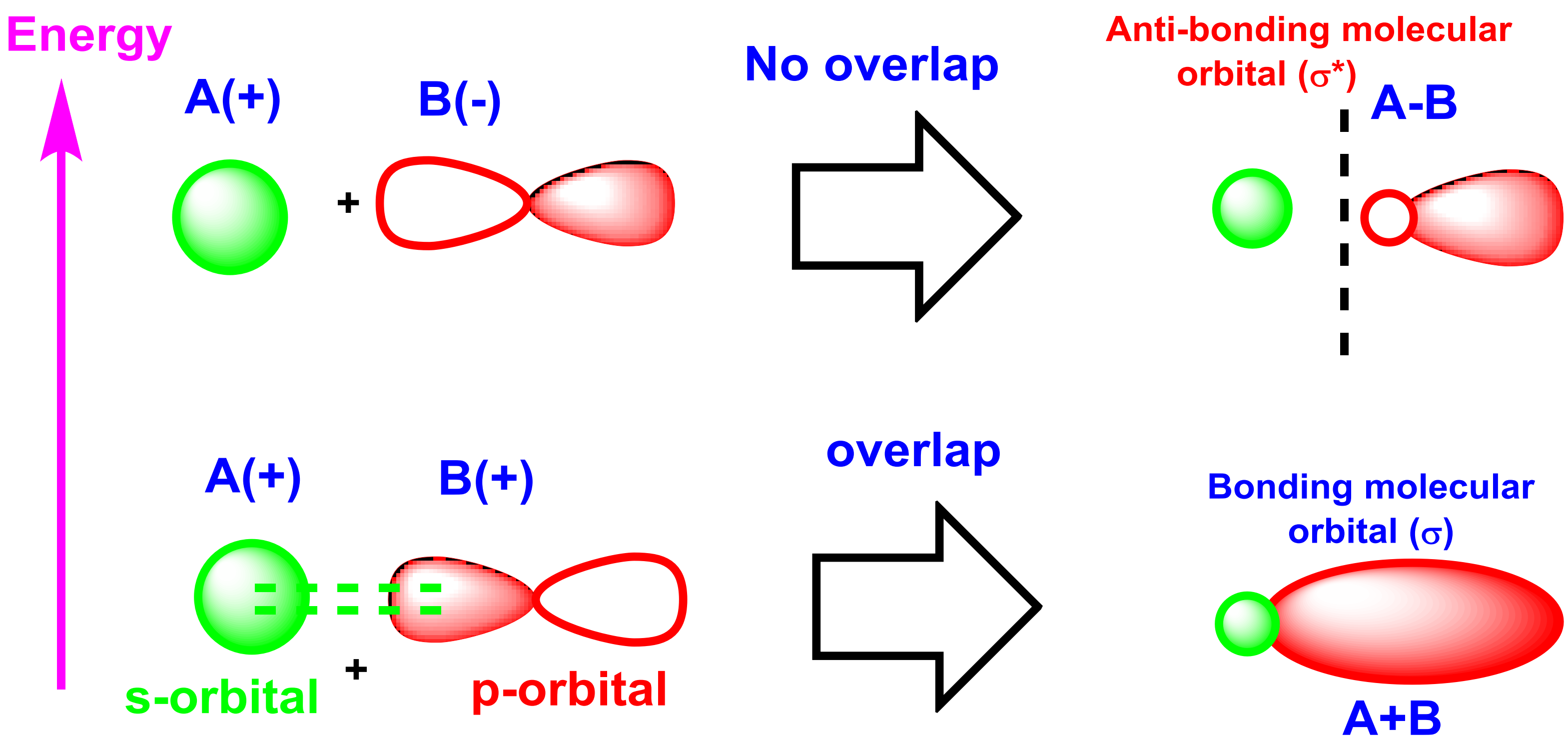
✓ 2. head-on overlap the s and a p orbitals



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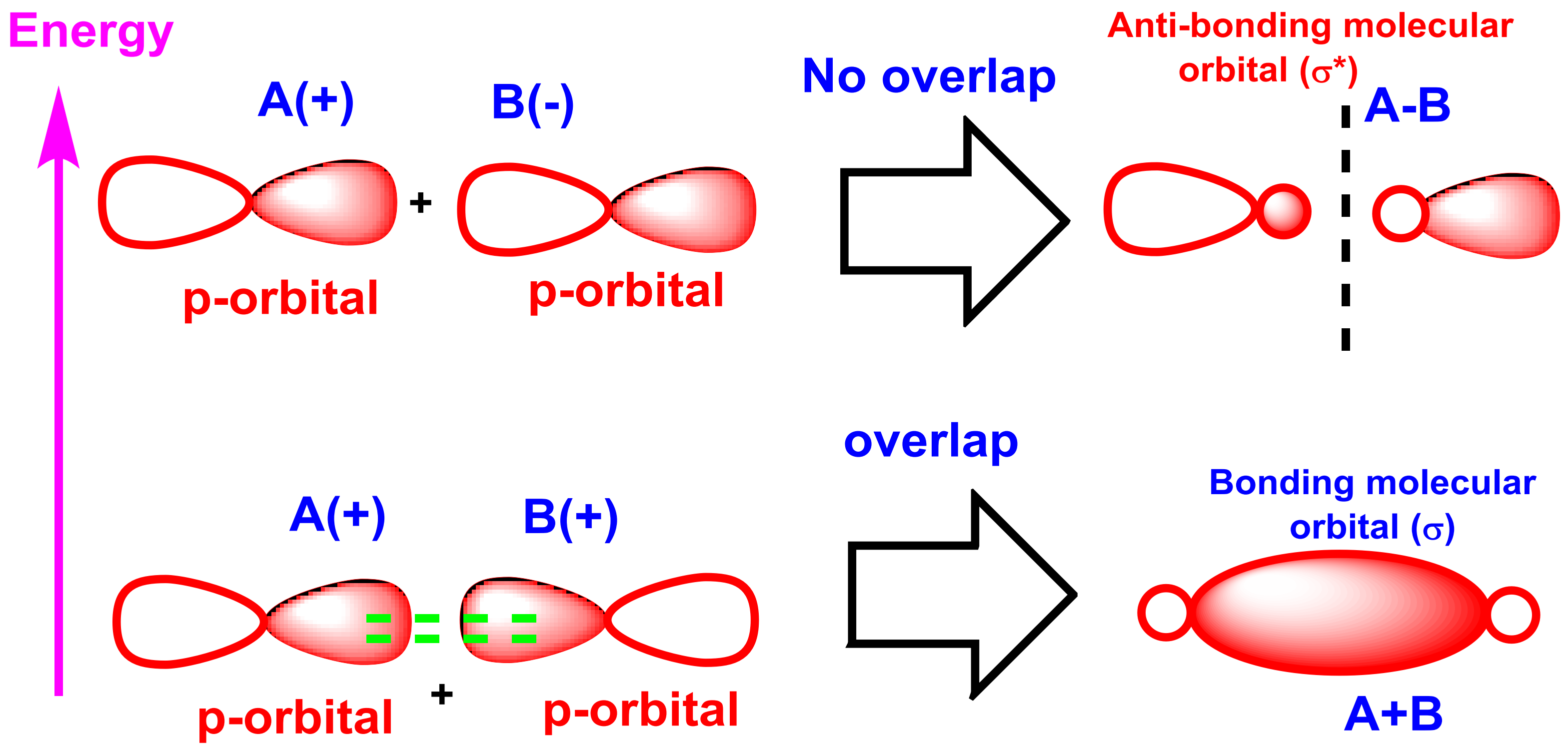
✓ 3. head-on overlap of two p orbitals



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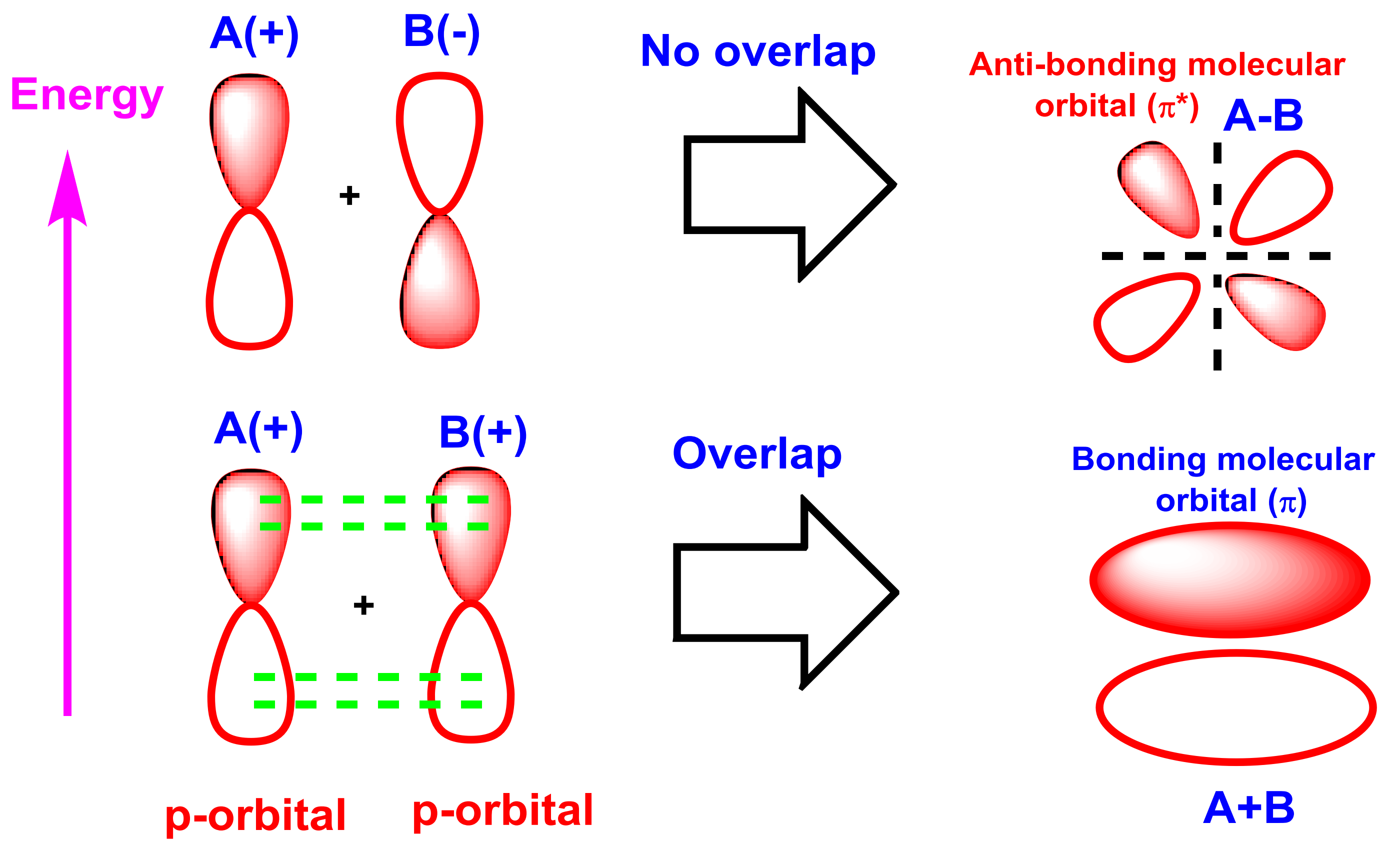
❖ Pi (π) bond is formed by side ways overlap of two p orbitals



✓ **Note:** If the p orbitals are perpendicular to each there is no overlap

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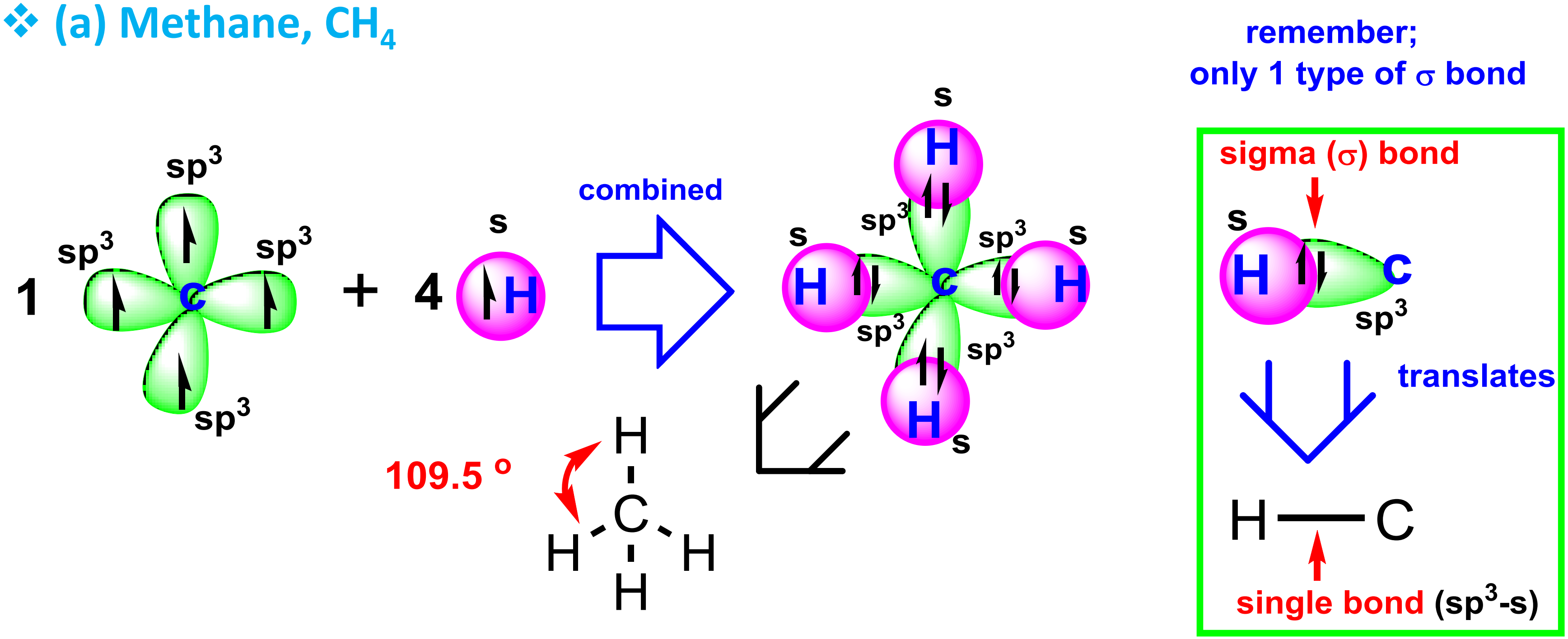
❖ **Covalent bond may be:**

- ✓ **(a) single bond (e.g A—B)**
- ✓ **(b) double bond (e.g A=B), and**
- ✓ **(c) triple bond (e.g A≡B)**

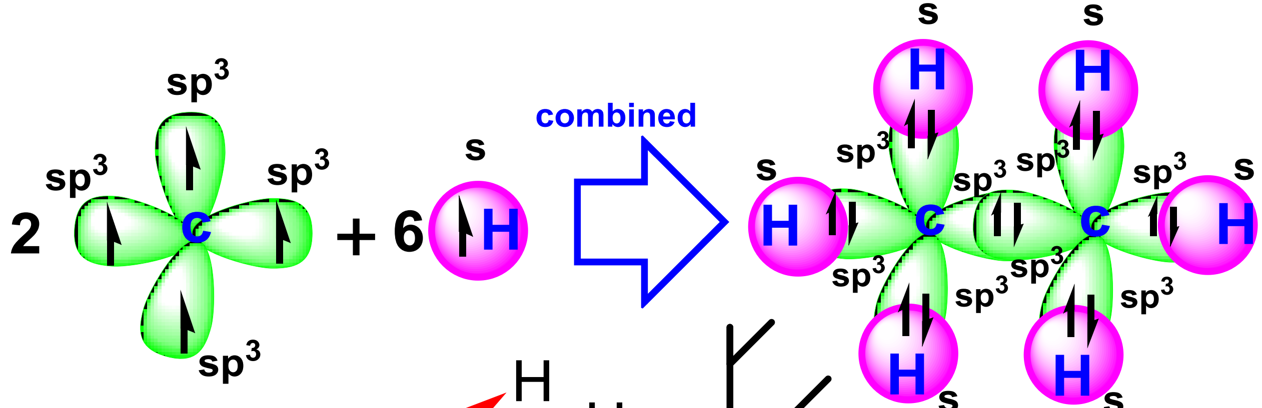
❖ **Notation: a line, — ; 1 line between 2 atoms shows 1 covalent bond, depicting 'sharing of 1 electron each' between 2 atoms**

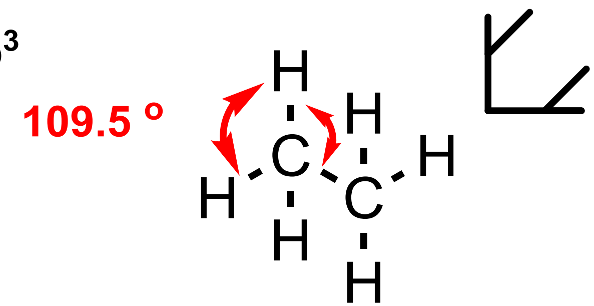
10.21 Molecular Orbital Pictures

- Having explored the hybridization states of carbon in organic compounds and the types of bonds (sigma or pi) associated, we can therefore construct the molecular orbital pictures for saturated compounds e.g methane, ethane etc..,and unsaturated compounds e.g ethene and ethyne
- Unsaturated compounds
- (a) Methane, CH_4



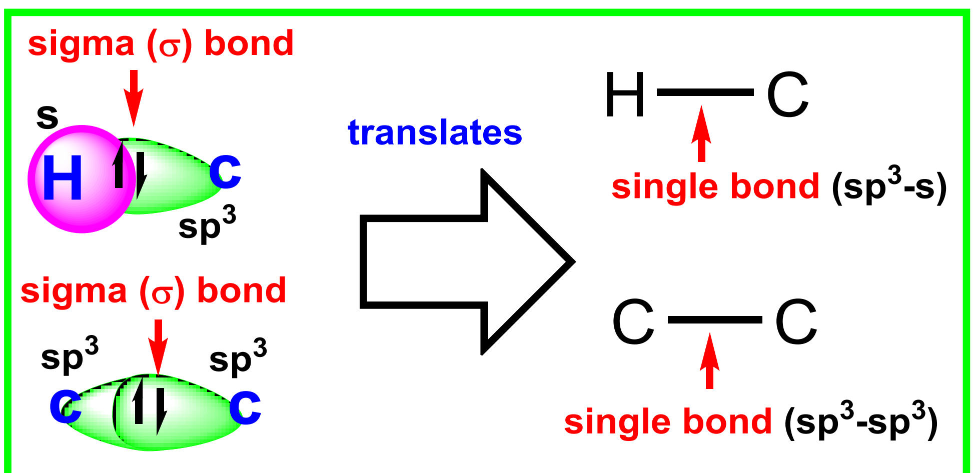
❖ (b) Ethane, C_2H_6





remember;

only 2 types of σ bond



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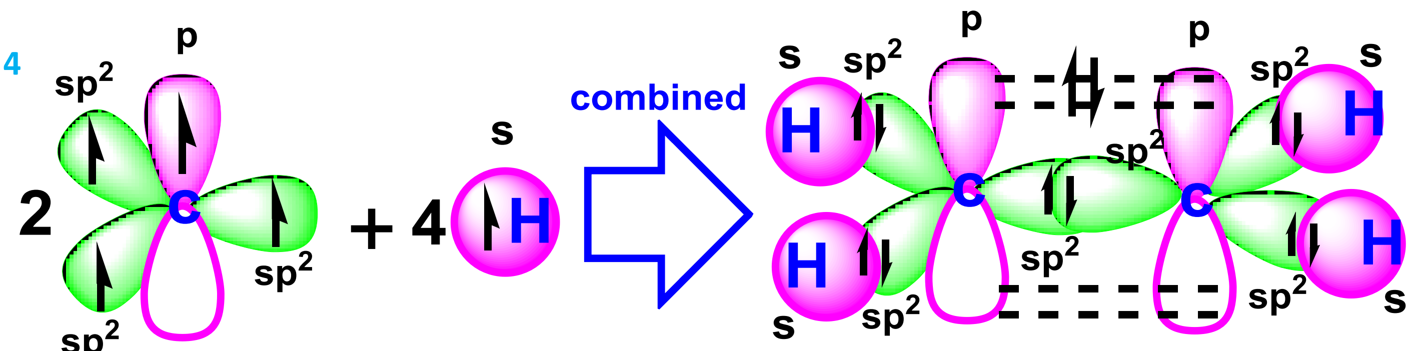
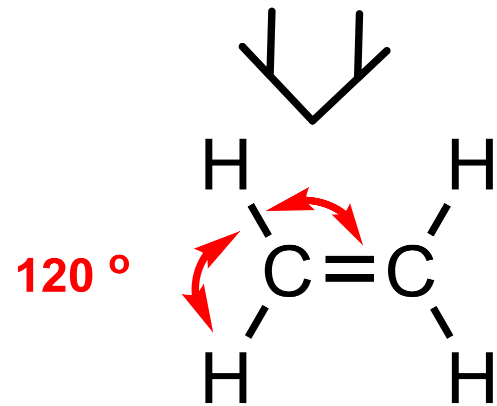
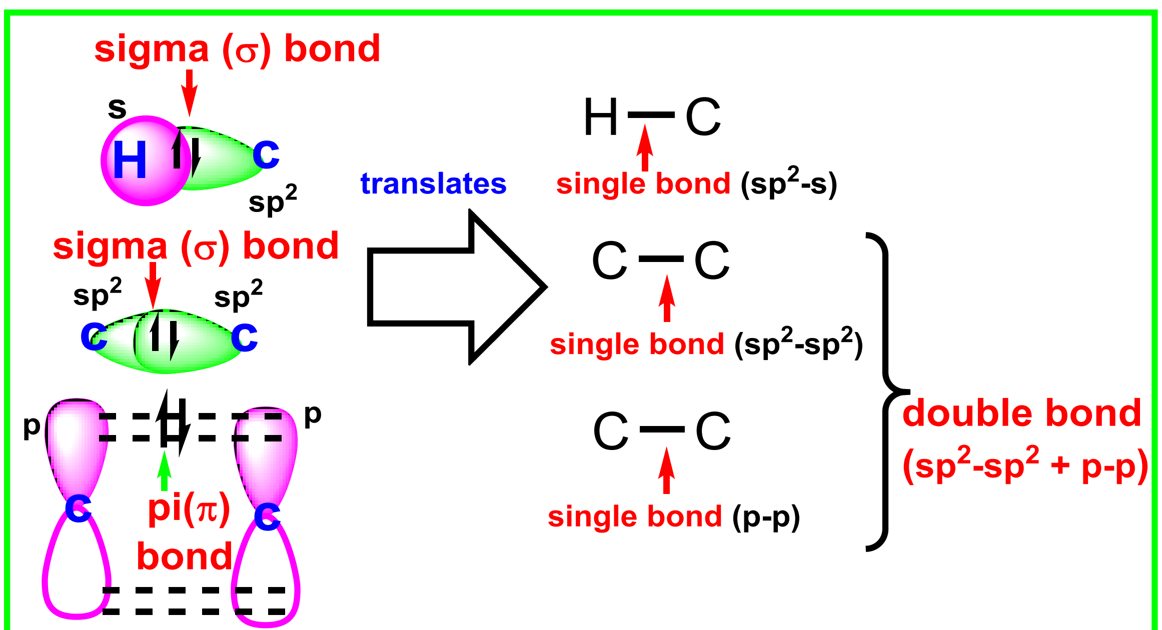
- **Ethene, C_2H_4**



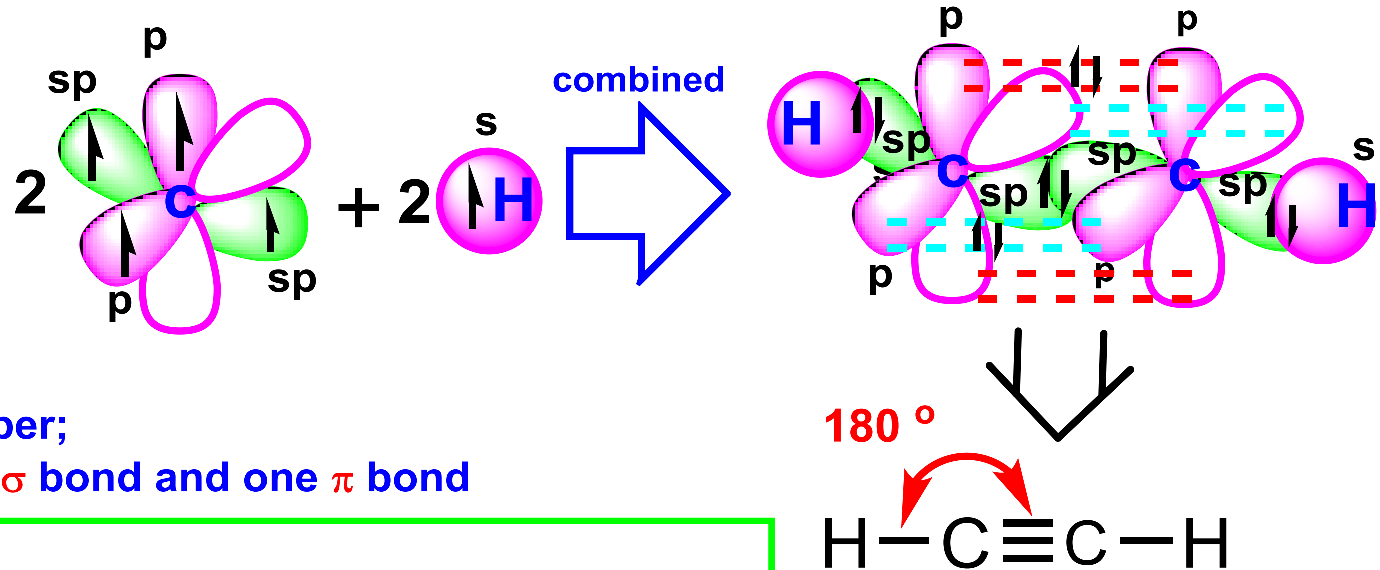


remember;
2 types of σ bonds and one π bond

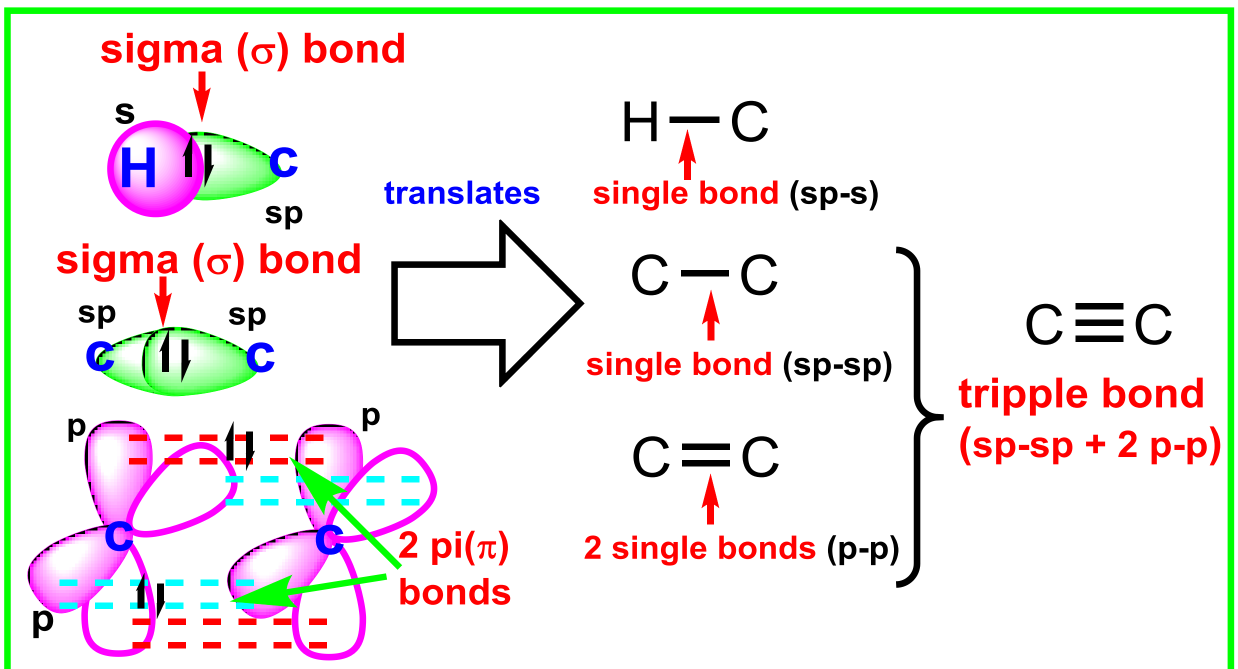


Contd……

- Ethyne, C_2H_2



remember;
2 types of σ bond and one π bond



Practice Questions

❖ **Consider the following compounds given below:**

(a) $H_2C{=}O$

formaldehyde

(b) $H_2C{=}C{=}O$

Ketene

(c) $H_2C{=}C{=}CH_2$

Allene

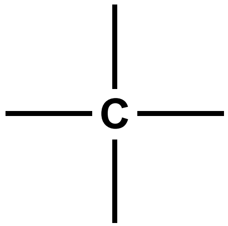
a) **Draw a fully labelled molecular orbital diagram for the three Organic Compounds given above.**

b) **State the hybridization states for all the bonds involved in the formation of the each of these compounds**

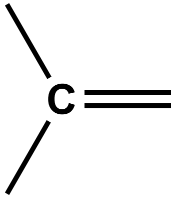
Summary

❖ Hybridization state of Carbon:

sp^3 = 4 single bonds (or connected to 4 atoms)



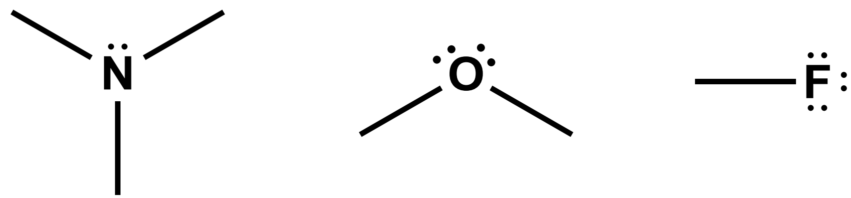
sp^2 = 2 single bonds and 1 double bond (or connected to 3 atoms)



sp = 1 single bond and 1 tripple bond or two double bonds (or connected to 2 atoms)

❖ Hybridization state of atoms other than carbon:

sp^3 = connected to 4 things (single bonds plus pair(s) of e^-)

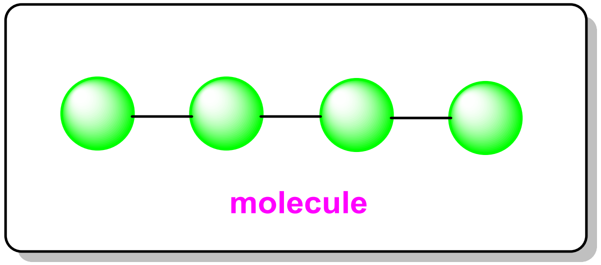


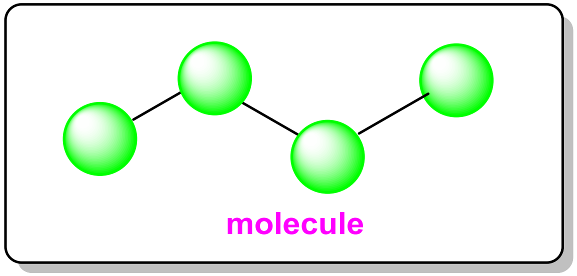
sp^2 = connected to 3 things (double bond plus pair(s) of e^-)

sp = connected to 2 things (tripple bond plus 1 pairof e^-)

10.3 Representation of Organic Compounds

❖ A structural formula or representation of a molecule, shows a detailed possible sequence of atomic connections in its molecule





❖ Structures of organic compounds are represented in several ways

✓ The Lewis or dot structure

✓ Complete or dash or Kekulé structure

✓ Condensed structure

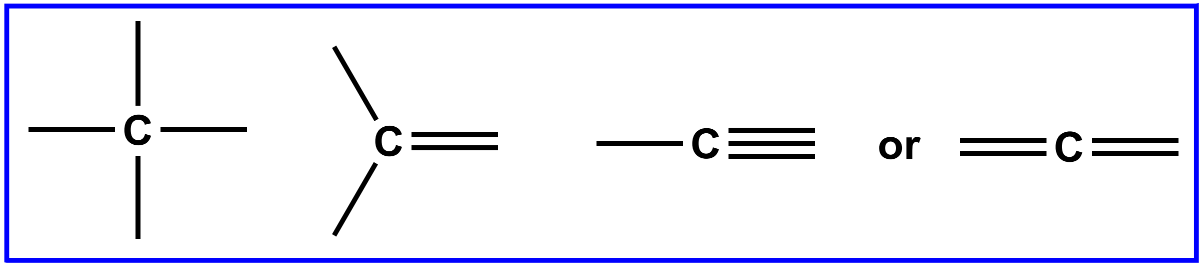
✓ Bond-line or skeletal structure

✓ 3 Dimensional (3-D) structure

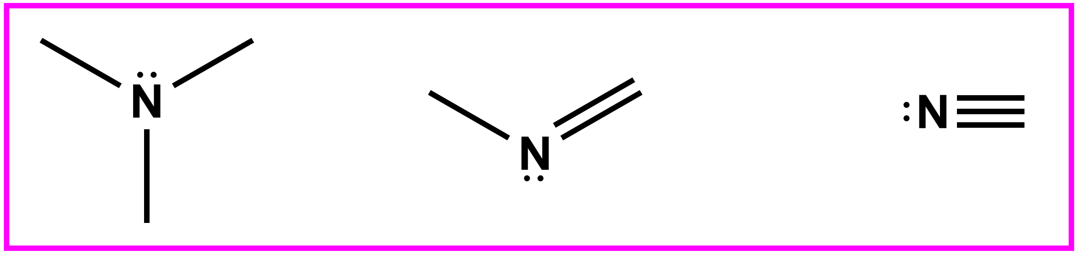
Contd……

- Before we go into the details of these structural representation of organic compounds, its important to know the number of bonds formed by each of the following atoms.

✓ Carbon (C) ; has 4 valence electrons and as result forms 4 bonds



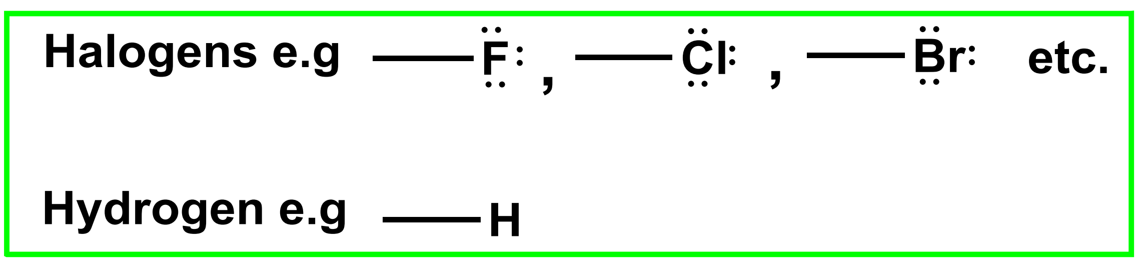
✓ Nitrogen (N); has 3 valence electrons and has a result forms 3 bonds



Contd……

- ✓ **Oxygen (O); has 2 valence electrons and has a result forms 2 bonds**

- ✓ **Hydrogen (H); and halogens (F, Cl, Br and I); have 1 valence electron and has a result forms 1 bond**

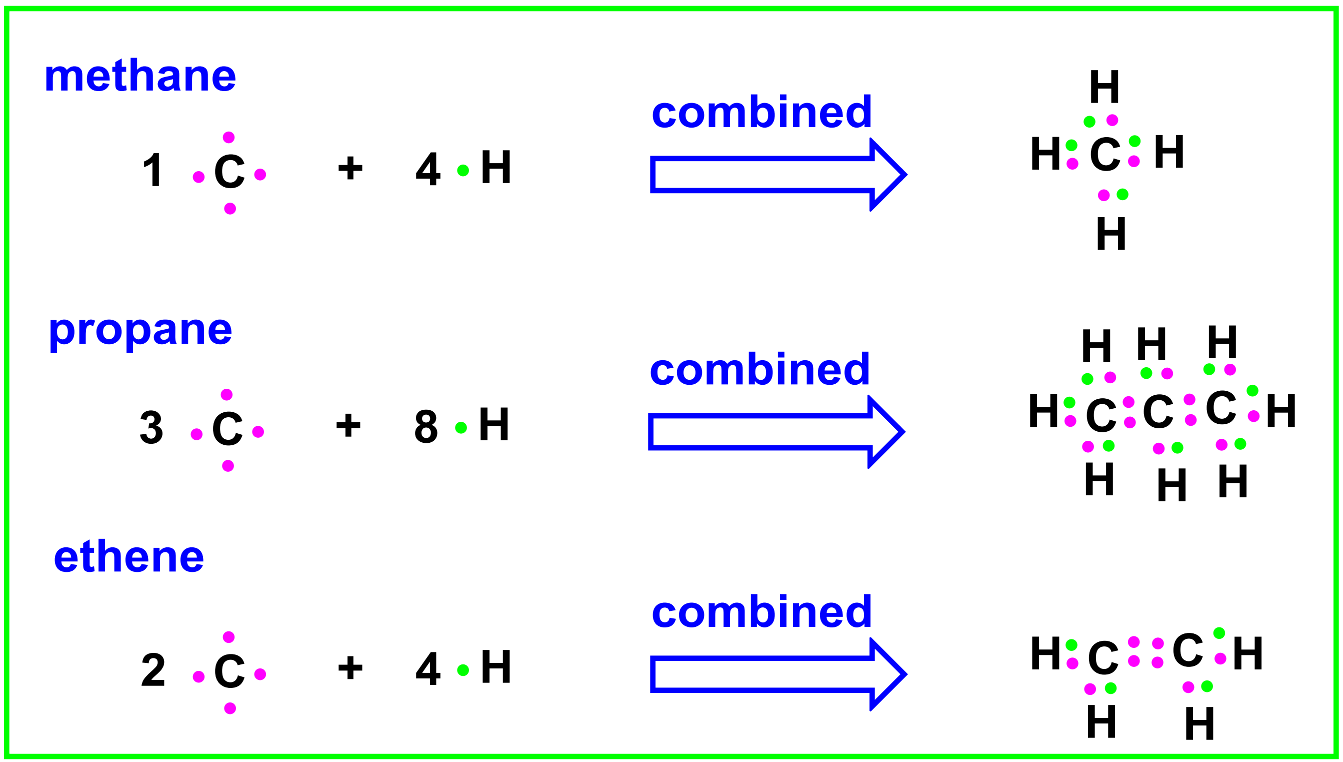


Contd……

(1) The Lewis or dot structural representation

- ✓ Valence electrons are represented as dots
- ✓ Lone pairs are shown

Examples: methane (CH_4), propane (C_3H_8) & ethene (C_2H_4)

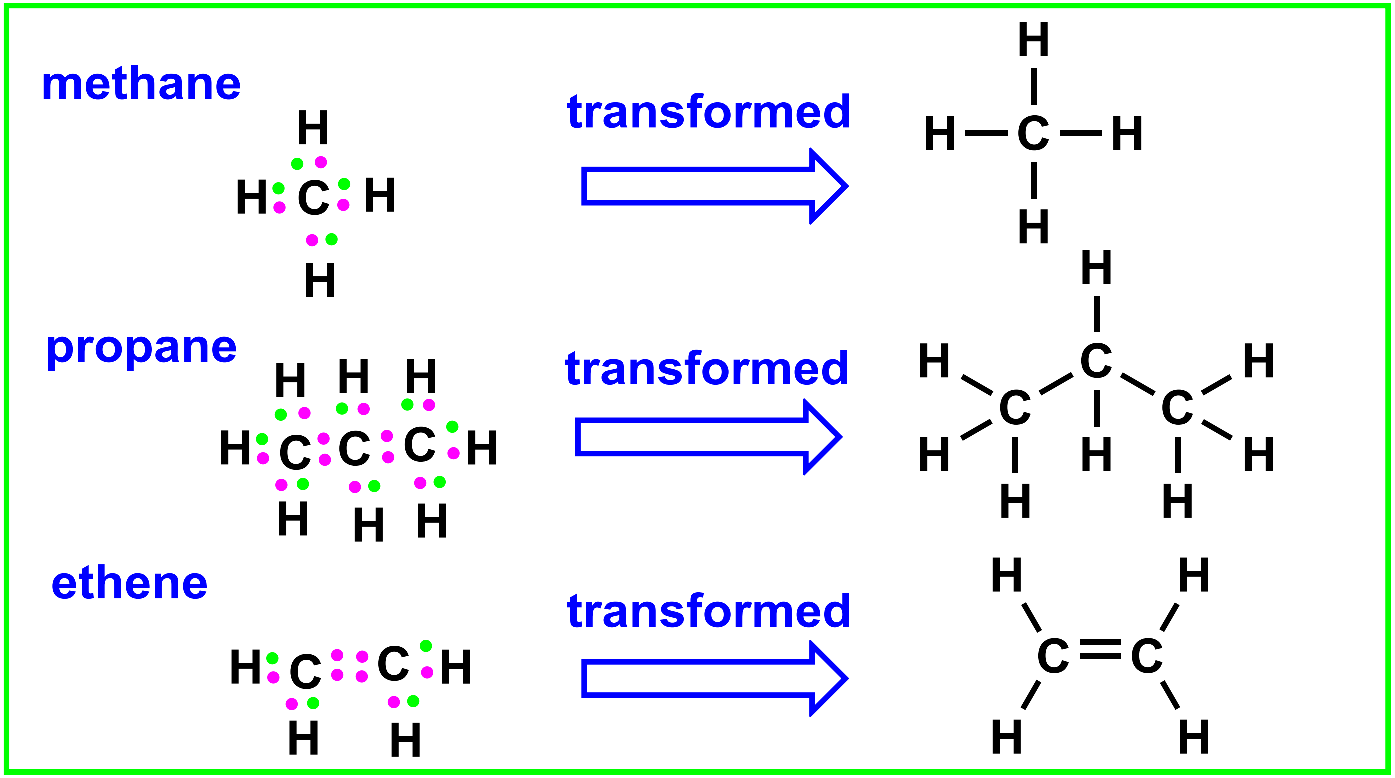


Contd……

(2) Complete or dash or Kekulé structural representation

- ✓ Bonding electron pairs are represented as a dash (line)
- ✓ Lone pairs are left out (unless they need to draw the attention to something)

Examples: methane (CH_4), propane (C_3H_8) & ethene (C_2H_4)

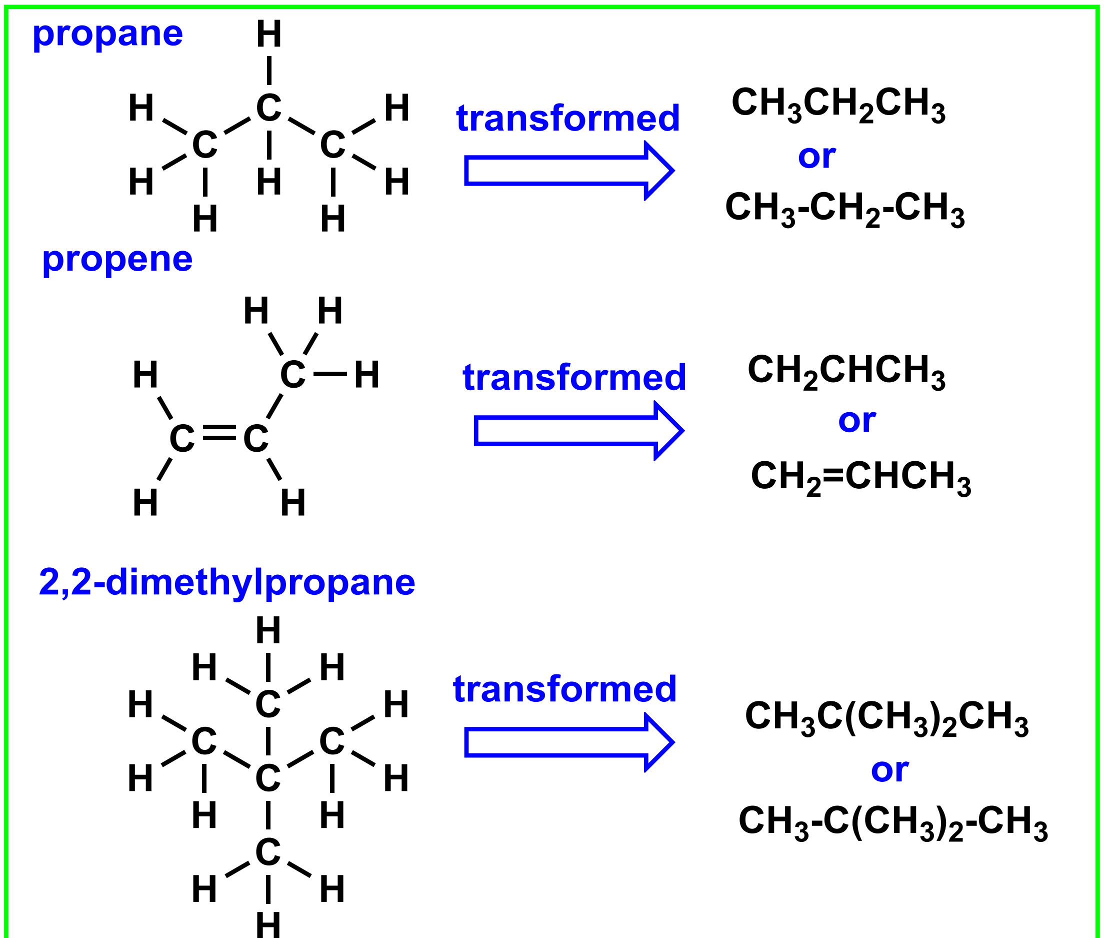


Contd……

(3) Condensed structural representation

- ✓ Indicates the number of identical groups attached to an atom followed by a subscript

Examples: propane (C_3H_8) ,propene (C_3H_6) & 2,2-dimethyl propane (C_5H_{12}),



Contd……

(4) Bond-line or skeletal structural representation

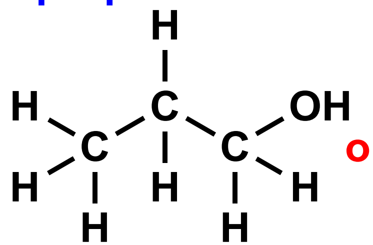
✓ In this type of representation for organic compounds;

- Carbon atom(s) and hydrogen atom(s) attached directly to carbon atoms are not shown
- Lines representing carbon to carbon bonds are drawn in a zigzag fashion
- Atoms other than carbon or hydrogen i.e nitrogen, oxygen, chlorine etc… are especially written or shown
- Hydrogen(s) attached to atoms other than carbon must be shown
- Terminals denotes methyl ($-CH_3$) groups and the line junctions denote carbon atoms bonded to appropriate number of hydrogen(s)

Contd……

Examples: propanol (C_3H_7OH),propene (C_3H_6) & 2,2-dimethylpropane (C_5H_{12})

1-propanol



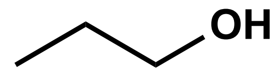
or

$CH_3CH_2CH_2OH$

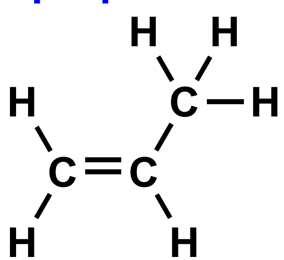
or

$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$

transformed



propene



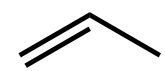
or

$CH_2CH_2CH_3$

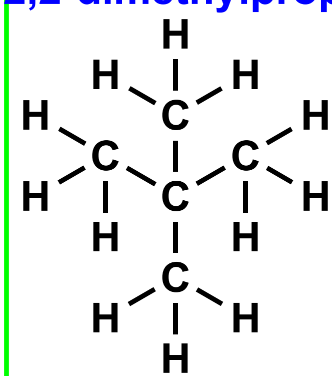
or

$CH_2{=}CHCH_3$

transformed



2,2-dimethylpropane



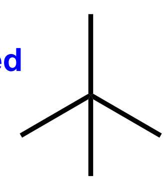
or

$CH_3C(CH_3)_2CH_3$

or

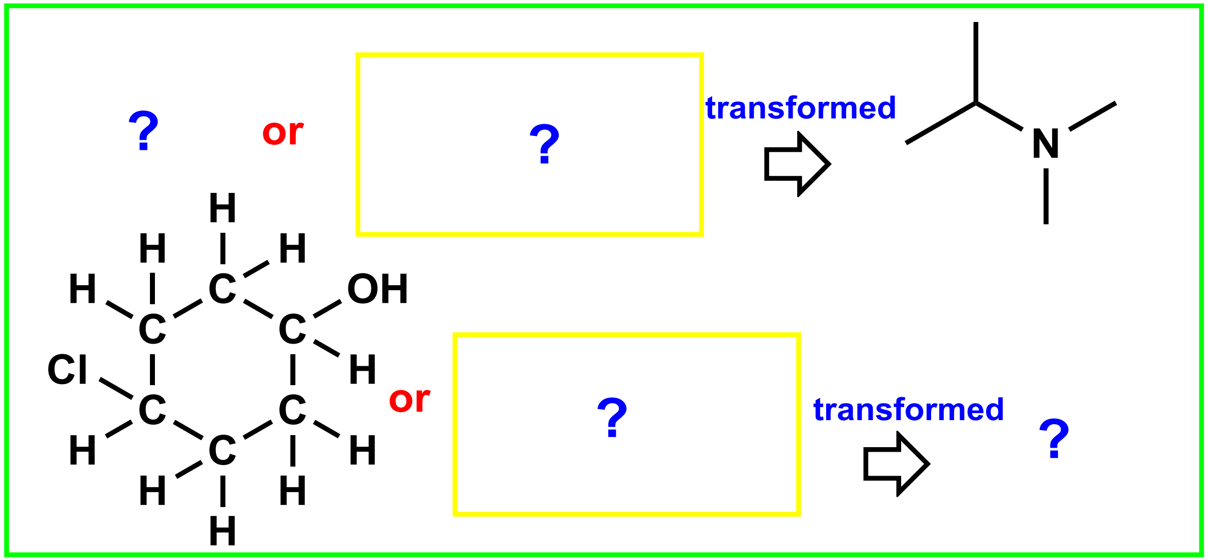
$CH_3\text{-}C(CH_3)_2\text{-}CH_3$

transformed

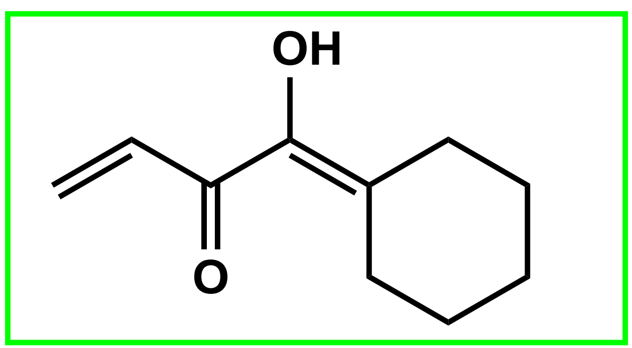


Practice Questions

1. Convert the following structures to their appropriate structural representation



2. How many hydrogens does the structure below have?

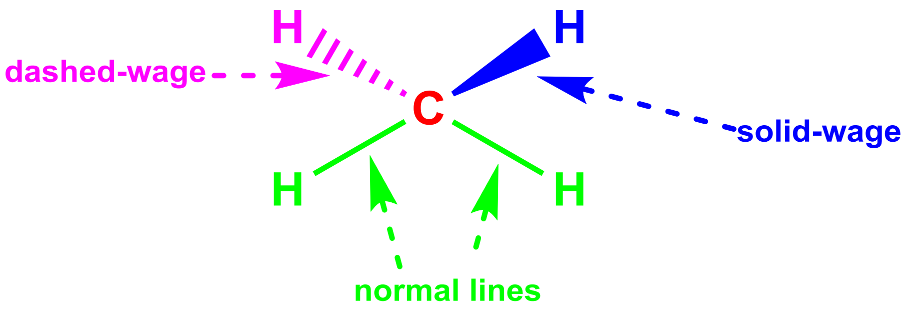


Contd……

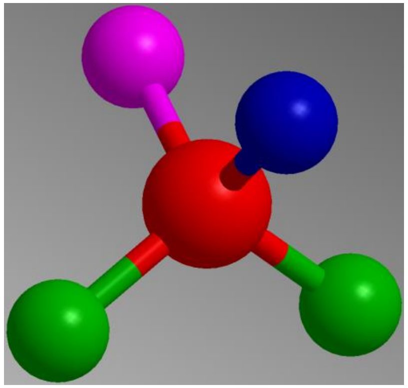
(5) (a) 3 Dimensional (3-D) structural representation

✓ Organic molecules are represented in three dimensional (3D) structures upon proper using of certain convention such as wedge formula.

Example; Consider methane CH_4



Plane of the paper



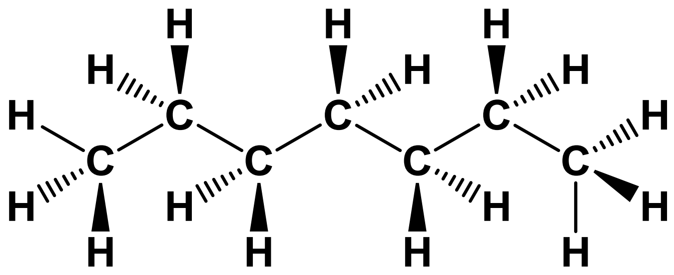
Note;

- **Solid-wage** indicates bonds projecting out of the plane of the paper and towards the observer
- **Dashed-wage** indicates bonds projecting out of the plane of the paper and away from the observer
- **Normal lines** indicates bonds lying in the plane of the paper

Contd……

(5) (b) Molecular Models

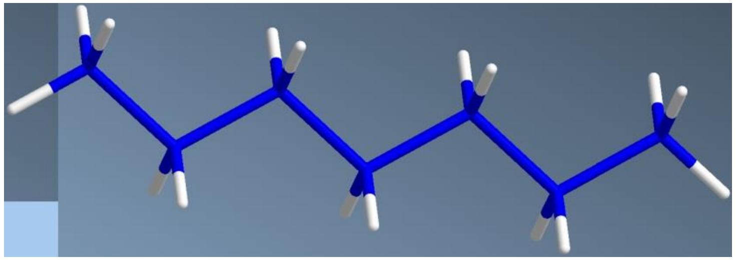
- ✓ These are physical devices made of wood, plastic or metal and are used for a better visualization and perception of three dimension of organic molecules
- ✓ They are three types of models commonly used; Framework model, Ball and Stick model and Space-filling model
- ✓ Lets use the structure of 3-D pentane as a typical example to explain these models



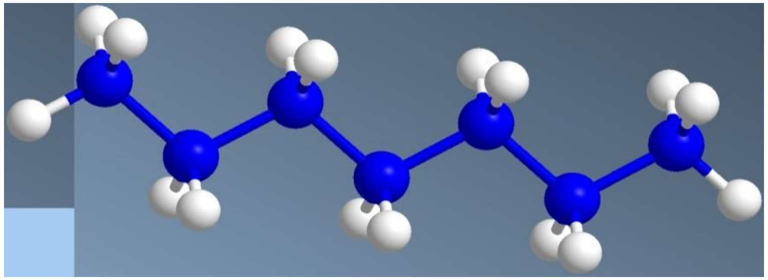
Pentane

Contd……

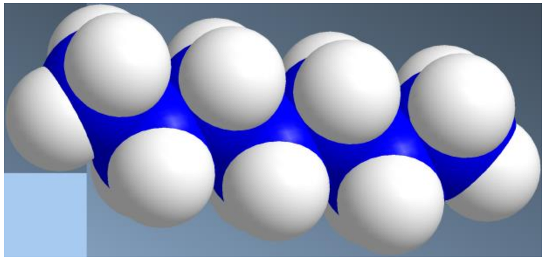
- **Framework model;** this model emphasizes the pattern of bonds of molecules and ignores the size of atoms or atoms of molecules



- **Ball and Stick model;** in this model ball represents atoms and sticks represents bonds



- **Space-filling model;** in this model bonds are not shown and it conveys the volume occupied by each atom



10.31 Formal Charge (FC)

- A **formal charge (FC)** is the **charge assigned** to an atom in a molecule, assuming that **all electrons** in all chemical bonds are equally shared between atoms, regardless of the **relative electronegativity.**

- **FC can be determined by using formula**

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

Or

$$FC = VE - NBE - \frac{1}{2}BE$$

10.31 Formal Charge (FC)

❖ **Example;**

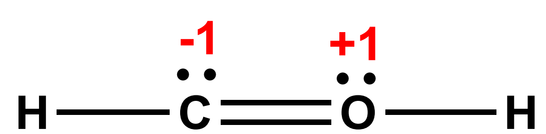
✓ **Calculate the formal charge of the oxygen (O) and carbon (C) atoms in the following molecule.**

FC for O atom $= VE - NBE - \frac{1}{2} BE$

$= 6 - 2 - \frac{1}{2}(6) = +1$

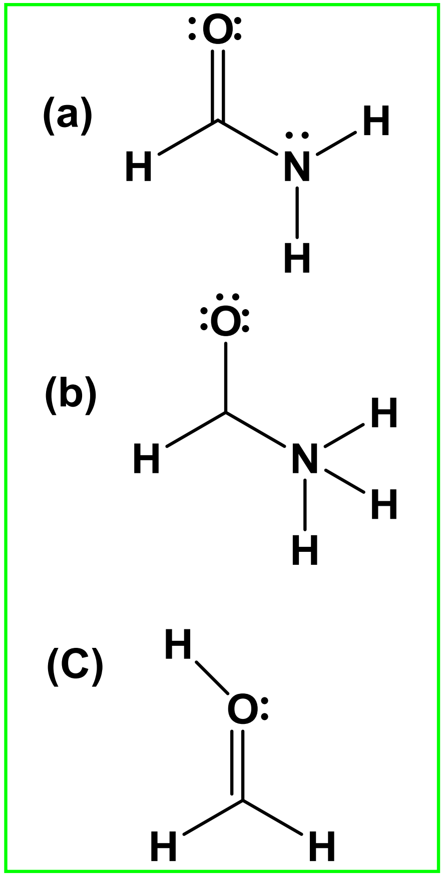
FC for C atom $= VE - NBE - \frac{1}{2} BE$

$= 4 - 2 - \frac{1}{2}(6) = -1$



Practice Questions

✓ Calculate the formal charge of the oxygen (O) , carbon (C) and nitrogen (N) atoms in each of the following molecules.



10.4 Functional Groups

- A **functional group** could be an **atom** or a **group of atoms** within a molecule that is capable for its characteristic **chemical reactions** and **physical properties**
- **Functional groups** contain at least one atom that is **not C** or **H**, usually **O** or **N** or **a halogen (F, Cl, Br and I).**
- **R** is used to represent a **carbon/hydrogen chain.**
- **R'** is used to represent a **carbon/hydrogen chain** that may be **same** or **different** on the same molecule
- The various types of **functional groups** are;

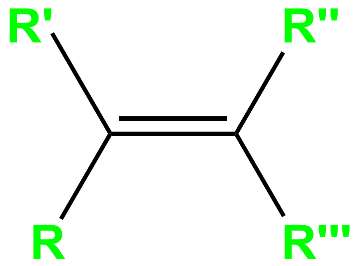
Contd……

1. Alkenes

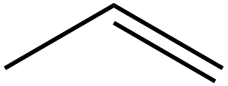
- ❖ **Alkenes are organic molecules made of carbon-carbon double bond (s)**

- ❖ **They have suffixes ending in *–ene***

General example



Specific example



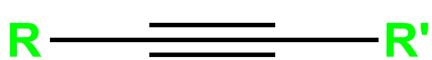
propene

Contd……

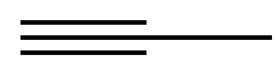
2. Alkyne

- Alkynes are organic molecules made of carbon-carbon triple bond (s)
- They have suffixes ending in *–yne*

General example



Specific example



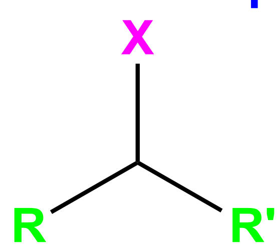
propyne

Contd……

3. Haloalkanes

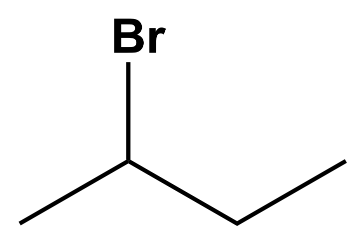
- These are hydrocarbons in which a halogen (F, Cl, Br and I) is attached to a carbon
- They are named as substituents e.g (fluoro for F , chloro for Cl, bromo for Br, and iodo for I atoms) followed by the name of the alkane

General example



where x = halogen (F, Cl, Br & I)

Specific example



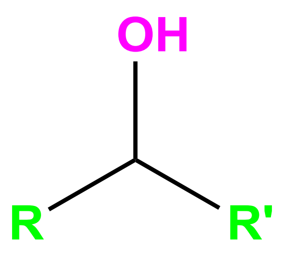
2-bromobutane

Contd……

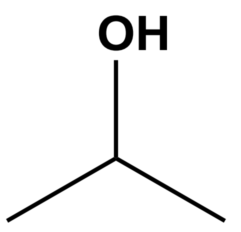
4. Alcohols

- These are hydrocarbons in which a hydroxyl group (-OH) is attached to a carbon
- Alcohols all have the ending "-ol"
- A number indicates to which carbon the functional group is attached.

General example



Specific example



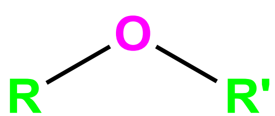
2-propanol

Contd……

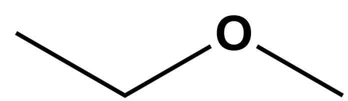
5. Ethers

- These are molecules where the hydrogen in an alcohol is instead replaced by a hydrocarbon group
- Ethers are named by naming the hydrocarbon on either side of the oxygen
- The last word in the name is "Ether"

General example



Specific example



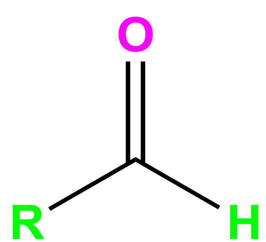
ethyl methyl ether

Contd……

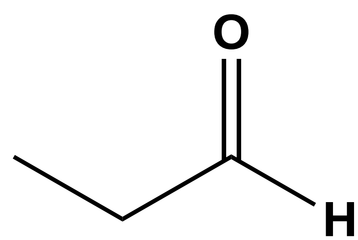
6. Aldehydes

- These are hydrocarbons in which the C and the O atoms are connected by a double-bond franked by a hydrocarbon group and hydrogen atom at the end of the chain
- The C=O group is called a "carbonyl" group
- Aldehydes have the ending "-al"

General example



Specific example



1-propanal

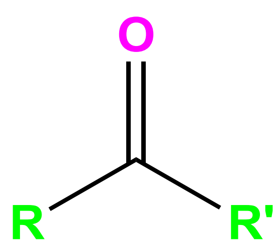
Contd……

7. Ketones

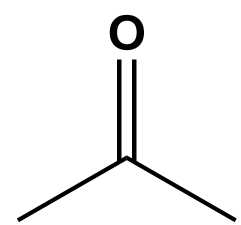
- These are hydrocarbons in which a "carbonyl" group is franked by two hydrocarbon groups

- Ketones have the ending "-one"

General example



Specific example



2-propanone

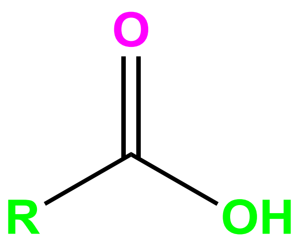
Contd……

8. Carboxylic acids

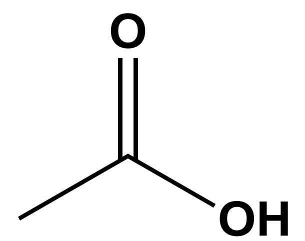
- These are hydrocarbon derivatives in which the a **"carbonyl"** group is franked by **a hydrocarbon group** or **hydrogen atom** and **a hydroxyl group (-OH)** at the end of the chain

- **Carboxylic acids** have the ending "-oic acid"

General example



Specific example



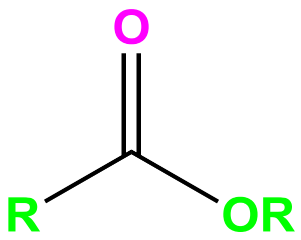
ethanoic acid

Contd……

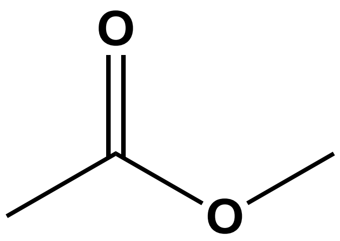
9. Esters

- These are carboxylic acid derivatives in which a "carbonyl" group is franked by a hydrocarbon group and an alkoxyl group (-OR) at the end of the chain
- Esters are tricky to name; the name of the group after O atom is the first followed by the word that includes the carboxyl group and ending in " oate "

General example



Specific example



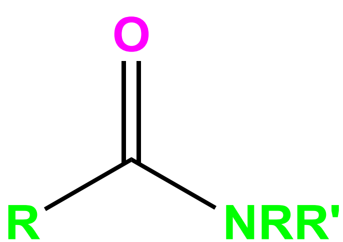
methyl ethanoate

Contd……

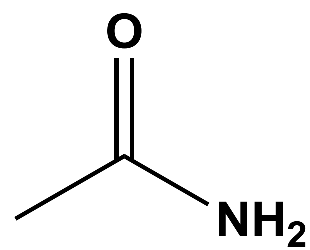
10. Amides

- These are carboxylic acid derivatives in which the a “carbonyl” group is franked by a hydrocarbon group and amino (-NH_2) or amine group at the end of the chain
- Amides have the ending “-amide”

General example



Specific example



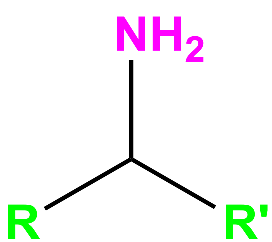
ethanamide

Contd……

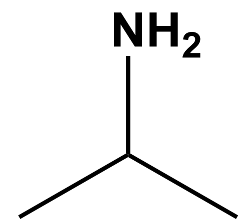
11. Amines

- These are hydrocarbons in which an amino group ($-NH_2$) is attached to a carbon
- Amines have the ending "-amine"
- A number indicates to which carbon the functional group is attached.

General example



Specific example



2-propanamine

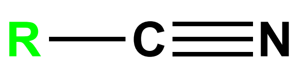
Contd……

12. Nitriles

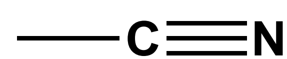
❖ These are hydrocarbons in which the carbon triply bonded to a nitrogen is attached to carbon

❖ Nitriles have the ending "-nitrile"

General example



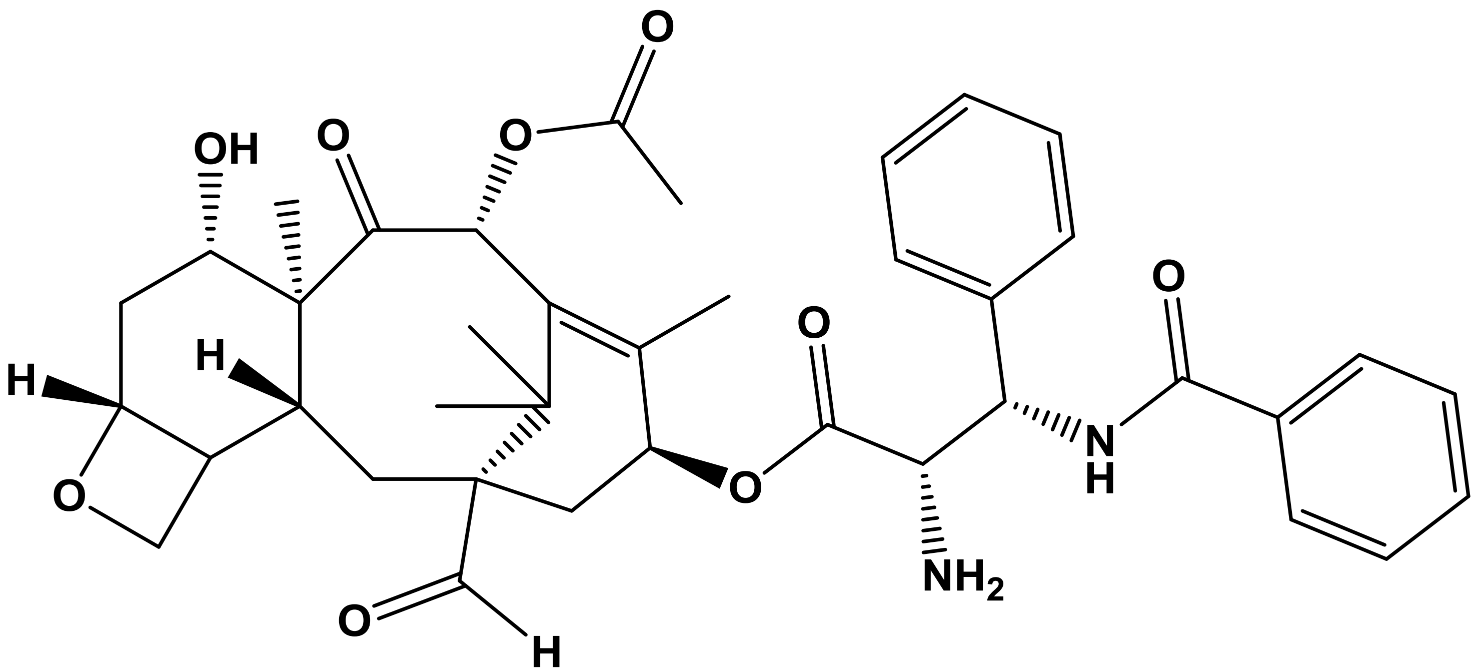
Specific example



ethanenitrile

Practice Question

1. **Identify, circle and name all the functional groups present in the molecule given below:**



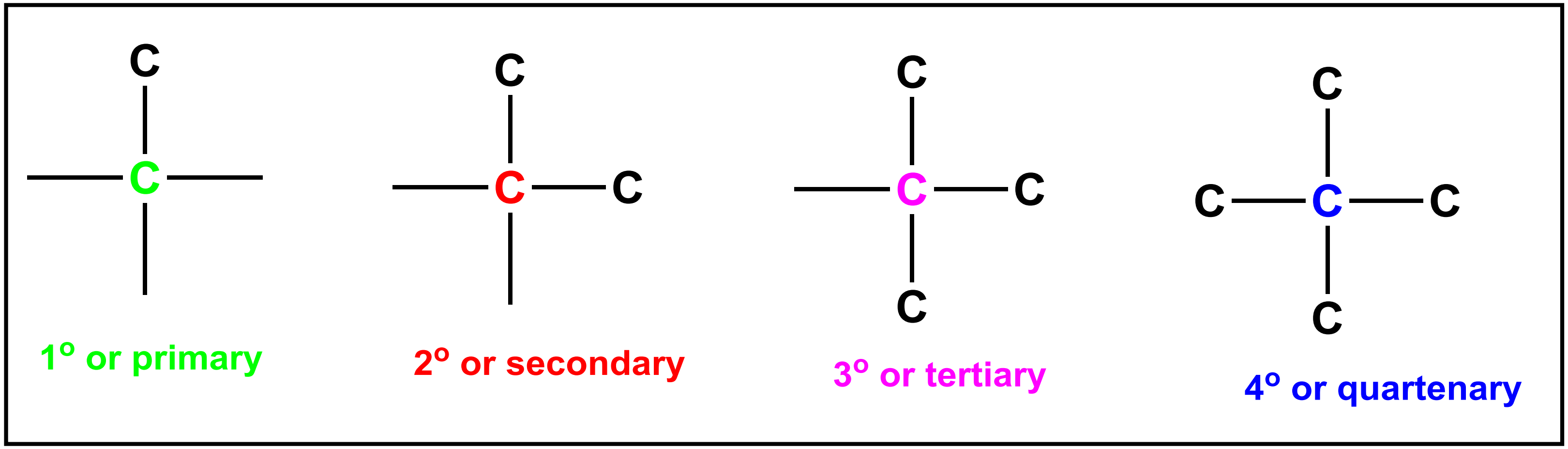
10.5 Classification of Carbon and Hydrogen atoms

❖ Carbons atoms

✓ Carbons have a special terminology to describe how many other carbons they are attached to;

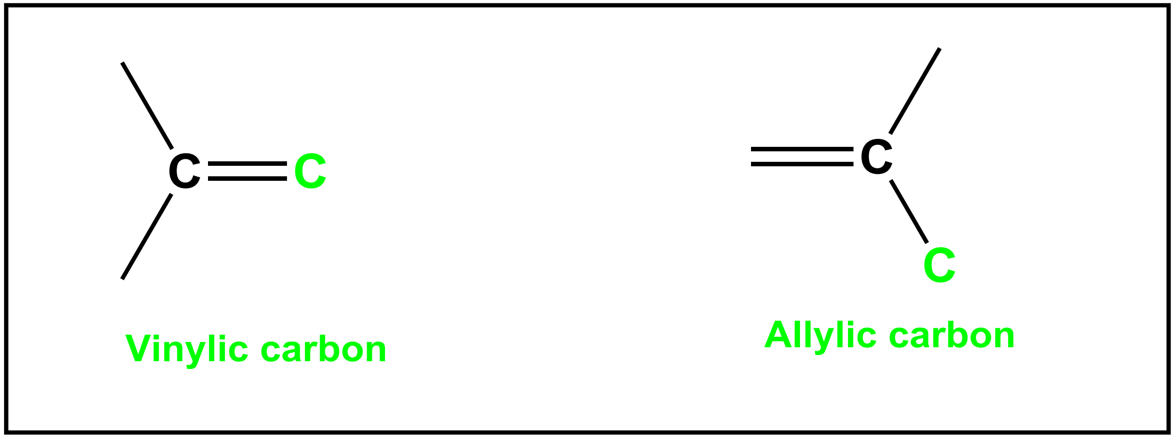
✓ Hence;

- Primary carbons (1°) are attached to one other C atom, secondary carbons (2°) are attached to two other C atoms, tertiary carbons (3°) are attached to three other C atoms, and quaternary carbons (4°) are attached to four other carbon atoms with an sp^3 hybridization state.



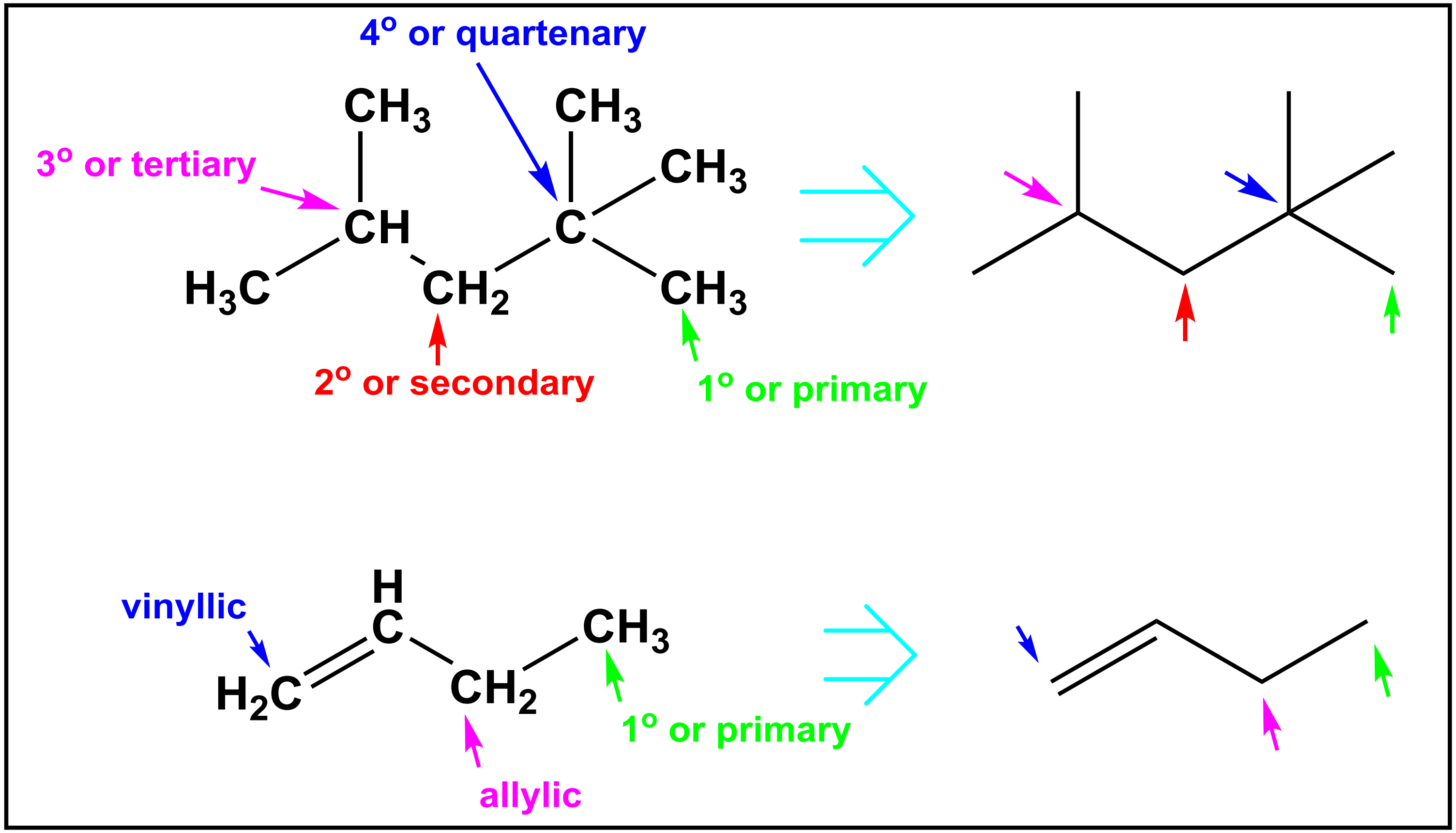
Contd……

- Besides, carbons can be described as either vinylic or allylic
- ✓ For instance;
- ○ Vinylic carbons are a class of carbons which has a double bond (with sp^2 hybridization state); while allylic carbons are another class of carbons which are directly attached to a doubly bonded C atom (with sp^2 hybridization state).



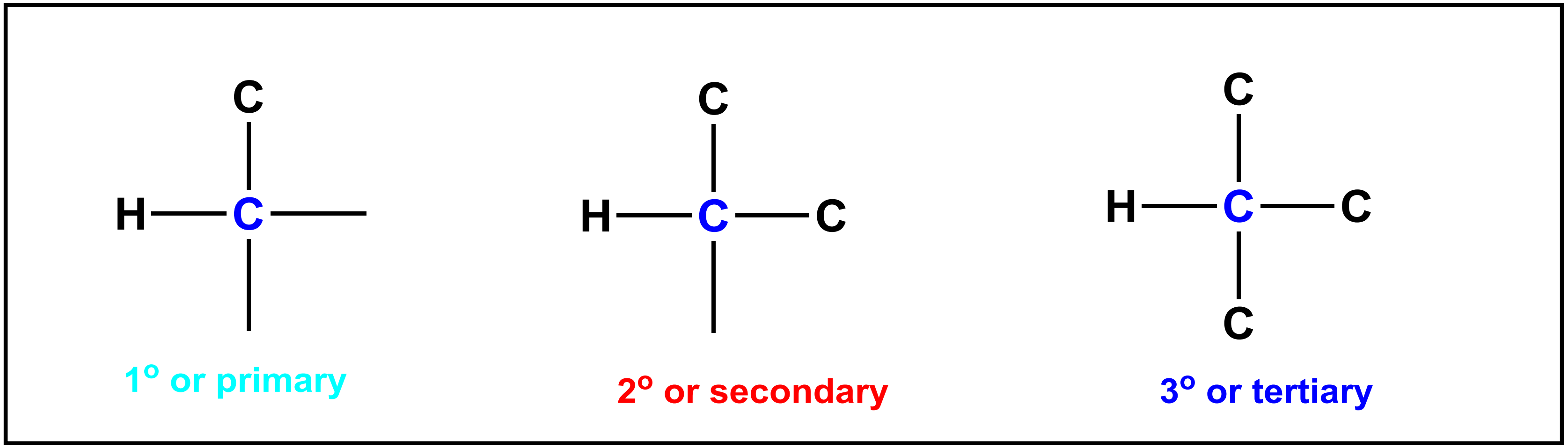
Contd……

❖ Consider the following molecules as an example;



Contd……

- Hydrogen atoms
- ✓ Hydrogen atoms are also classified in this manner.
- For instance; Primary hydrogens (1°) are attached to carbons bonded to one other C atom, secondary hydrogens (2°) are attached to carbons bonded to two other C atoms and tertiary hydrogens (3°) are attached to carbons bonded to three other C atoms sp^3 hybridization state

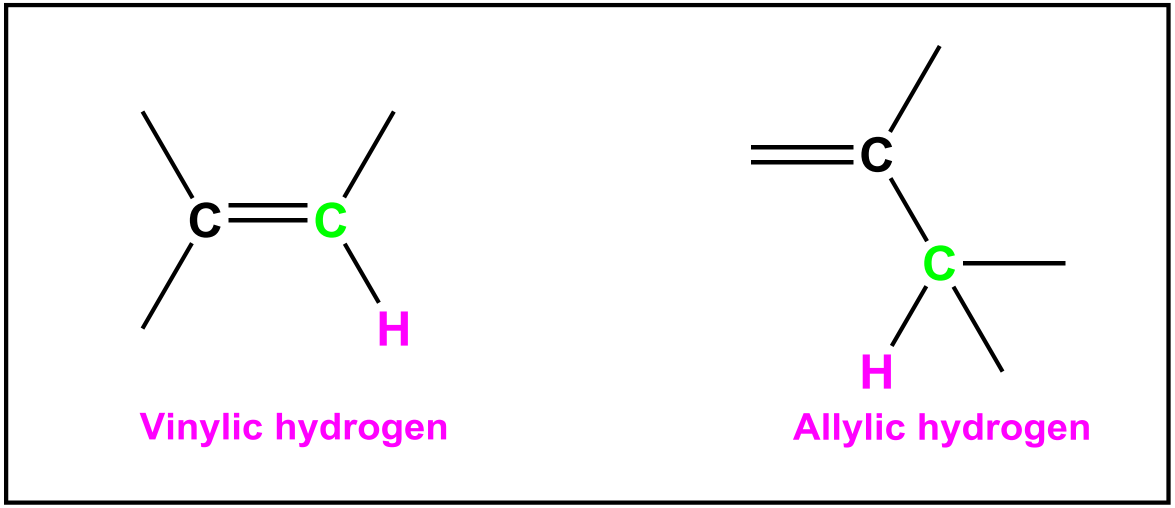


Contd……

- In a similar fashion, hydrogens can be described as either vinylic or allylic

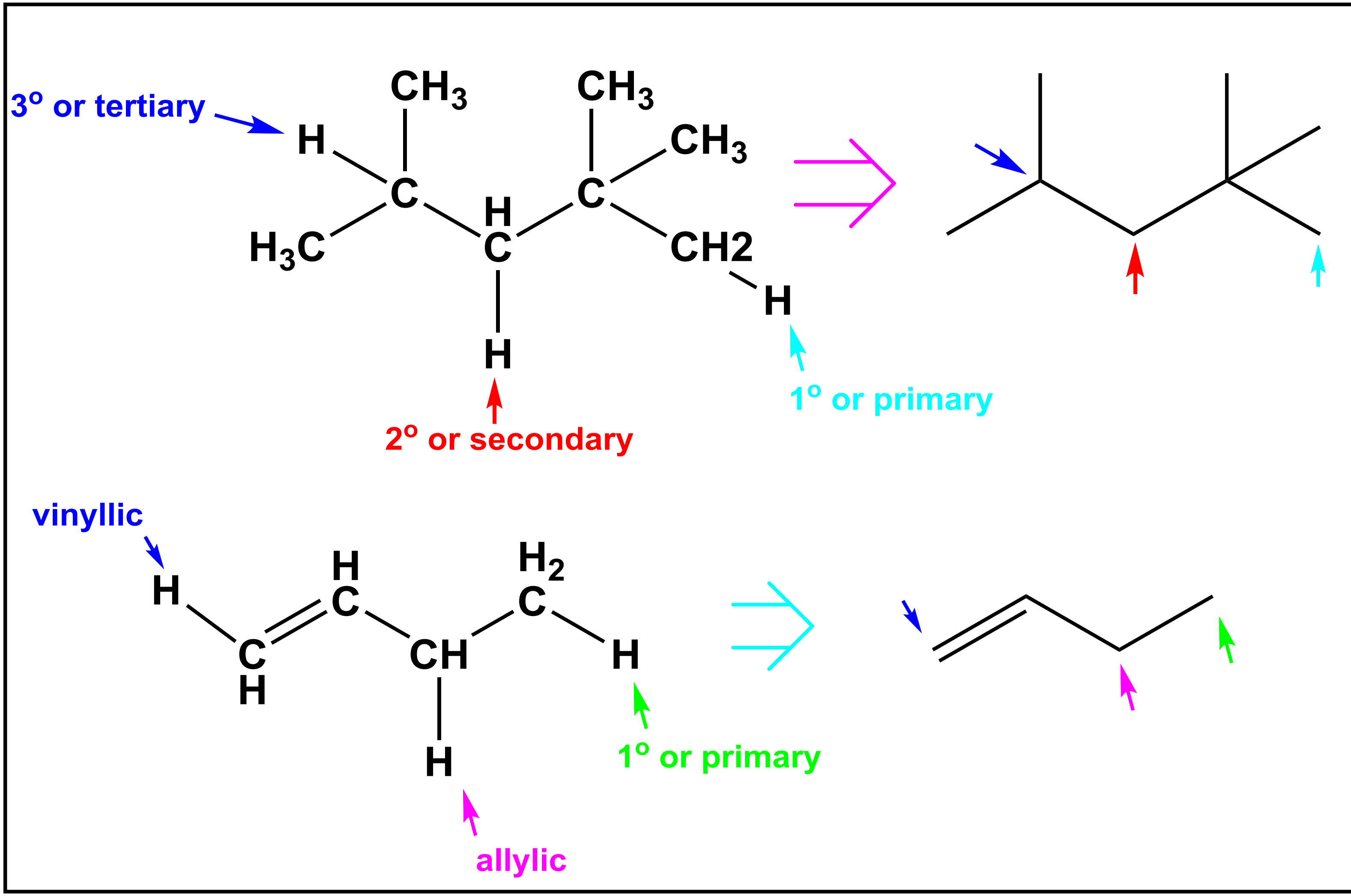
✓ For instance;

○ Vinylic hydrogens are a class of hydrogens which are directly attached to the vinyl carbon; while allylic hydrogens are another class of carbons which are directly attached to an allylic carbon



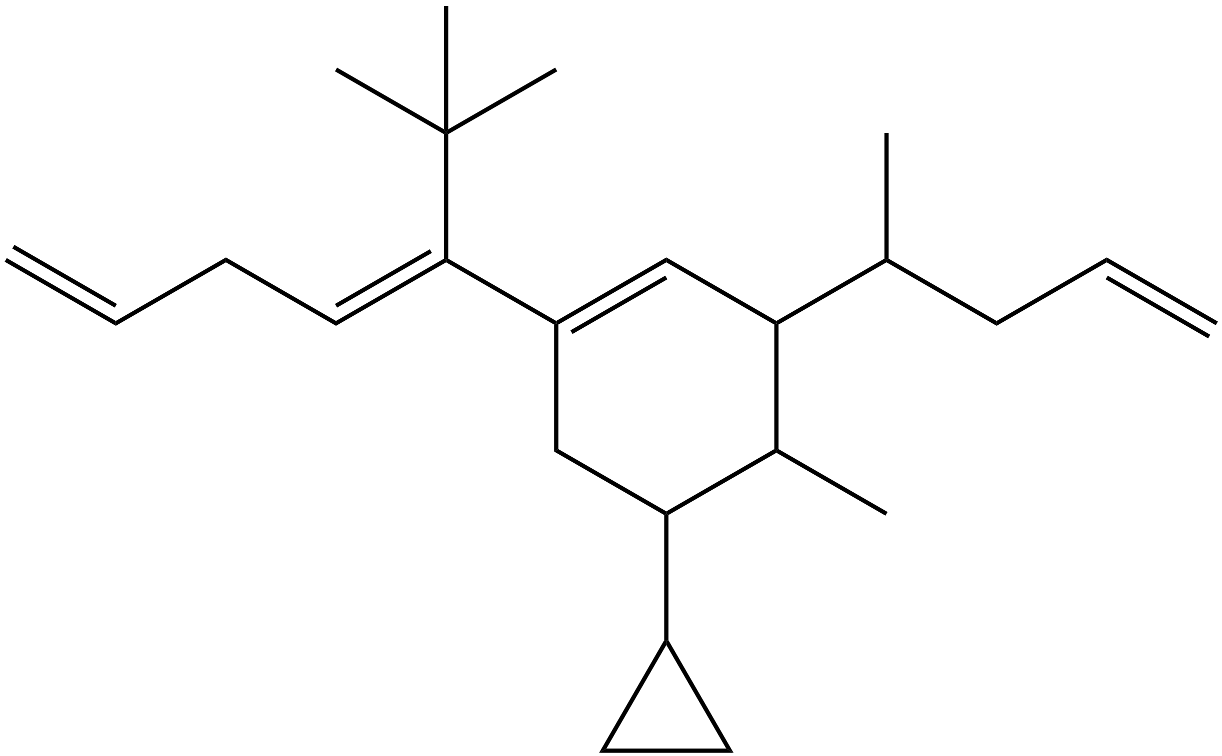
Contd……

❖ Consider the following molecule as an example;



Practice Question(s)

1. **Identify, circle and state the types of carbons and hydrogens that are present in the molecule given below:**
2. **What is the total number of carbons and hydrogens for each type identified in question 1?**



10.6 Index hydrogen deficiency (IHD)

- Index Hydrogen Deficiency (IHD) is used to determine from a molecular formula ($C_nH_aX_bO_cN_d$) the number of single or multiple bonds or rings in an organic molecule.
- It can be calculated using the formula;

$$IHD = \frac{2C+2+N-H-X}{2}$$

where: C = # carbon atoms

N = # nitrogen atoms

H = # hydrogen atoms

X = # halogen atoms

- Note: Oxygen (O) or sulphur (S) atoms are not included in the calculation

Contd……

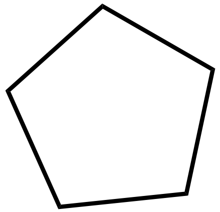
- Interpretation of the IHD values can be broken down as follows

✓ IHD = 0; means all the bonds in the molecule are single bonds

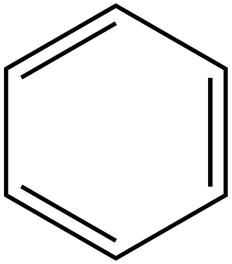
✓ IHD = 1; means the molecule contains either a ring or a double bond

✓ IHD = 2; means the molecule contains a triple bond or 2 rings or a ring and a double bond

✓ IHD = 4; means the molecule contains an aromatic ring



ring



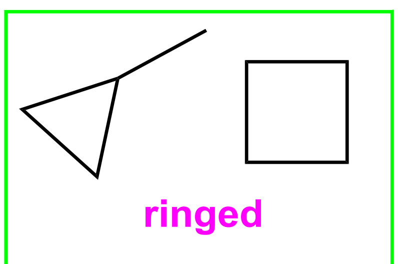
aromatic ring

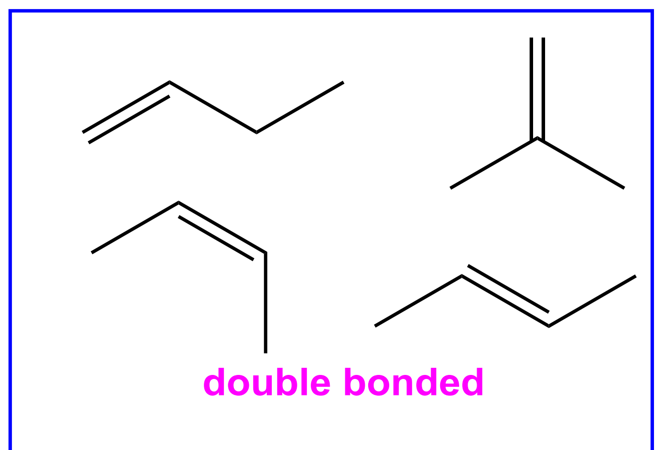
Contd……

- **Example;**
- **Calculate the IHD for the compound with the molecular formula, (C_4H_8) and deduce the possible isomeric structures**

$$IHD = \frac{2C+2+N-H-X}{2} = \frac{2(4)+2+0-8-0}{2} = \frac{2}{2} = 1$$

- **Interpretation;** **compound contains a double bond or a ring**
- **Six (6) possible isomeric structures**





10.7 Alkanes

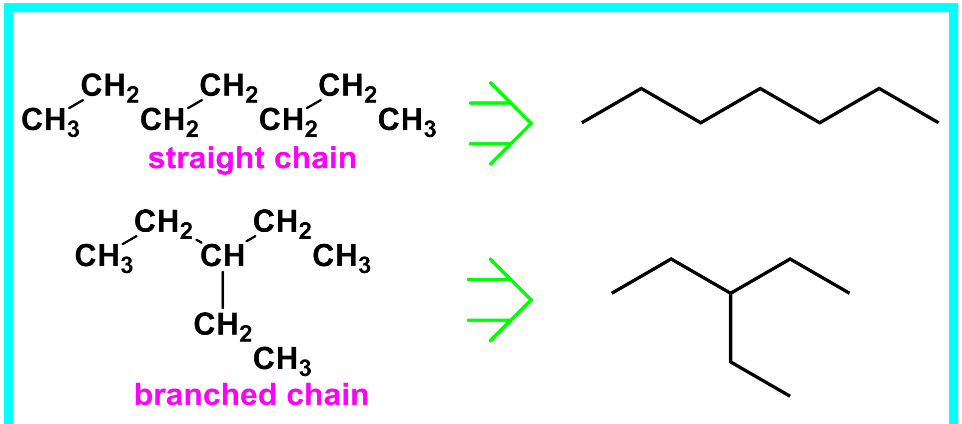
❖ Alkanes

- ✓ Alkanes are aliphatic hydrocarbons having only C-C and C-H sigma (σ) bonds
- ✓ Because their carbon atoms can be joined together in chains or rings and as such they can be categorized as acyclic or cyclic

❖ Acyclic alkanes

- ✓ Alkanes have the molecular formula C_nH_{2n+2} for linear structures and C_nH_{2n+2} (where $n > 3$) for branched chains of carbon atoms
- ✓ They are also called saturated hydrocarbons because they have the maximum number of hydrogen atoms per carbon

❖ Examples



Contd……

❖ Summary of straight chain alkanes

Number of C atoms	Molecular formula	Name (*n*-alkane)	Number of constitutional isomers
1	CH_4	methane	—
2	C_2H_6	ethane	—
3	C_3H_8	propane	—
4	C_4H_{10}	butane	2
5	C_5H_{12}	pentane	3
6	C_6H_{14}	hexane	5
7	C_7H_{16}	heptane	9
8	C_8H_{18}	octane	18
9	C_9H_{20}	nonane	35
10	$C_{10}H_{22}$	decane	75

❖ **Note:** memorize the names of these ten alkanes

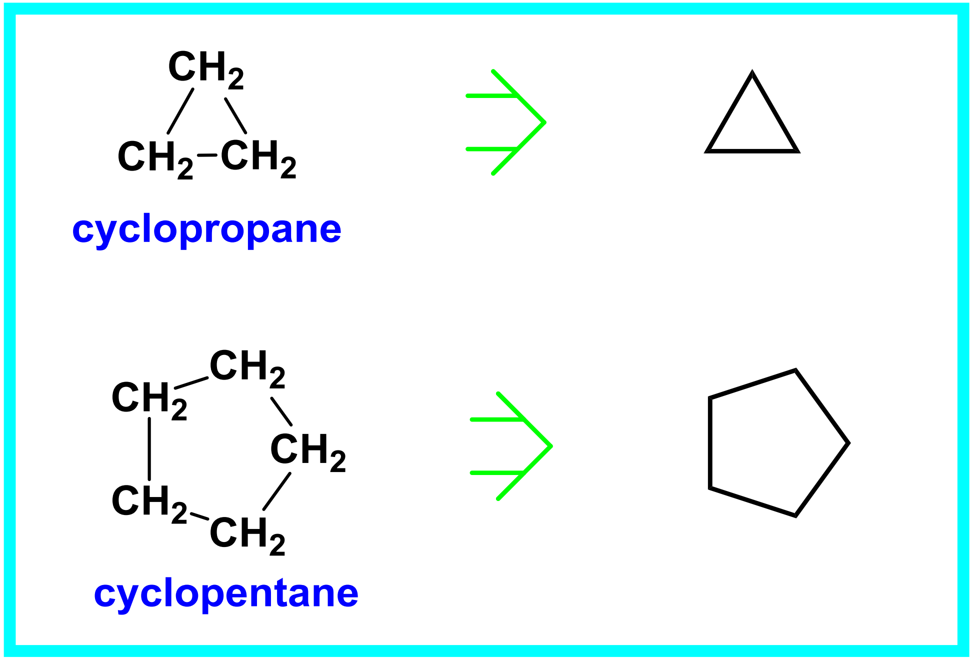
Contd……

- **Cycloalkanes**

✓ **These contain carbons joined in one or more rings**

✓ **Because their general formula is C_nH_{2n} (where n > 2) as a result they have two fewer H atoms than an acyclic alkane with the same number of carbons**

✓ **Example**



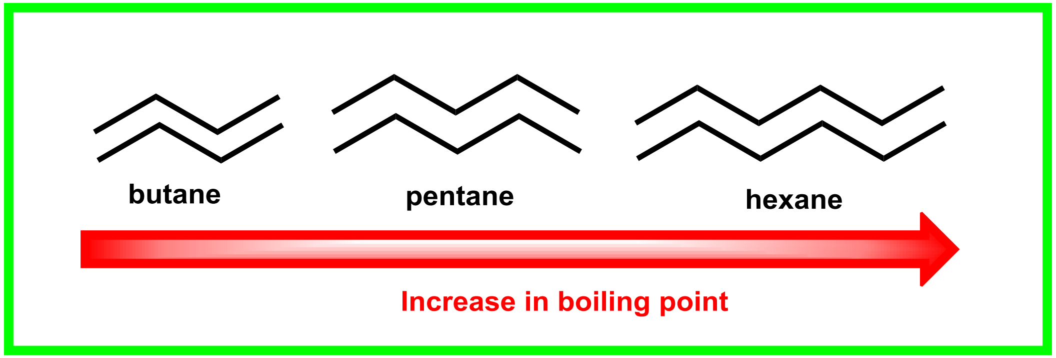
10.71 Physical properties

- **Physical state**
- Alkanes with;
- $C_1 — C_4$ chains are gases
- $C_5 — C_{17}$ chains are liquids
- C_{18} and above are solids; at room temperature
- **Solubility**
- Alkanes are insoluble in water but soluble in non-polar solvents e.g ether
- **Density**
- Alkanes are less dense than water and as a result float on water

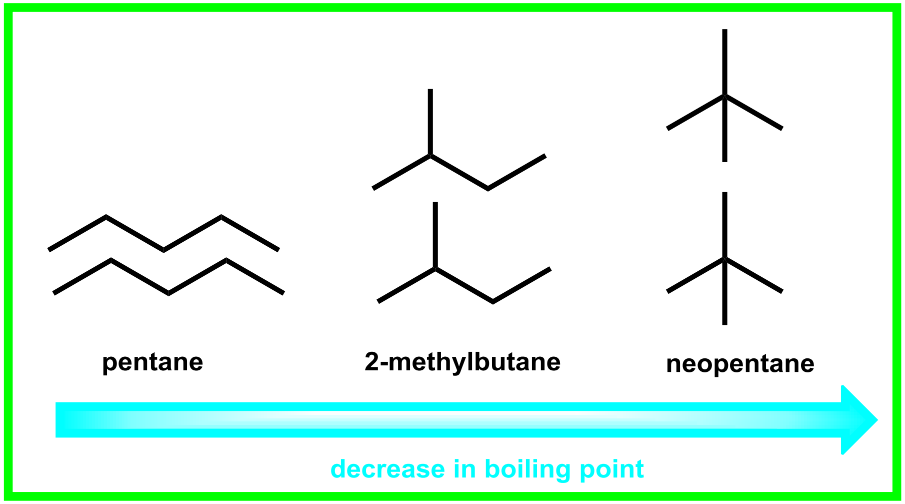
Contd……

❖ **Boiling point**

✓ The boiling point in alkanes increases as carbon chain length increases due to increase of van der waals forces of attraction e.g



✓ And decreases with increase in the branching e.g



10.72 Isomers

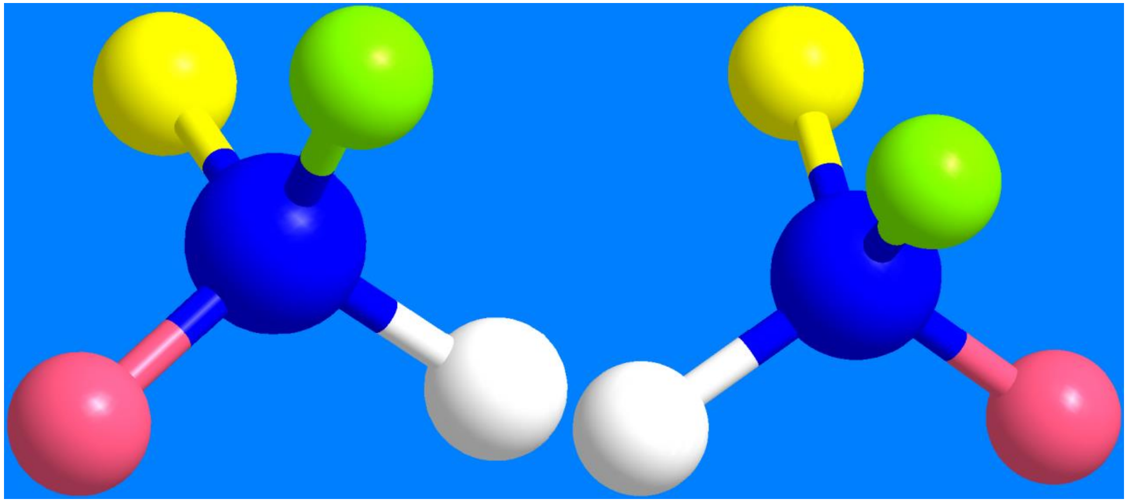
❖ **Isomers**

✓ **These are compounds which have the same molecular formula but different arrangement of atoms**

❖ **They are two types; (i) stereoisomers and (ii) constitutional isomers**

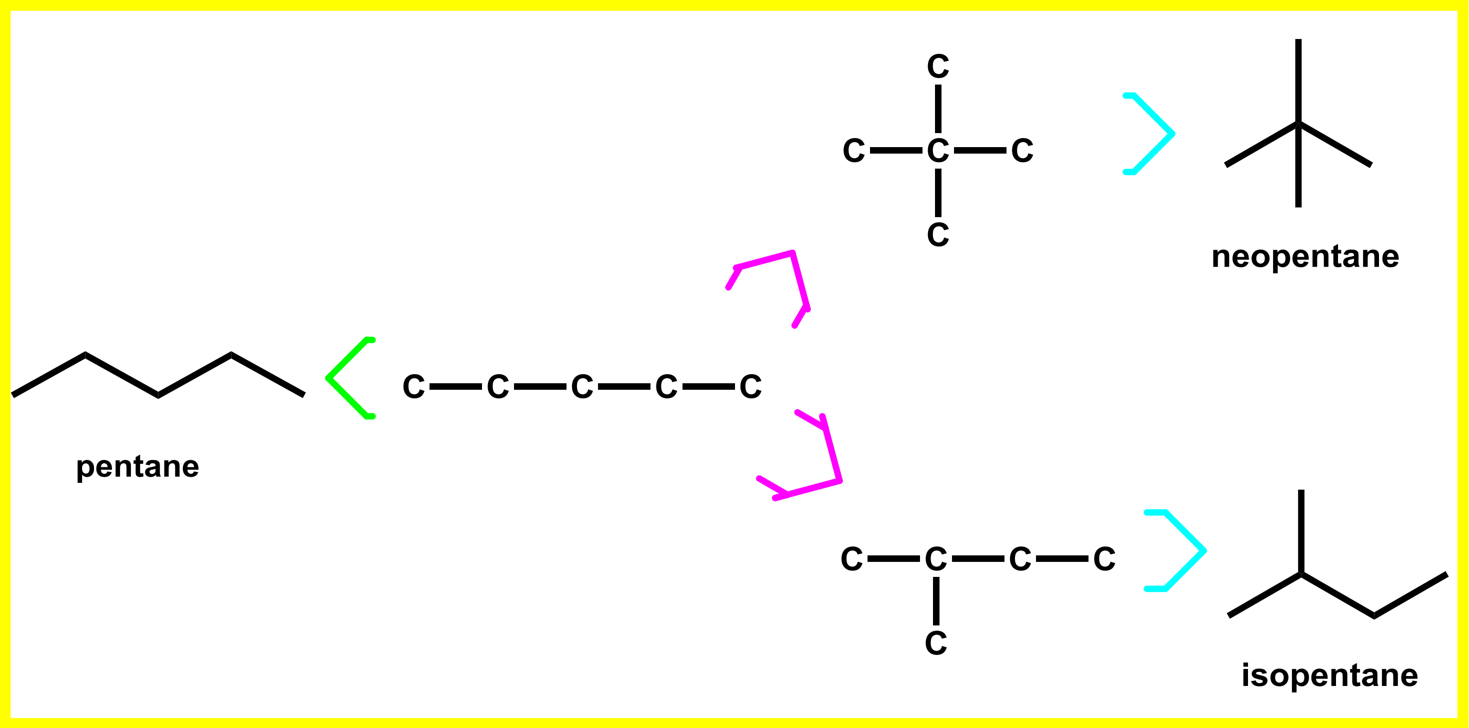
✓ **Stereoisomers**

- **These are isomers which have the same number of atoms but differ in the spatial arrangement of atoms**



Contd……

- Constitutional isomers
- These are isomers which same number of atoms but differ in the connectivity of these atoms
- Consider pentane with the molecular formula, C_5H_{12},



10.73 Naming alkanes

- The name of every organic molecule has three parts

✓ The parent name indicates the number of carbons in the longest continuous carbon chain in the molecule.

✓ The suffix indicates what functional group is present.

✓ The prefix reveals the identity, location, and number of substituents attached to the carbon chain

prefix + parent + suffix

what and where are the sustituents?

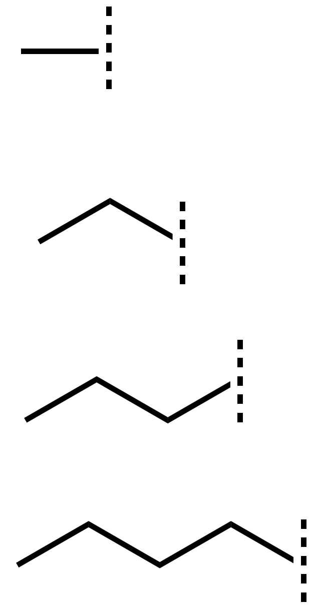
What is the longest carbon chain?

what is the functional group?

Contd……

- Naming substituents
- Carbon substituents bonded to a long carbon chain are called alkyl groups
- ✓ An alkyl group is formed by removing one hydrogen from an alkane
- ✓ To name an alkyl group, change the *-ane* ending of the parent alkane *to -yl*
- ✓ Hence;

Alkane		Alkyl group	
CH_4	methane	CH_3-	methyl
CH_3CH_3	ethane	CH_3CH_2-	ethyl
$CH_3CH_2CH_3$	propane	$CH_3CH_2CH_2$-	propyl
$CH_3CH_2CH_2CH_3$	butane	$CH_3CH_2CH_2CH_2$-	butyl



Contd……

❖ Naming three- and four-carbon alkyl groups is more complicated because the parent hydrocarbons have more than one type of hydrogen atom

✓ propane

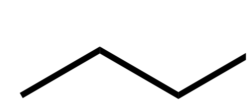
2^o 1^o

$CH_3CH_2CH_3$

propane

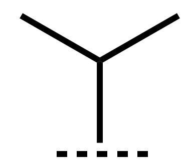
$CH_3CH_2CH_2-$

propyl



CH_3CHCH_3

*iso*propyl



✓ Butane

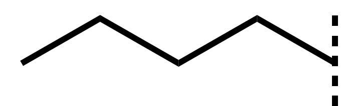
2^o 1^o

$CH_3CH_2CH_2CH_3$

butane

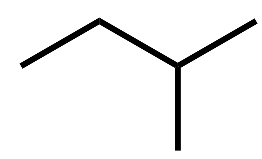
$CH_3CH_2CH_2CH_2-$

butyl



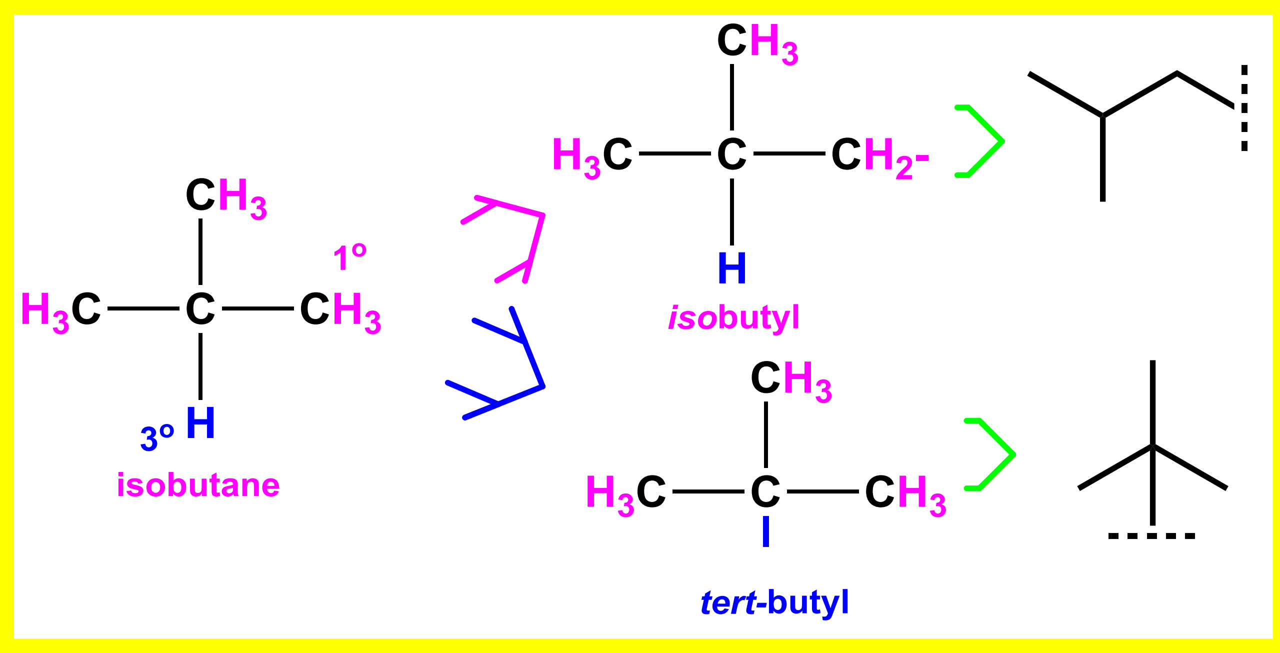
$CH_3CH_2CHCH_3$

sec-butyl



Contd……

✓ Isobutane



❖ Note that alkyl groups as substituents are abbreviated as;

❖ Methyl (Me), Ethyl (Et), Propyl (Pr), Butyl (bu), *iso*Propyl(*i*-Pr), *sec*-Butyl (*sec*-bu), *iso*butyl (*i*-bu) and *tert*-Butyl (*tert*-bu)

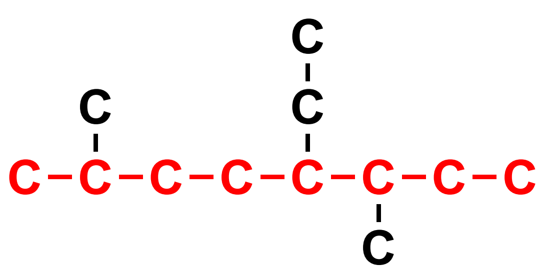
Contd……

- There are four IUPAC rules for naming alkanes

✓ Rule (1); Find the parent chain and add the suffix

- Find the longest continuous carbon chain, and name the molecule by using the parent name for that number of carbons
- To the name of the parent, add the suffix -ane for an alkane

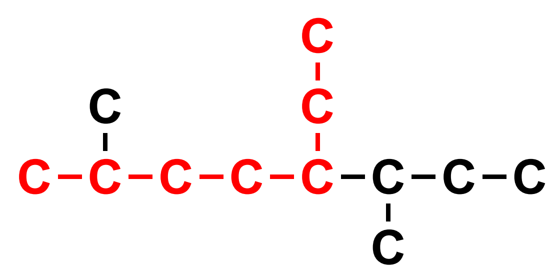
Correct



8 atoms in the longest chain

8 C's → octane

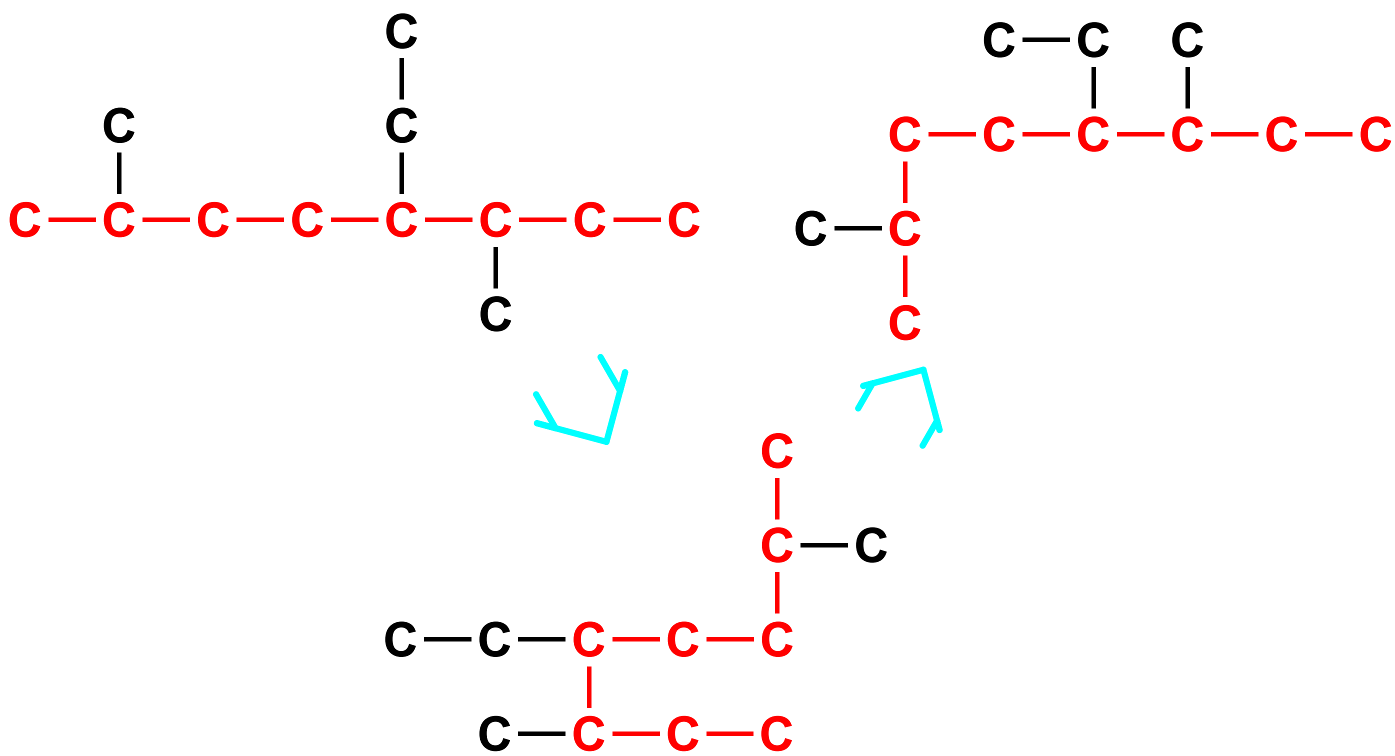
Incorrect



7 atoms in the longest chain

Contd……

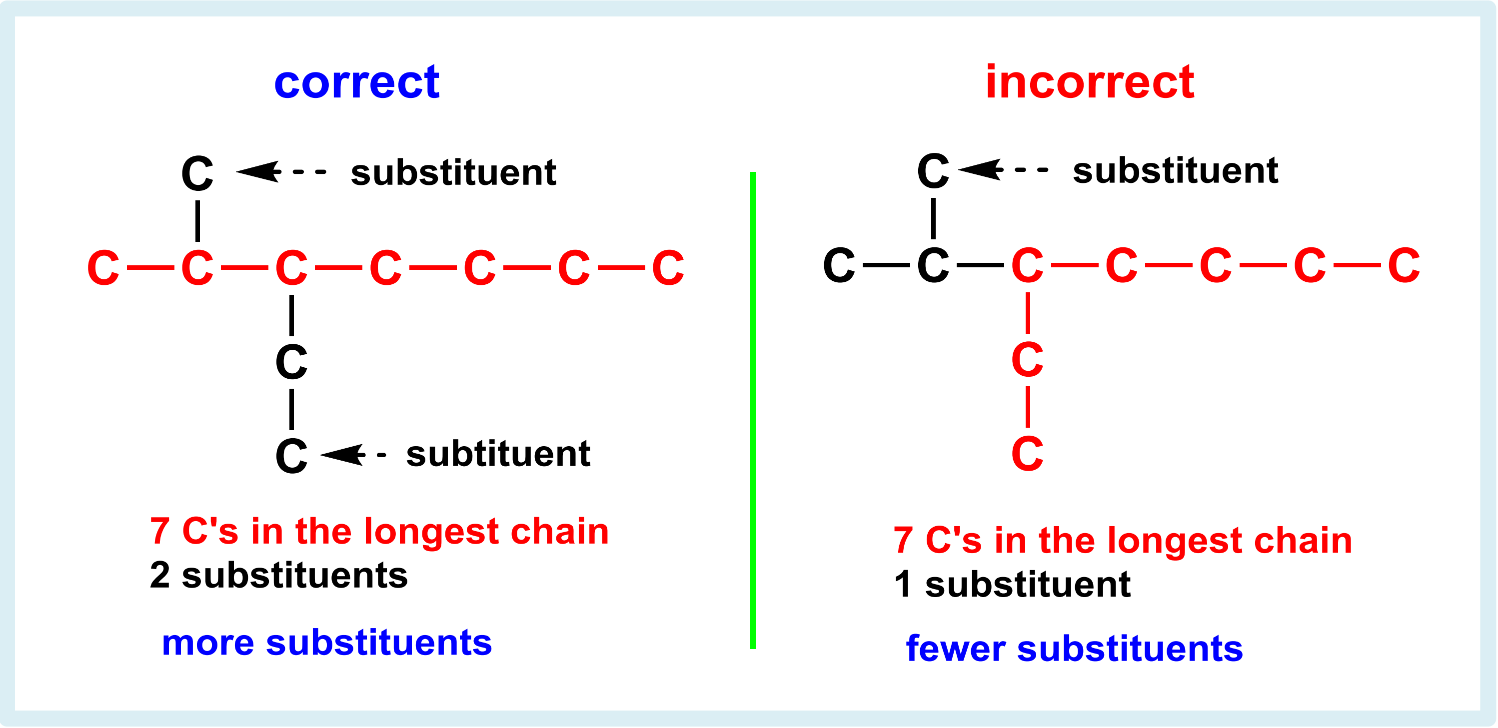
- It does not matter if the chain is straight or has bends



8 C's in the longest chain of each representation

Contd……

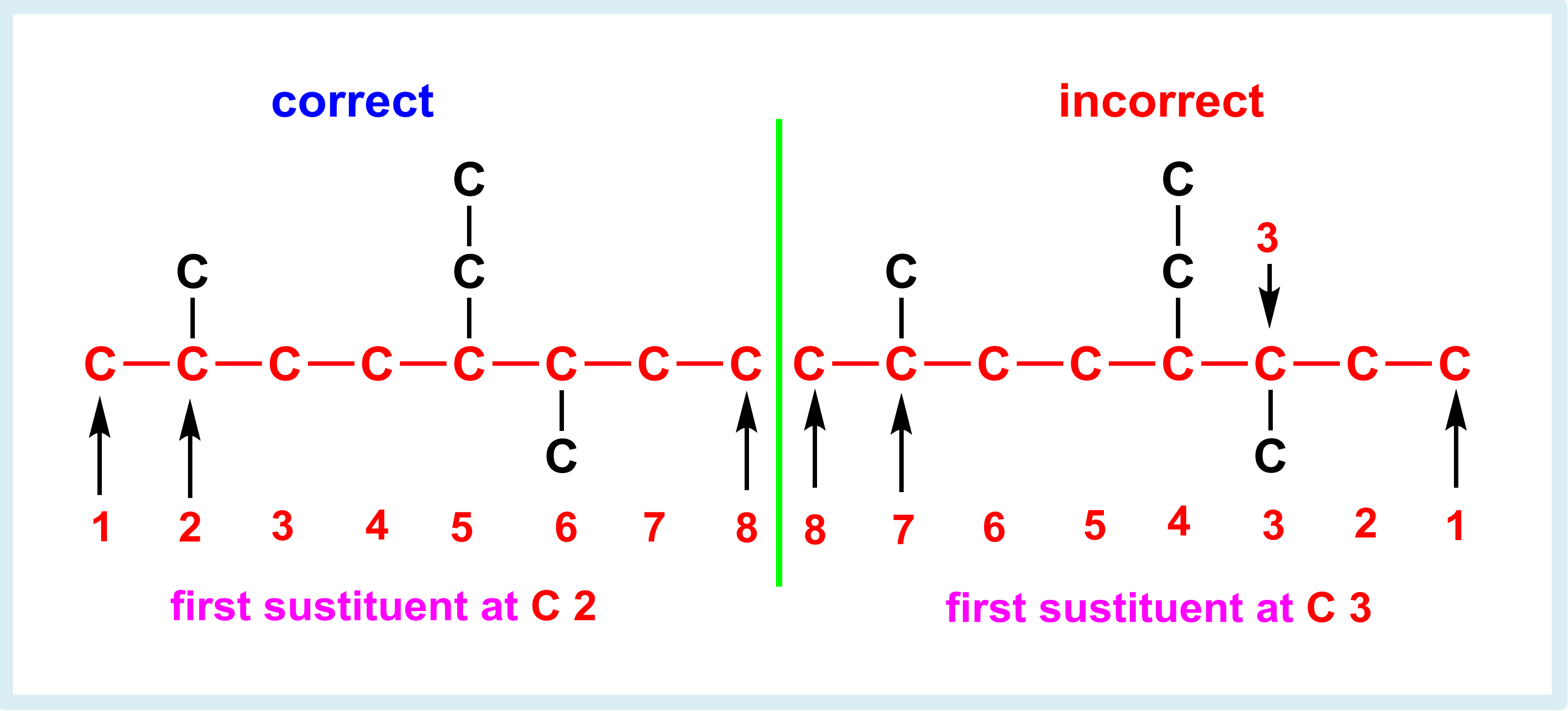
- If there are two chains of equal length, pick the chain with more substituents



Contd……

✓ Rule (2); Number the atoms in the carbon chain

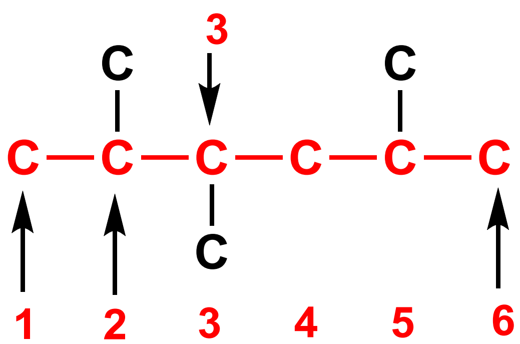
- Number the longest chain to give the first substituent the lower number



Contd……

- If the first substituent is the same distance from both ends, number the chain to give the second substituent the lower number

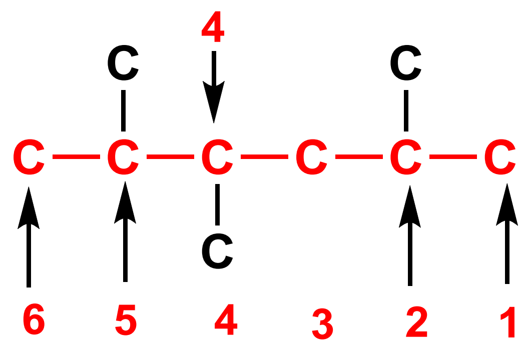
correct



CH_3 groups at C2, C3 and C5

Here C3 is a lower number

incorrect

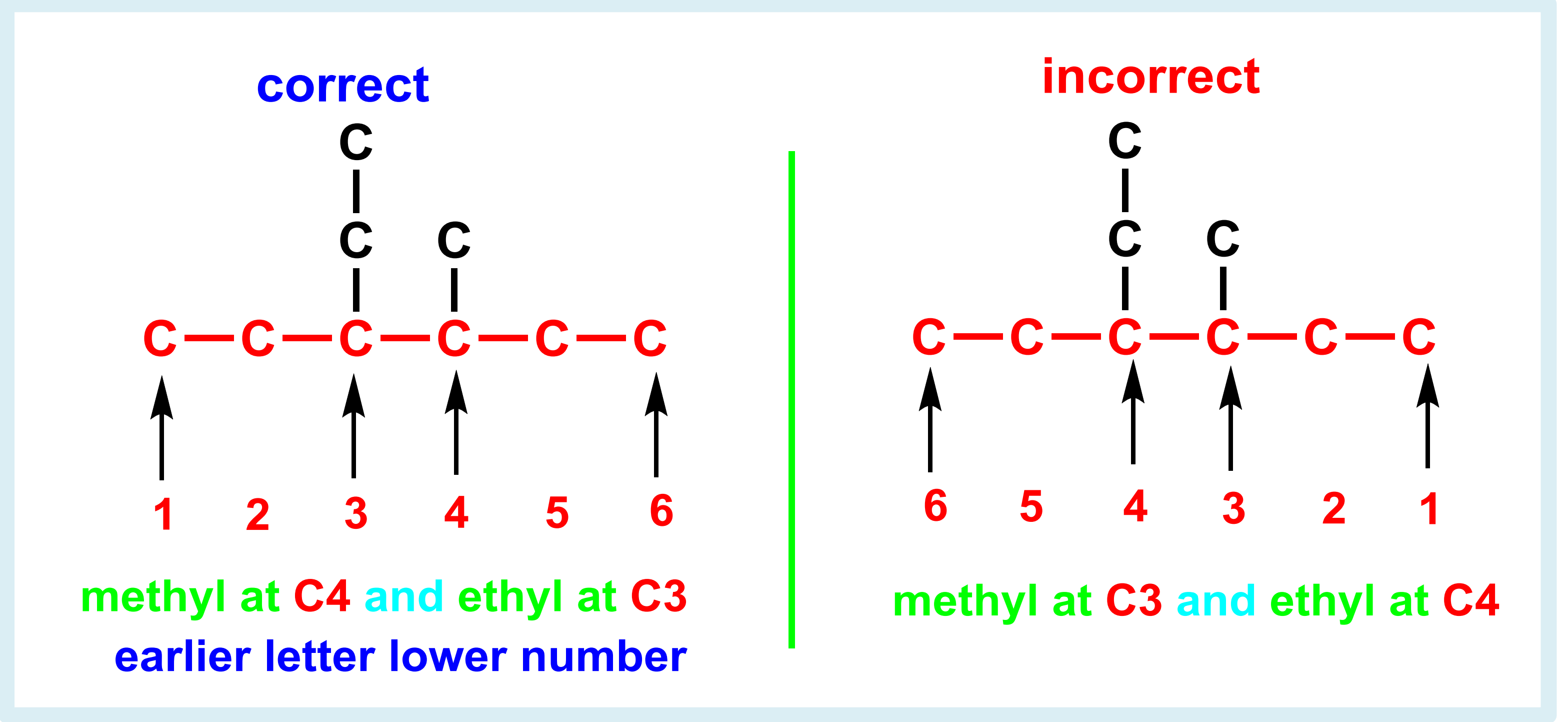


CH_3 groups at C2, C4 and C5

Here C4 is a higher number

Contd……

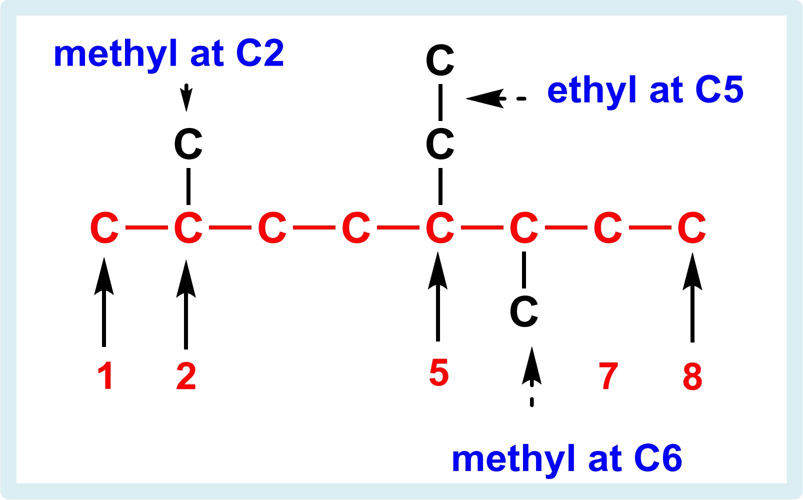
- When numbering a carbon chain results in the same numbers from either end of the chain, assign the lower number alphabetically to the first substituent



Contd……

✓ **Rule (3); Name and number the substituents**

- **Name the substituents as alkyl groups, and use the numbers from rule 2 to designate their location**



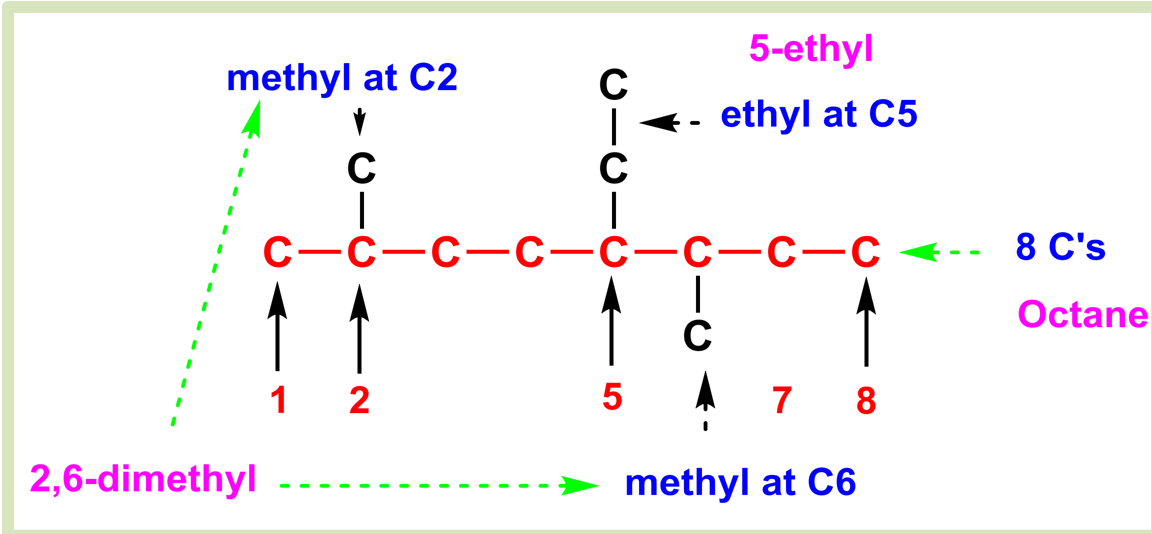
- **Each substituent needs its own number.**
- **If two or more identical substituents are prefixes to indicate how many: di- for two groups, tri- for three groups, tetra- for four groups, and so forth. The preceding molecule has two methyl substituents, and so its name contains the prefix di- before the word methyl → dimethyl**

Contd……

- ✓ Rule (4); Combine substituent names and numbers + parent + suffix.
- Precede the name of the parent by the names of the substituents.
- Alphabetize the names of the substituents, ignoring all prefixes except iso, as in isopropyl and isobutyl.
- Precede the name of each substituent by the number that indicates its location.
- There must be one number for each substituent.
- Separate numbers by commas (,) and separate numbers from letters by hyphens (-).
- The name of an alkane is a single word, with no spaces after hyphens or commas.

Contd……

- Identify the pieces of the compound from rule 1-3;



- Then, put the pieces of the name together

substituent names and numbers	+	parent	+	suffix
5-ethyl-2,6-dimethyl		oct		ane

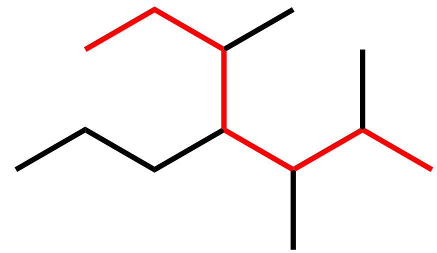
(Alphabetize; e for ethyl and m for methyl)

8 C's alkane = octane

- And the name is; 5-ethyl-2,6-dimethyloctane

Contd……

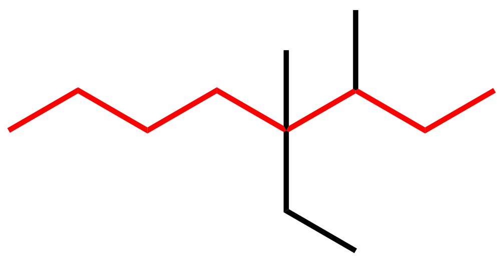
- **Specific examples;**



2,3,5-trimethyl-4-propylheptane

(Pick the long chain with more substituents and alphabetize the e of ethyl before the m of methyl,and m of methyl before the p of propyl)

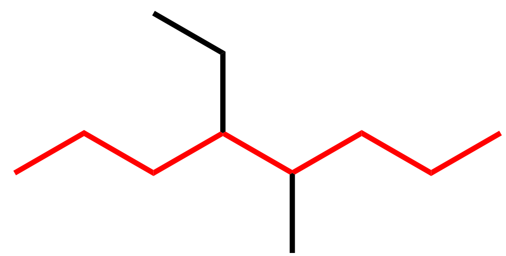
Not 3,5,6-trimethyl-4-propylheptane



4-ethyl-3,4-dimethyloctane

(Alphabetize the e of ethyl before the m of methyl)

Not 5-ethyl-5,6-dimethyloctane



4-ethyl-5-methyloctane

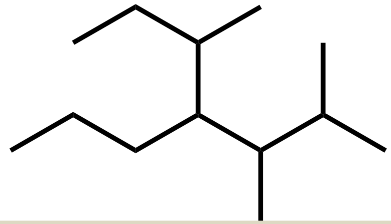
(Assign the lower number to the 1st sustituent alphabetically: the e of ethyl before the m of methyl)

Not 5-ethyl-4-methyloctane

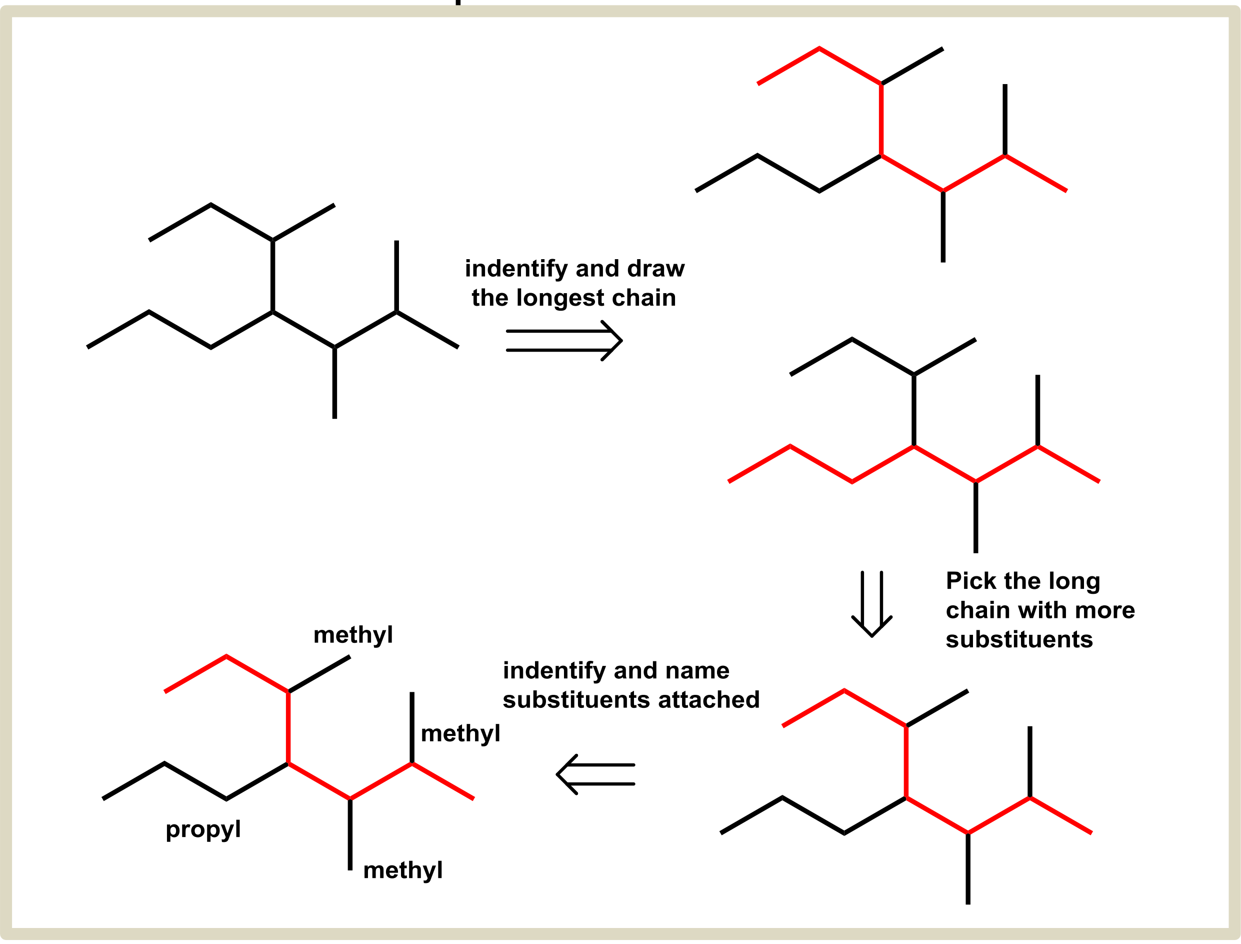
- **Note: the carbon atom of each long chain are drawn in red**

Contd……

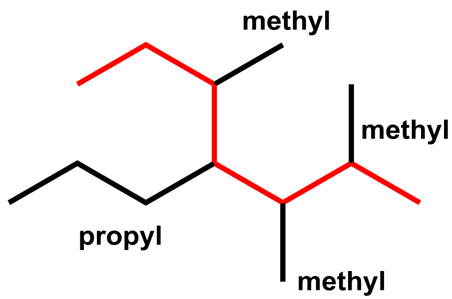
- Give the IUPAC name for the compound given below.



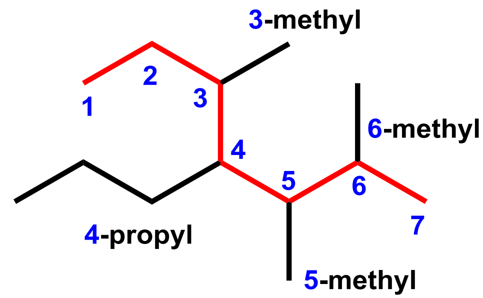
- Analysis



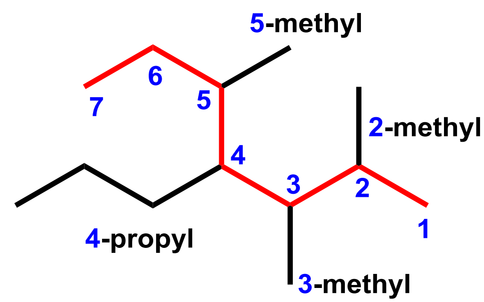
Contd......



number the substituents, alphabetize and generate name



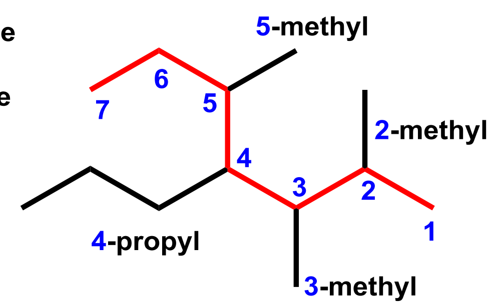
3,5,6-trimethyl-4-propyl



2,3,5-trimethyl-4-propyl

Pick the chain with lower numbering

complete the name by adding the parent name at the end

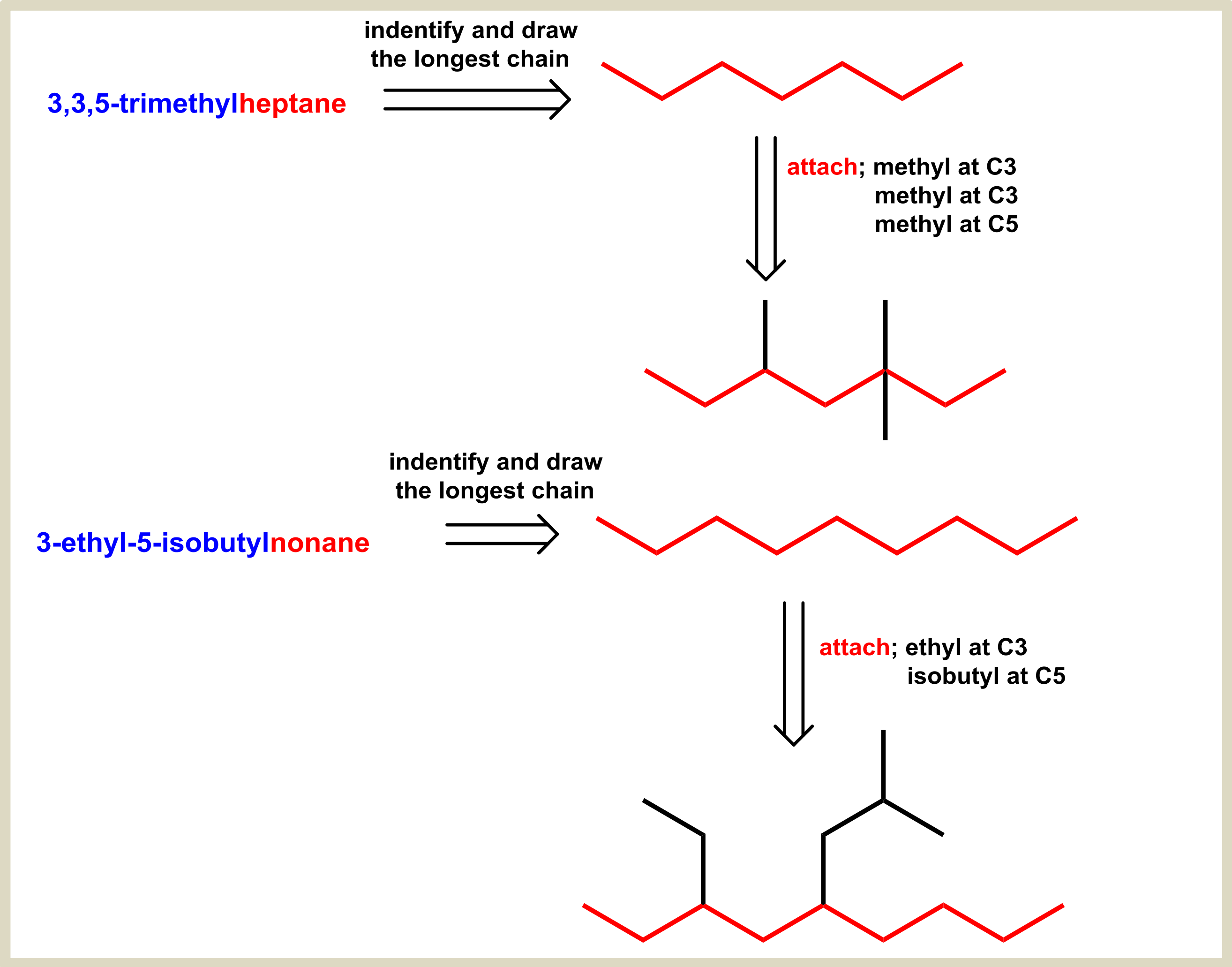


2,3,5-trimethyl-4-propyl

2,3,5-trimethyl-4-propylheptane

Contd……

- Give structures corresponding to each IUPAC name

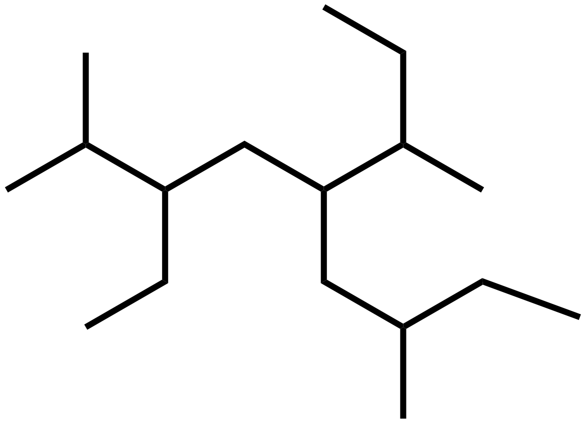


- **Note:** the carbon atom of each long chain are drawn in red

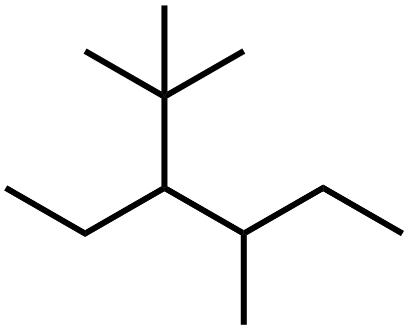
Practice Question(s)

1. **Give the IUPAC name for each of the compound.**

(a)



(b)



2. **Give the structure corresponding to each IUPAC name.**

(a) 3-ethyl-2,7-dimethyl-5-propyloctane

(b) 4-(*tert*-butyl)-3-methylheptane

10.74 Naming cycloalkanes

- Cycloalkanes are named by using similar rules, but the prefix cyclo- immediately precedes the name of the parent.

prefix + cyclo- + parent + suffix

- prefix: what and where are the sustituents?
- parent: What is the longest carbon chain?
- suffix: what is the functional group?

HOW TO Name a Cycloalkane Using the IUPAC System

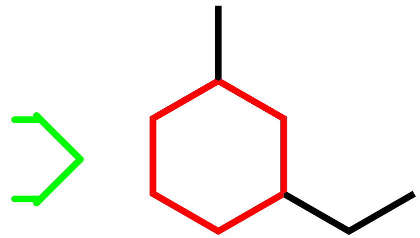
✓ Rule 1: Find the parent cycloalkane

- Count the number of carbon atoms in the ring and use the parent name for that number of carbon

Contd……

- Add the prefix cyclo- and the suffix -ane to the parent name

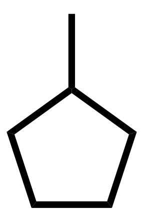
6 C's in the ring



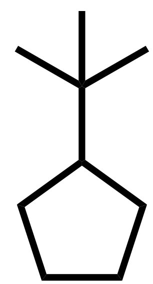
cyclohexane

✓ **Rule 2: Name and number the substituents**

- No number is needed to indicate the location of a single substituent



methylcyclopentane



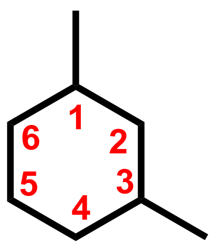
tert-butylcyclopentane

Contd……

- For rings with more than one substituent, begin numbering at one substituent and proceed around the ring clockwise or counterclockwise to give the second substituent the lower number.

Correct

numbering clockwise

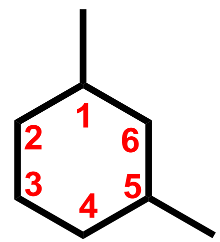


CH_3 group at C1 and C3

1,3-dimethylcyclohexane

Incorrect

numbering counterclockwise



CH_3 group at C1 and C5

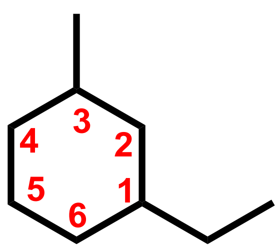
1,3-dimethylcyclohexane

Contd……

- With two different substituents, number the ring to assign the lower number to the substituents alphabetically

Correct

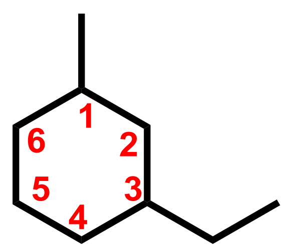
begin numbering at the ethyl group



ethyl group at C1
methyl group at C3

earlier letter → lower letter

Incorrect



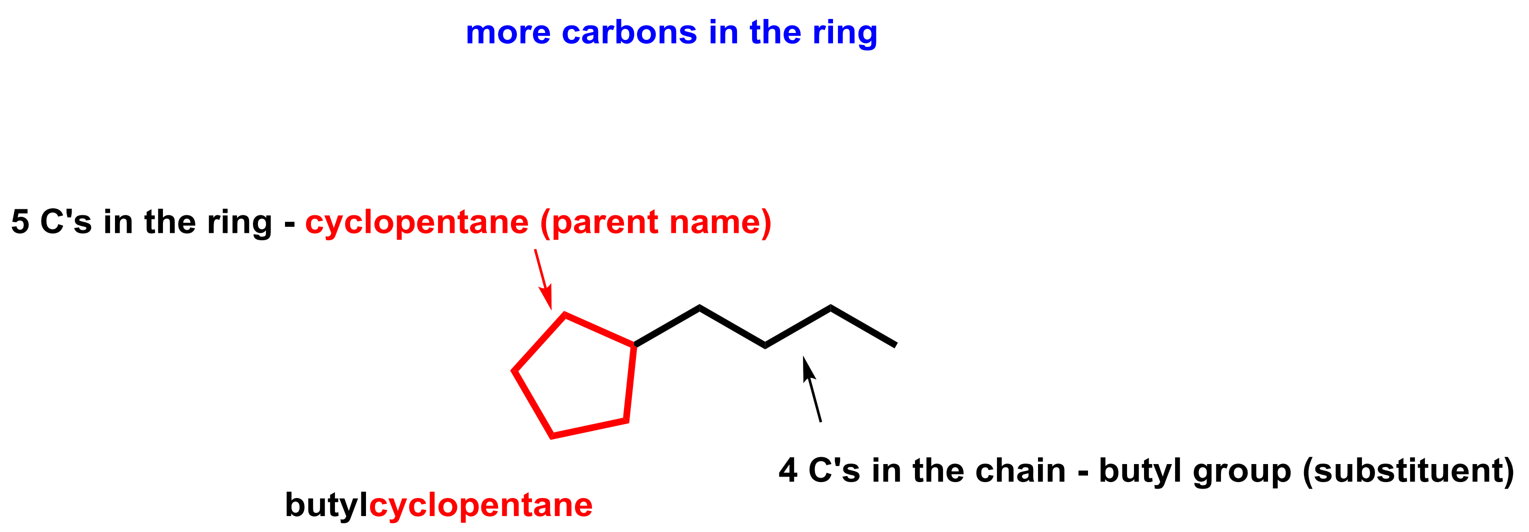
begin numbering at the methyl group

methyl group at C1
ethyl group at C3

Contd……

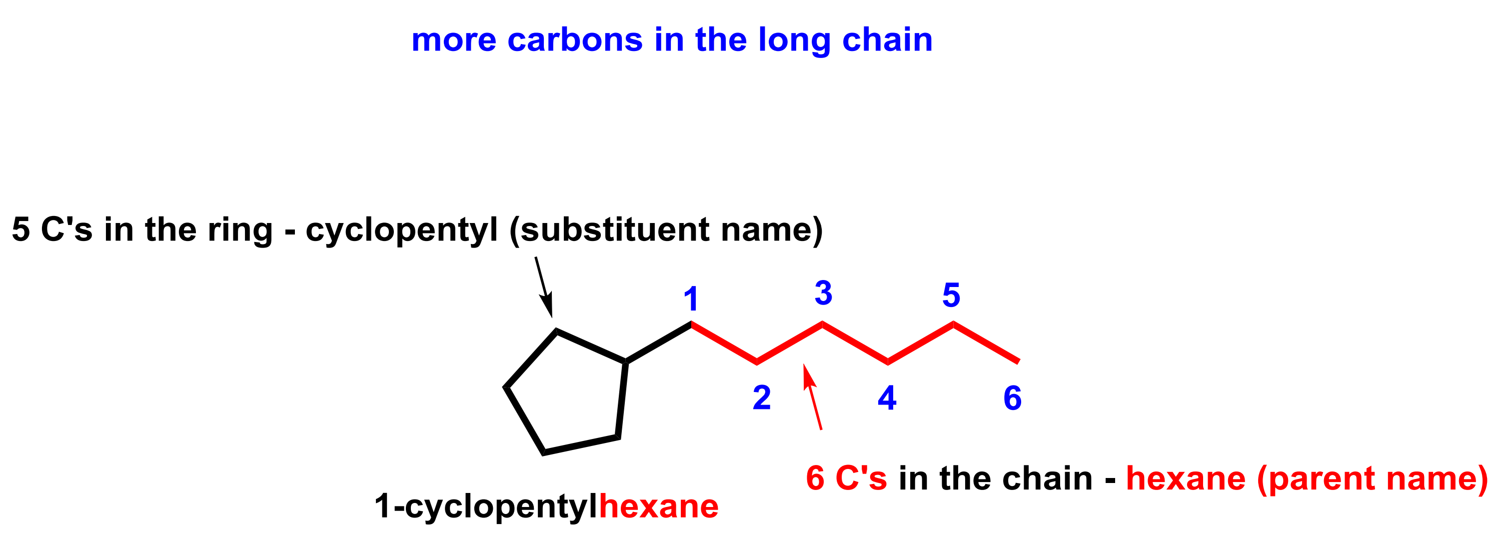
- ✓ Rule 3: When an alkane is composed of both a ring and a long chain, what determines whether a compound is named as an acyclic alkane or a cycloalkane?

- If the number of carbons in the ring is greater than or equal to the number of carbons in the long chain, the compound is named as a cycloalkane



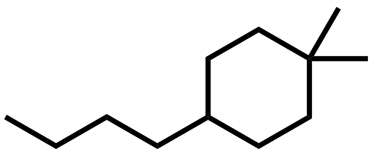
Contd……

❖ If the number of carbons in the long chain is greater than the number of carbons in the ring, the compound is named as an acyclic alkane

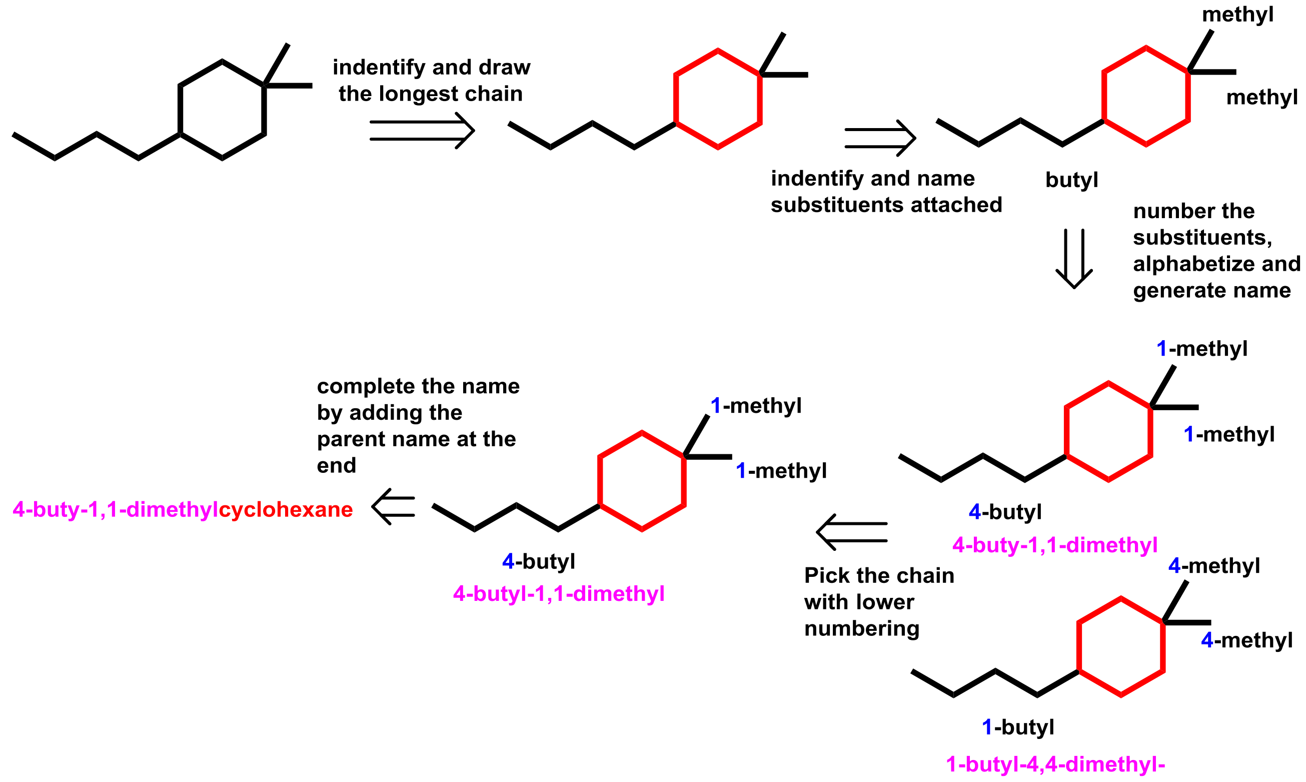


Contd……

- Give the IUPAC name for the compound given below



- Analysis

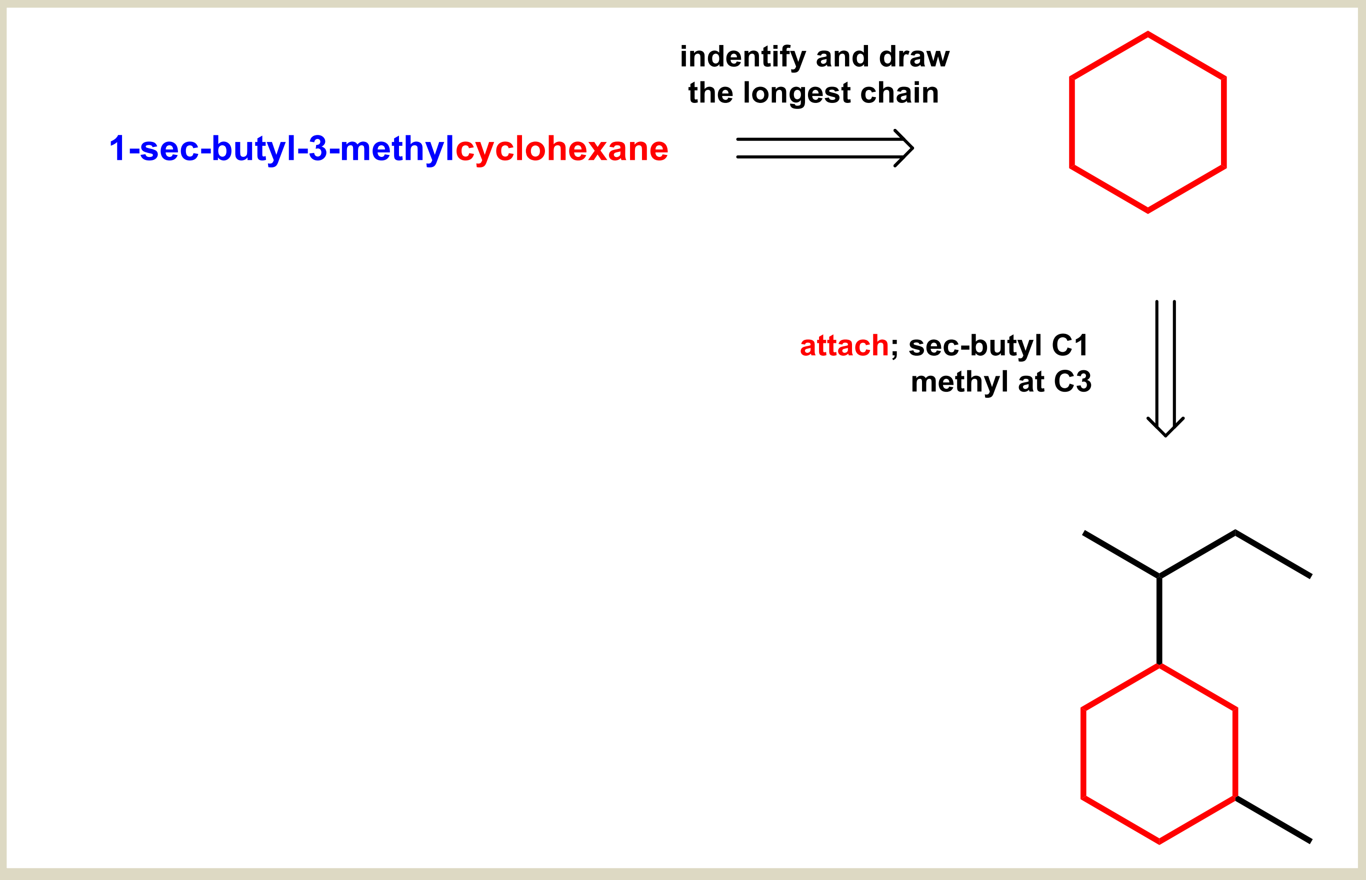


Contd……

- **Give structure corresponding to IUPAC name given below**

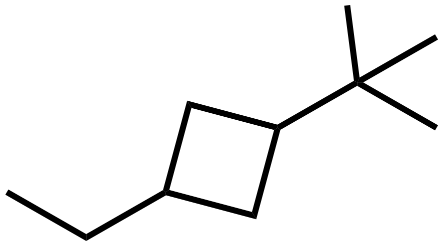
1-*sec*-butyl-3-methylcyclohexane

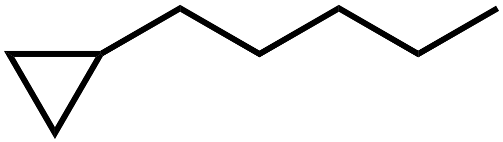
- **Analysis**



Practice Question(s)

1. Give the IUPAC name for each of the compound.

(a) 

(b) 

2. Give the structure corresponding to each IUPAC name.

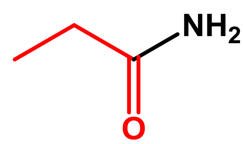
(a) 2-ethyl-2,3-dimethyl-5-propylcyclopentane

(b) 1-sec-butyl-3-isopropylcyclopentane

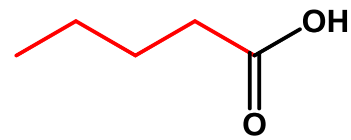
10.75 Naming Other Compounds With Functional Groups

- If the suffix of the functional group starts with a vowel, remove the –e from the parent alkane name

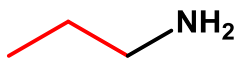
1-butanol



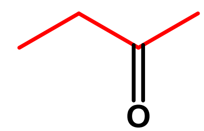
propanamide



pentanoic acid

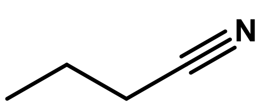


1-propanamine

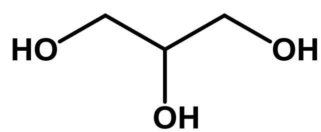


2-butanone

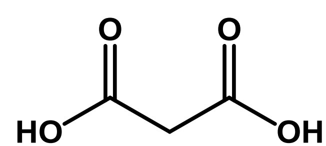
- Do not remove the –e from the parent alkane name in a case where the suffix starts with a consonant or there are two or more of a functional group necessitating the use of di, tri etc



butanenitrile



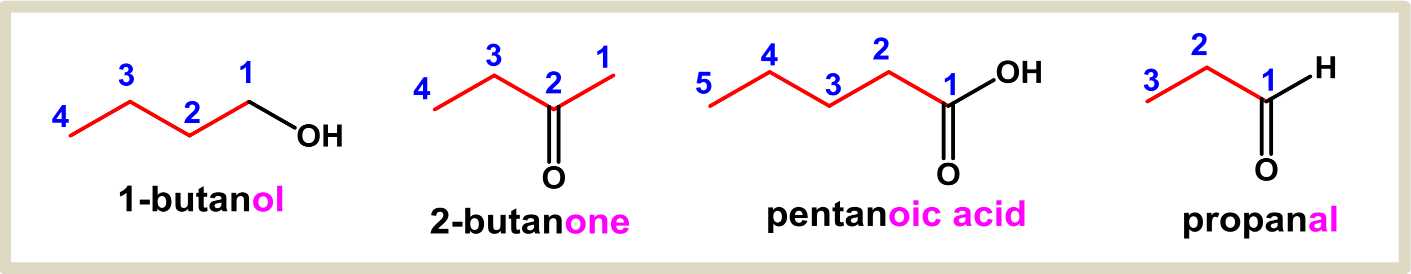
1,2,3-propanetriol
or
propane-1,2,3-triol



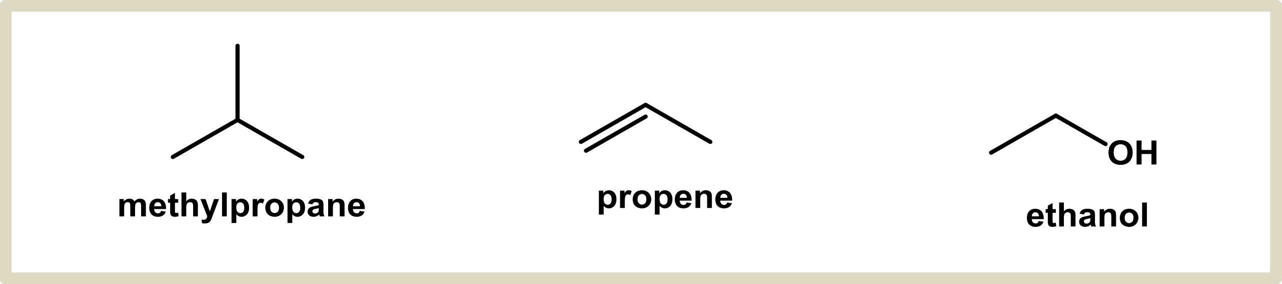
1,3-propanedioic acid
or
propane-1,3-dioic acid

Contd……

The position of the functional group on the carbon chain is given by a number – counting from the end of the molecule that gives the functional group the lowest number. For aldehydes, carboxylic acids & nitriles, the functional group is always on carbon 1

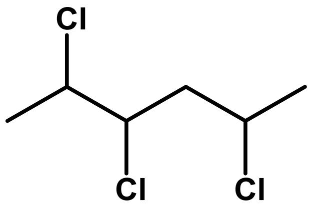


❖ **We only include numbers, however, if they are needed to avoid ambiguity.**

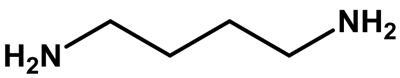


Contd……

- The designations di-, tri-, tetra-, penta- or hexa- should be used where there are two or more of the same group

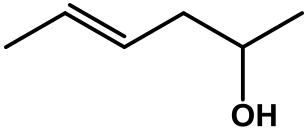


2,3,5-trichlorohexane



butane-1,4-diamine
or
1,4-butanediamine

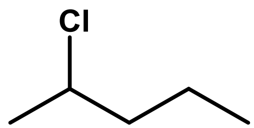
- Numbers and words are separated by dashes or hyphens. Commas are used to separate the numbers. If there is more than one functional group or side chain, the groups are listed in alphabetical order (ignoring any di, tri. Etc)
- The suffix for alkenes can go in front of other suffixes



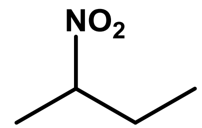
hex-4-en-2-ol

Contd……

- Some groups such as –Cl, -Br, -F and $-NO_2$ are always considered as substituents even when no other functional group is present

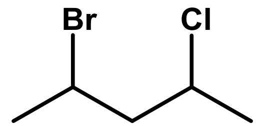


2-chloropentane



2-nitrobutane

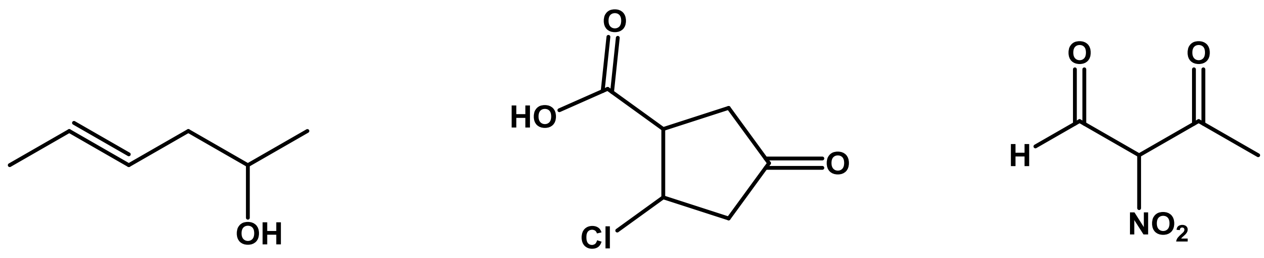
- Where two groups of the same priority are located on identical positions from either end of the parent chain, the group whose prefix comes first in the alphabetical order is assigned the lowest number



2-bromo-4-chloropentane

10.75 Polyfunctional Compounds

- Polyfunctional compounds are organic compounds that contain two or more functional groups.
- Examples;



✓ Nomenclature

- Principal functional group

- One of the functional groups in a polyfunctional compound is selected as a principal functional group while all other functional groups are treated as substituents.

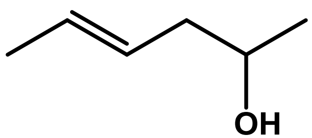
Contd……

✓ **Priority Ranking of Principle Functional Groups (remember)**

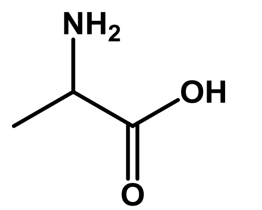
increasing priority ↑	Class	Suffix Name	Prefix Name
	Carboxylic acid	-oic acid	Carboxy
	Ester	-oate	Alkoxycarbonyl
	Amide	-amide	Amido
	Nitrile	-nitrile	Cyano
	Aldehyde	-al	Oxo (=O)
	Aldehyde	-al	Formyl (—CH=O)
	Ketone	-one	Oxo (=O)
	Alcohol	-ol	Hydroxy
	Amine	-amine	Amino
	Alkene	-ene	Alkenyl
	Alkyne	-yne	Alkynyl
	Alkane	-ane	Alkyl
	Ether	—	Alkoxy
	Alkyl halide	—	Halo

Contd……

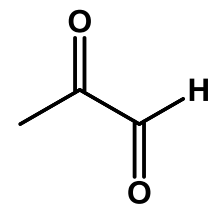
✓ How can we apply the knowledge of priority ranking of principle functional groups?



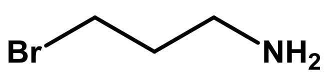
hex-4-en-2-ol
or
4-hexen-2-ol



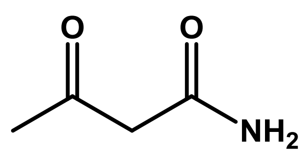
2-aminopropanoic acid



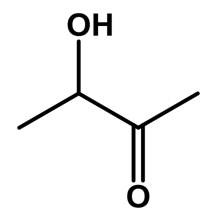
2-oxopropanal



3-bromopropan-1-amine
or
3-bromo-1-propanamine



3-oxobutanamide



3-hydroxybutan-2-one
or
3-hydoxy-2-butanone

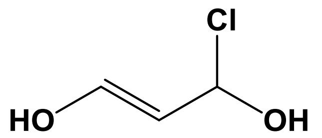
Contd……

✓ **Numbering the principal chain**

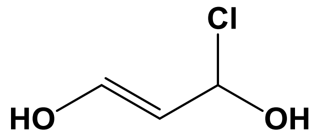
❖ **In numbering the principal chain present in a polyfunctional compound, the principal functional group gets the lowest possible number followed by double bond, triple bond and substituent**

✓ **Order of priority:**

Principle functional group > double bond > triple bond > substituents



3-chloroprop-1-ene-1,3-diol



(not 1-Chloroprop-2-ene-1,3-diol)

❖ **Note**; Alphabetize *iso* and *cyclo* but do not alphabetize *di, tri, tert* and *sec*

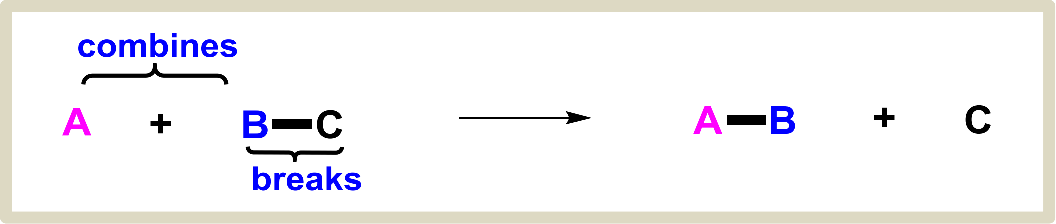
10.8 Introduction to Reaction Mechanisms

What is a reaction mechanism?

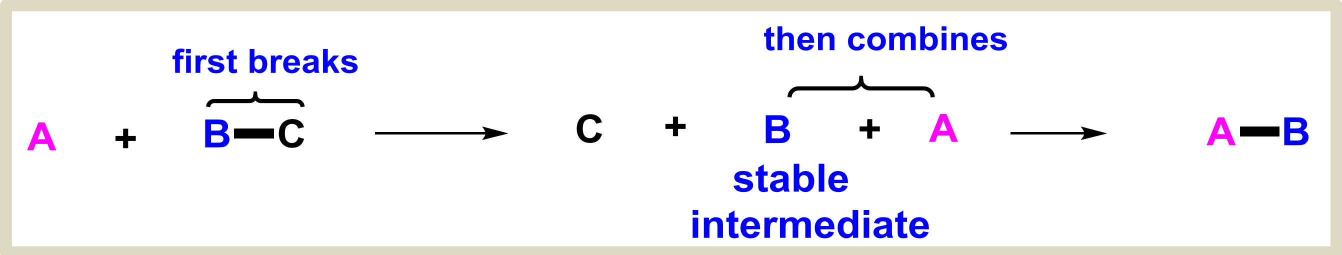
- A reaction mechanism is a step-by-step description of how reactants are microscopically converted into products in a chemical reaction. Each step will involve some kind of bond breaking and/or bond making. Pushing electrons is an excellent, graphic way to describe each step.

- Bond breaking and/or bond making may occur in;

✓ (i) one step or concerted reaction



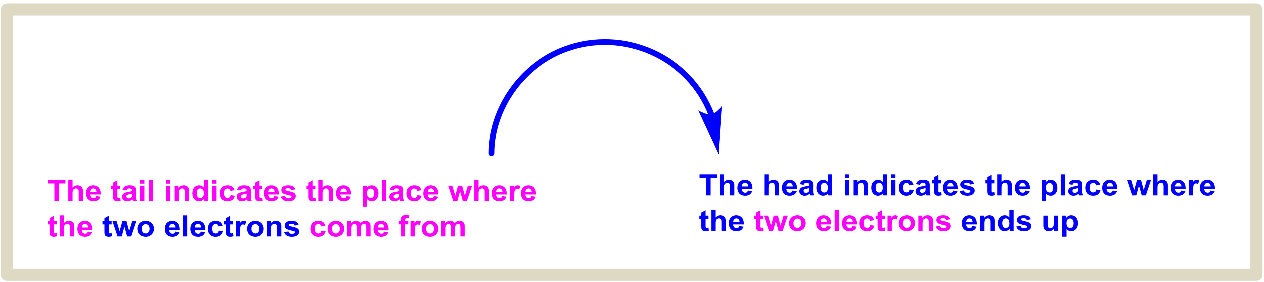
✓ (ii) stepwise reaction (series of steps)



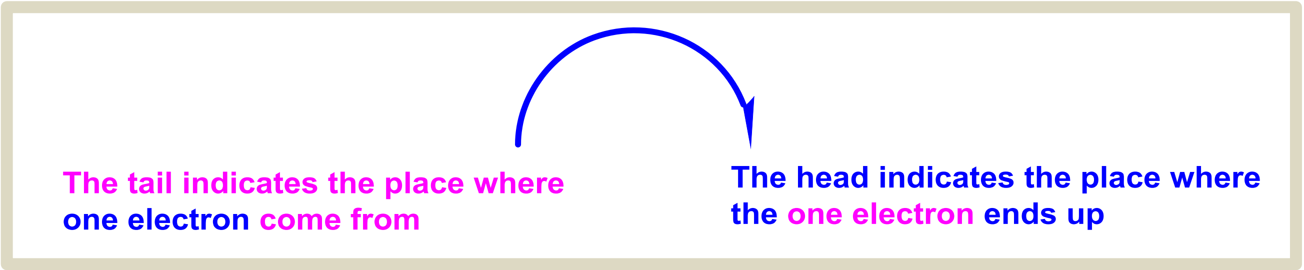
Contd……

- The pushing of electrons in a reaction mechanism can be squarely represented by using the curved arrow natation.
- The curved arrow natation simply show the follow of one electron or two electrons
- For example;

✓ (i) A double barbed arrowhead indicates the movement of two electrons

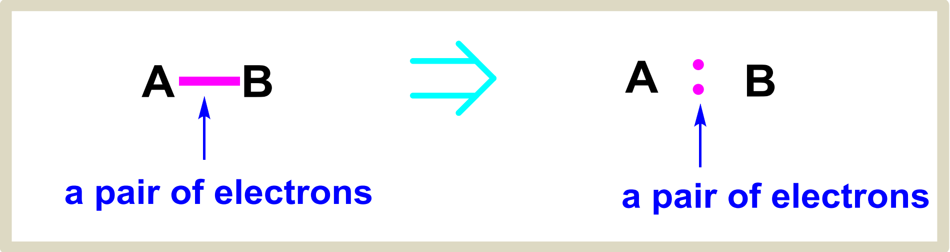


✓ (ii) A single-barbed arrowhead indicates the movement of one electron

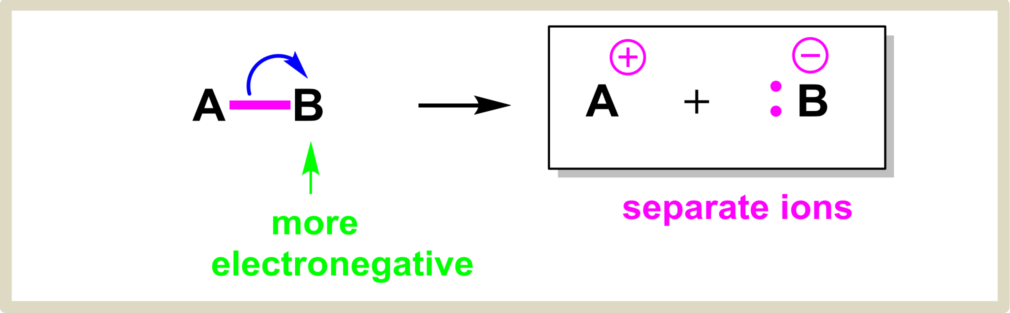


Contd……

- Lets apply the concept of curved arrow natation to bond breaking in a single bond
- ✓ Remember a single bond can be represented as;

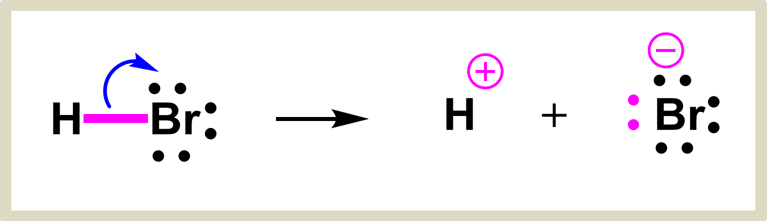


- The breaking of a single bond in any reaction may occur in two ways;
- ✓ (i) Heterolytic bond cleavage is where the bond connecting two atoms A and B is split to produce two separate ions due to unequal sharing of a pair of electrons (possibly coming from atoms having electronegativity differences)
- In this case a double barbed arrowhead is used



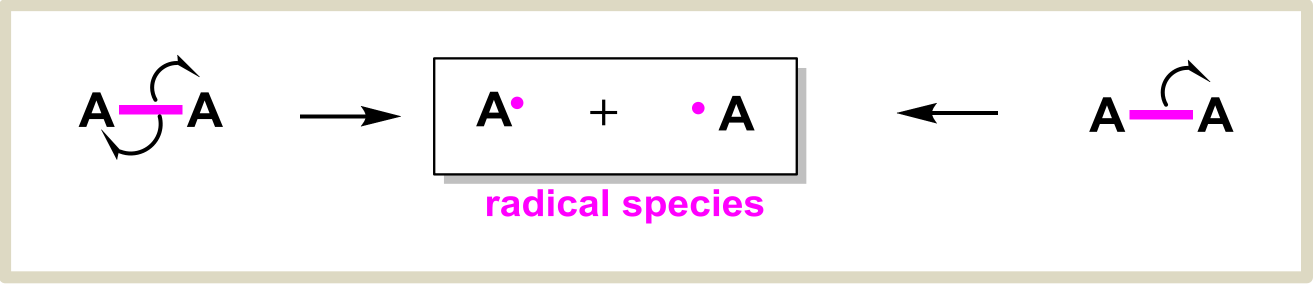
Contd……

- Specific case;



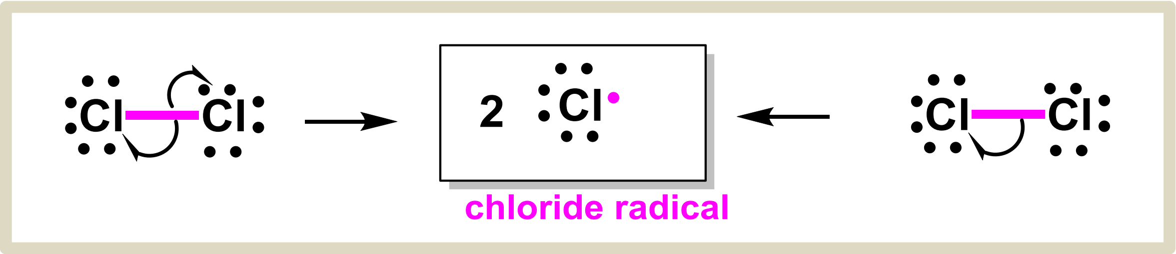
- (ii) Homolytic bond cleavage is where the bond connecting two atoms A and B is split into separate radical species (unpaired species) due to equal sharing of a pair of electrons (possibly coming from atoms having similar electronegativities)

❖ In this case a single barbed arrowhead is used



Contd……

❖ Specific case;



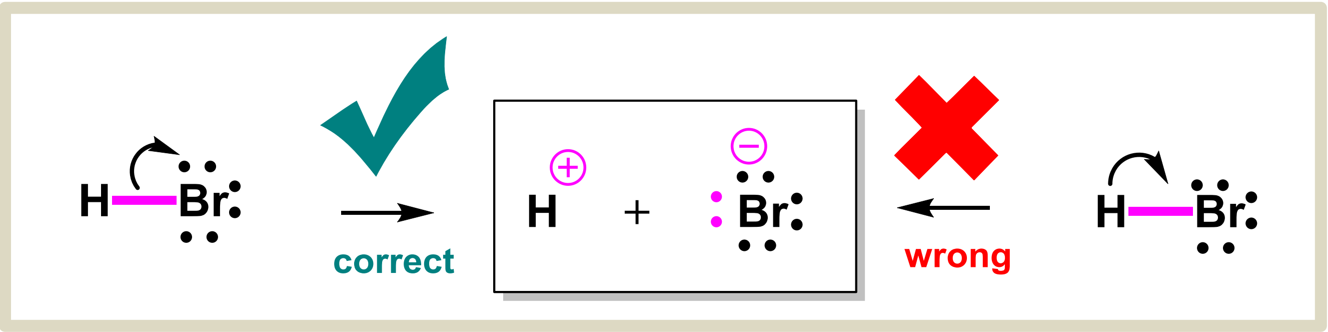
❖ Note:

✓ In general, radical species are very reactive species (scavengers) due to an incomplete octet configuration

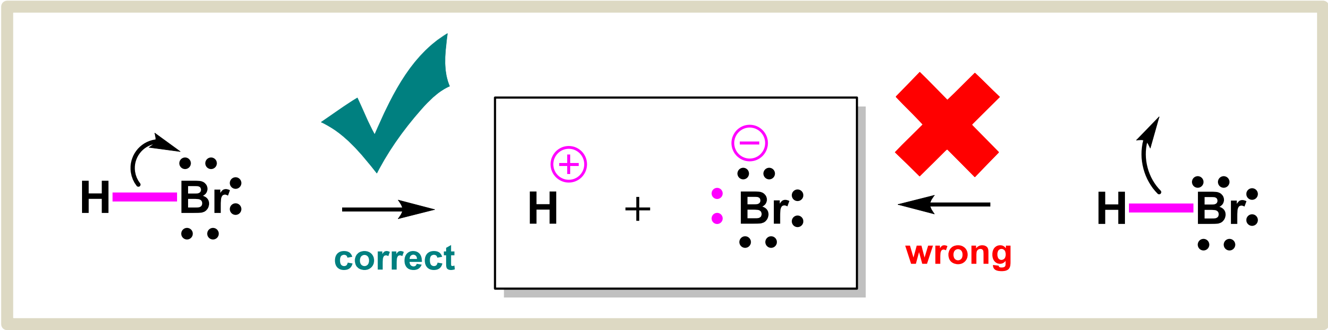
✓ All reactions involving free radical mechanism uses a single barbed arrow head

Contd......

- ✓ **Never use a curved arrow to show the movement of an atom**

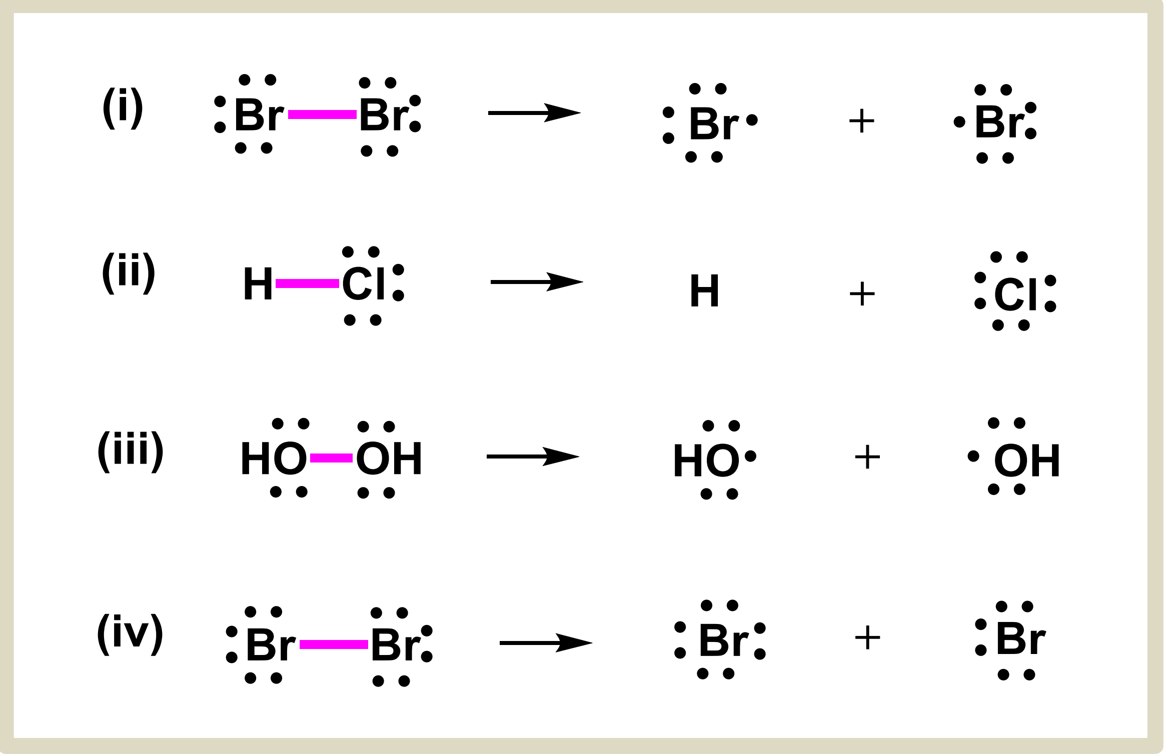


- ✓ **Never draw the head of the curved arrow pointing in space**



Practice Question(s)

1. State whether the highlighted bond has broken homolytically or heterolytically? By using the correct curved arrow notation show how? And state the charges on the ionic species formed if possible.

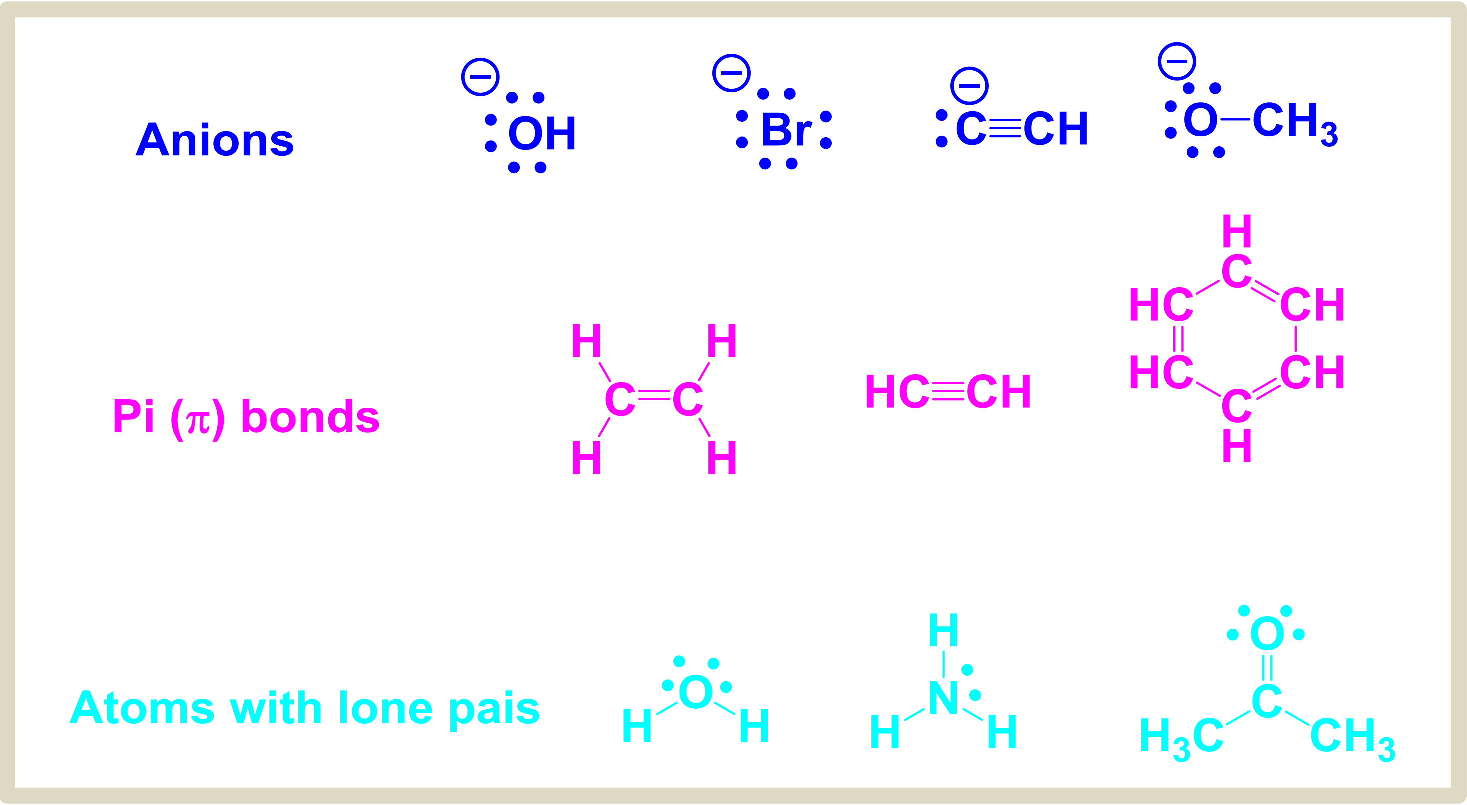


10.81 Classification of Reagents

- They are mainly two types of reagents in organic chemistry namely; (i) Nucleophiles (electron rich site) and (ii) Electrophiles (electron poor site)
- (i) Nucleophiles
- ✓ Translation; Nucleus loving species
- ✓ Chemical meaning; reacts with positively charged or partially positive atoms (electrophiles: electron loving)
- ✓ Characteristics: Nucleophilic atoms will have either lone pairs or pi (π) bonds that can be used to form new bonds with electrophiles

Contd……

- ✓ **Examples;**



Contd……

- ❖ (ii) Electrophiles

- ✓ Translation; Electron loving species

- ✓ Chemical meaning; reacts with sources of electrons (nucleophiles: nucleus loving)

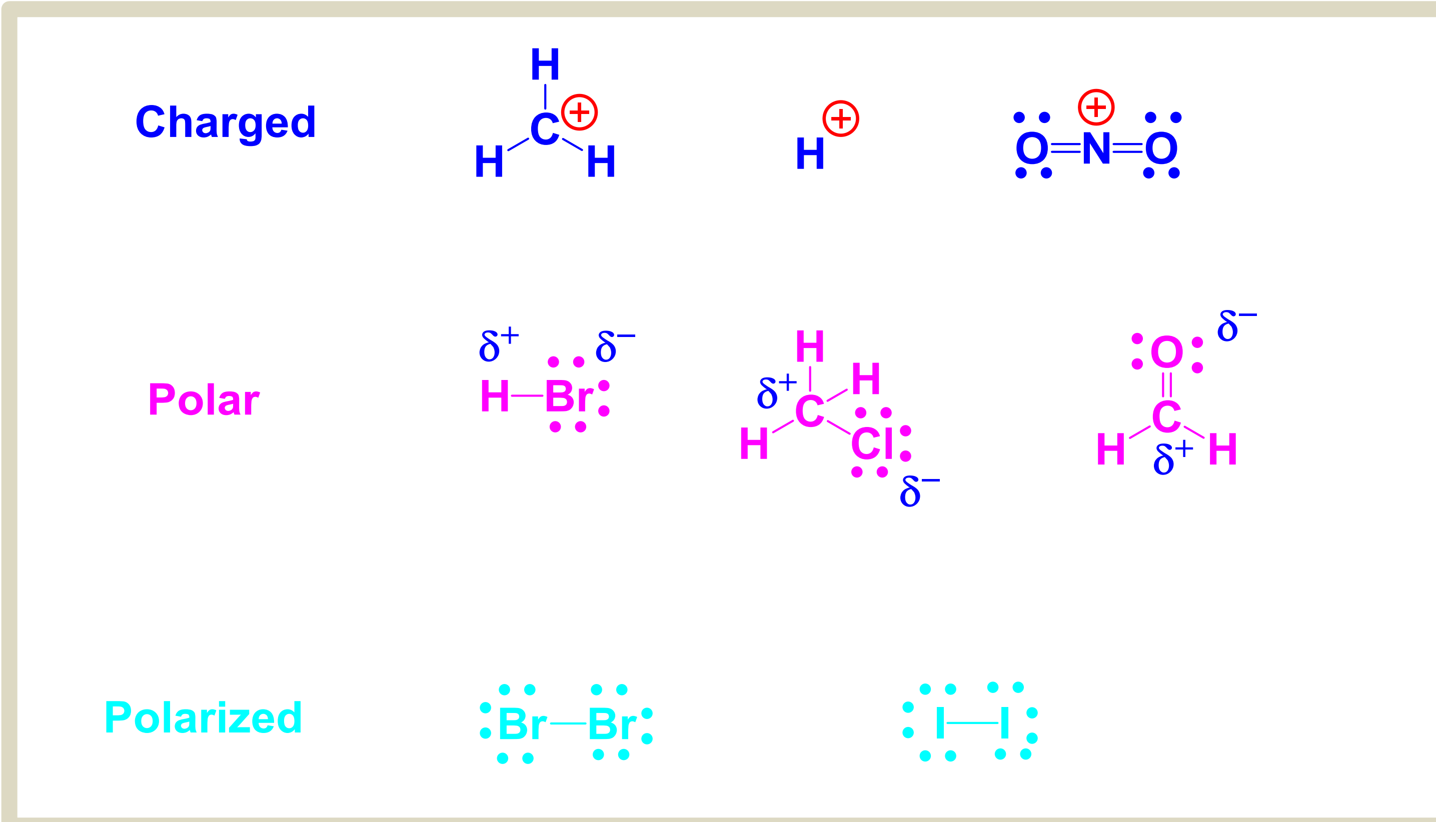
- ✓ Characteristics: Electrophilic atoms will have

  - a postive charge or partially positive charge or a very polarisable bond

  - empty orbital or heterolytically breakable bond (as a leaving group)

Contd……

✓ **Examples;**



❖ **Note: Electrons will always flow from a nucleophile (electron rich site) to an electrophile (electron poor site) in a chemical reaction**

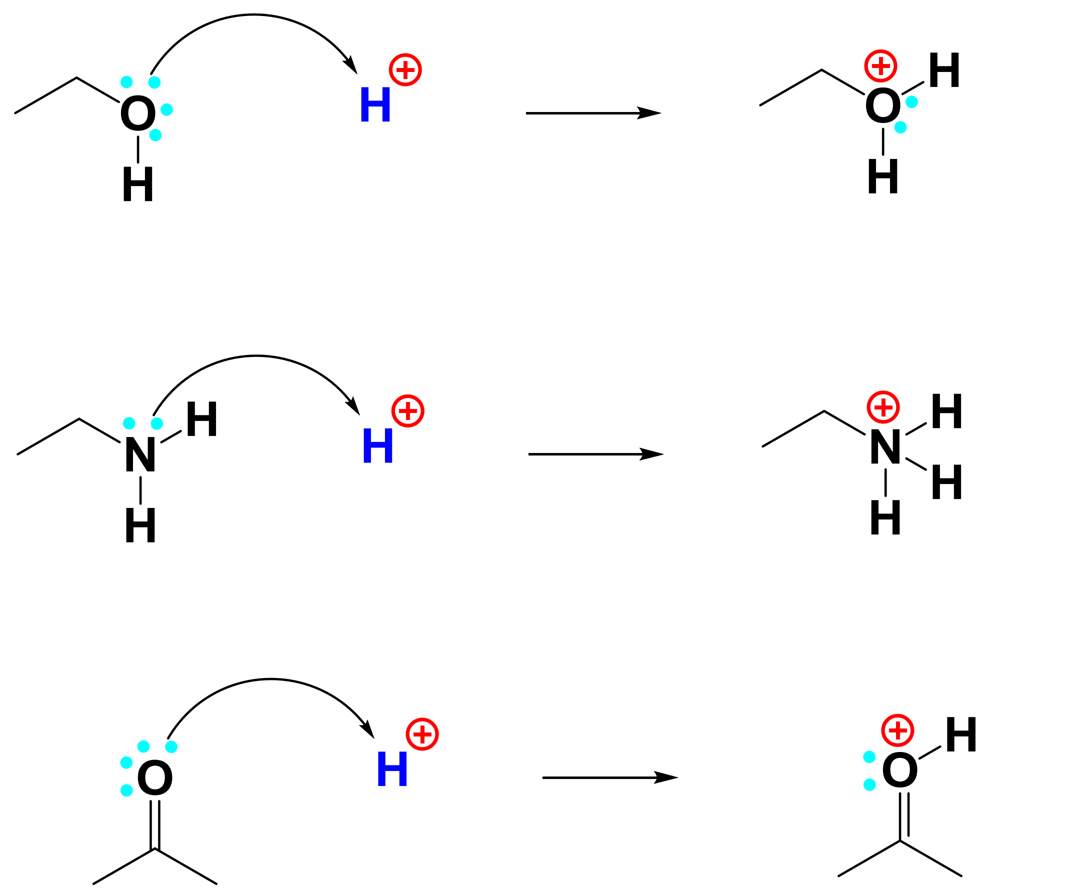
10.82 Arrow Pushing Mechanism and Bond Making/breaking

❖ Electron rich site in one molecule reacts with electron poor site in another molecule

(i)

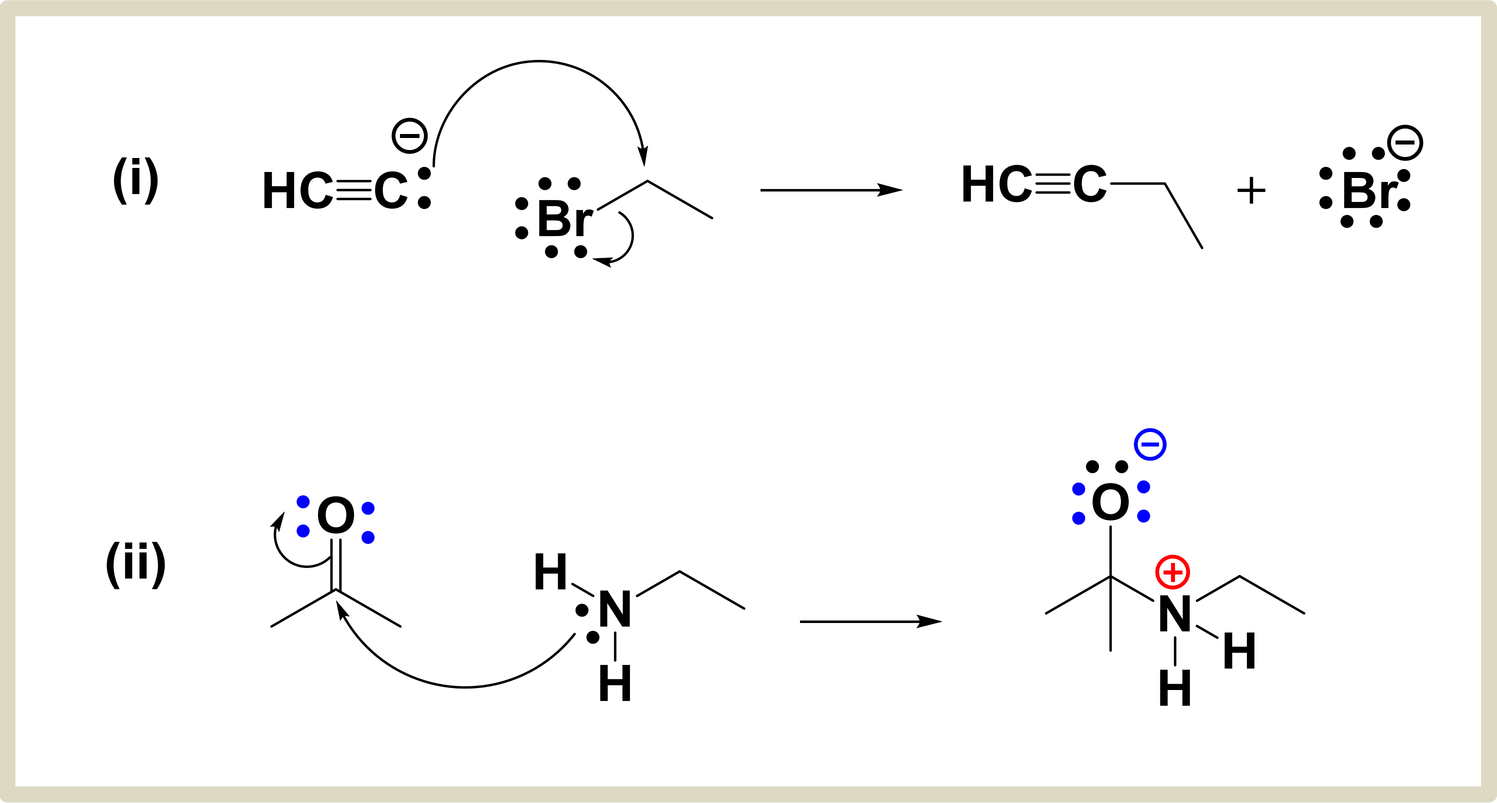
(ii)

(iii)



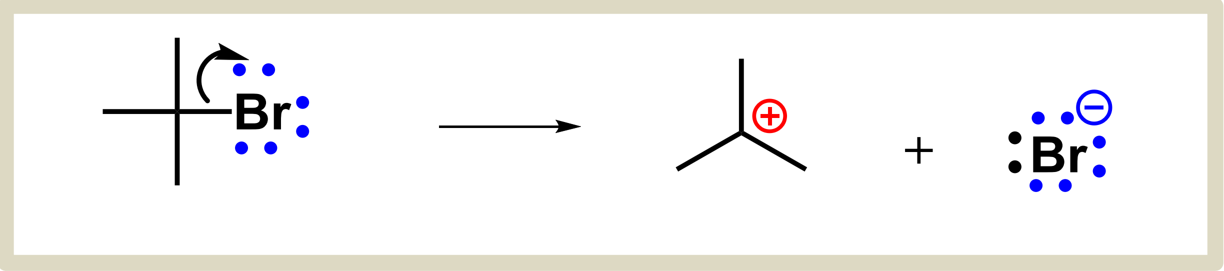
Contd……

- A bond is broken when one atom leaves with both electrons from the former bond



Contd……

- A bond is broken when one atom carries both electrons from the former bond



10.9 Reactions of Alkanes

- Alkanes are saturated hydrocarbons with the general formula, C_nH_{2n+2}
- They are obtained from crude oil by fractional distillation, cracking and reformation
- Alkanes are used as fuels
- As fuels they release heat energy when;

✓ Completely combusted (burnt) in (excess oxygen)

$$C_2H_6\,(g) + {}^{7}/_{2}\,O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(l)$$

✓ Incompletely combusted (burnt) in (limited oxygen)

$$C_2H_6\,(g) + {}^{5}/_{2}\,O_2\,(g) \rightarrow 2CO\,(g) + 3H_2O\,(l)$$

10.91 Free Radical Substitution Reactions of Alkanes

- Generally, because the C-C and C-H bonds in alkanes are relatively strong, alkanes do not react with many reagents
- In the presence of UV (Ultra Violet) light, alkanes react with chlorine to form a mixture of products with the halogens substituting the hydrogen atom
- General reaction

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

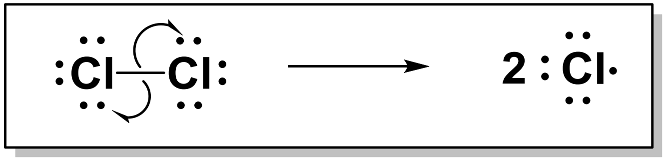
- Note; this is the overall reaction, but a more complex mixture of products is usually formed

$$CH_3CH_3 \quad CH_2Cl_2 \quad CHCl_3 \quad CCl_4$$

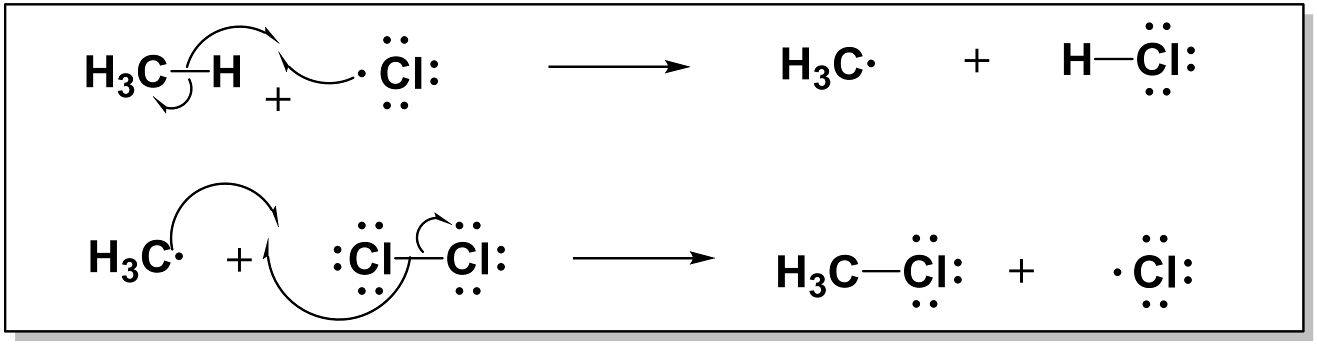
Contd……

- **Mechanism**

- **Step 1; Initiation reaction**

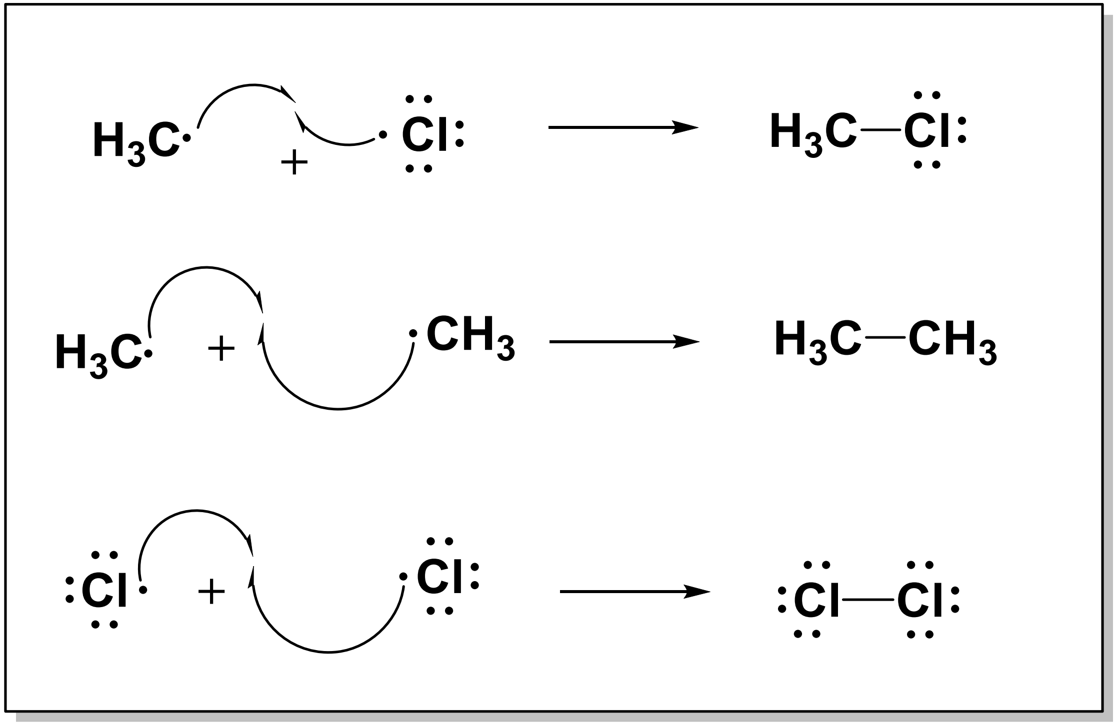


- **Step 2; Propagation**



Contd……

❖ **Step 3; termination**



Practice Question(s)

❖ Write a detailed mechanism for the following reactions;

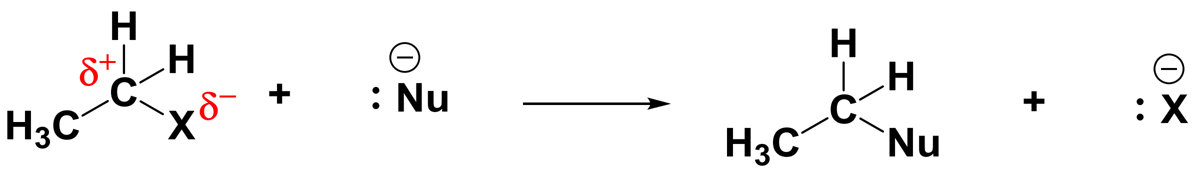
(i) $CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$

(ii) $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$

11.92 Substitution reaction of Halogenoalkane

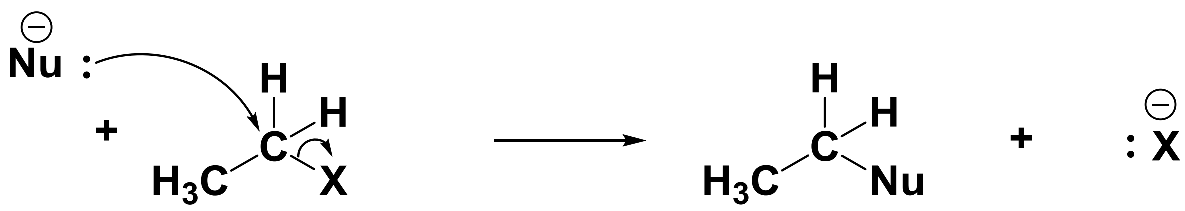
❖ Halogenoalkanes undergo substitution reactions with nucleophiles (Nu)= OH, CN, H_2O, NH_3 etc..

❖ General reaction



where x = Cl, Br or I

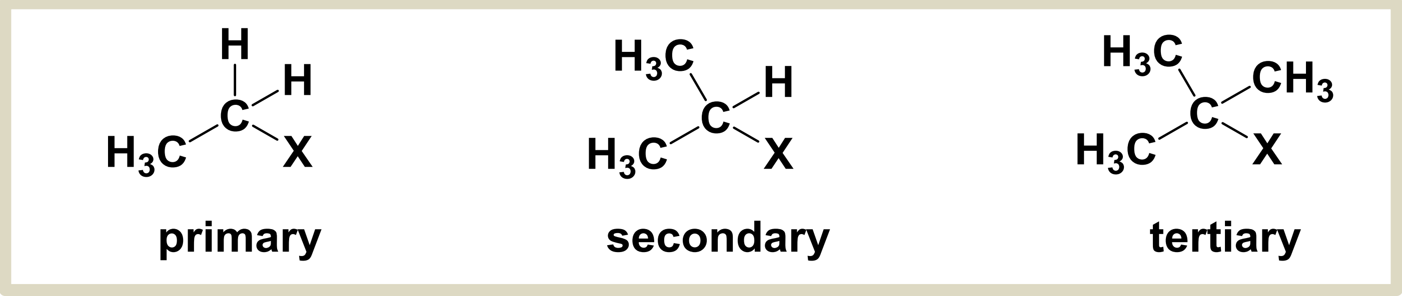
❖ Mechanism



where x = Cl, Br or I

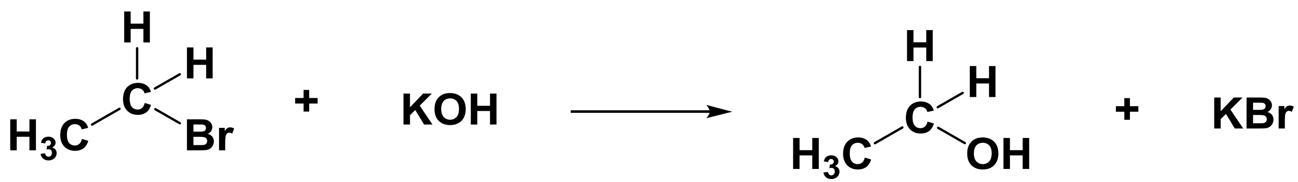
Contd……

- Nucleophilic substitution with aqueous hydroxide ions results in the transformation of the haloalkane to an alcohol
- They are two types of nucleophilic substitution reaction involving the reaction of halogenoalkanes with aqueous hydroxide ions namely; Nucleophilic Unimolecular Substitution (S_N1) and Nucleophilic bimolecular Substitution (S_N2)
- This depends on the structure of halogenoalkane
- For example; tertiary halogenoalkane undergo S_N1 while secondary and primary halogenoalkane undergo S_N2

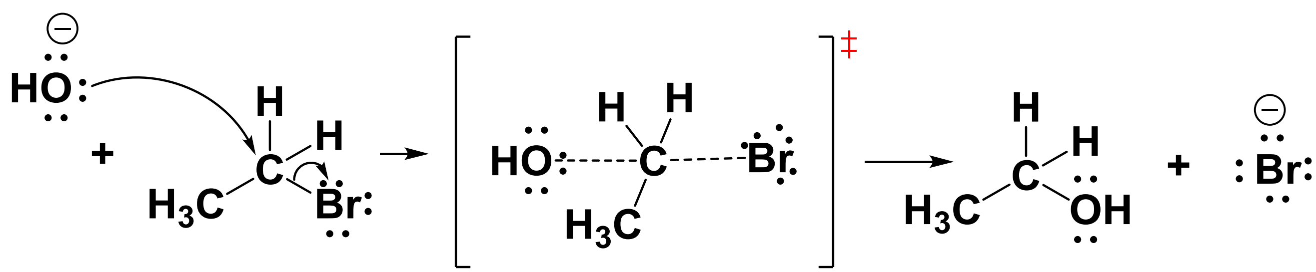


Contd......

- **Specific reaction (S_N2)**



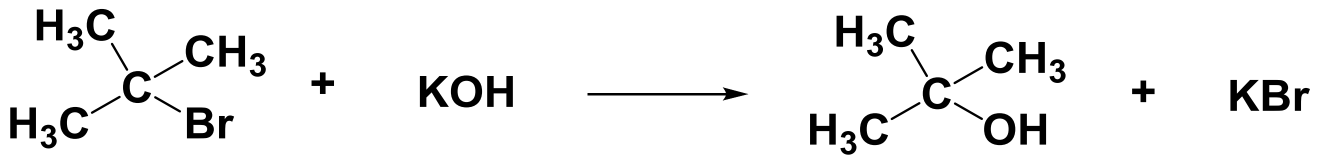
- **Mechanism**



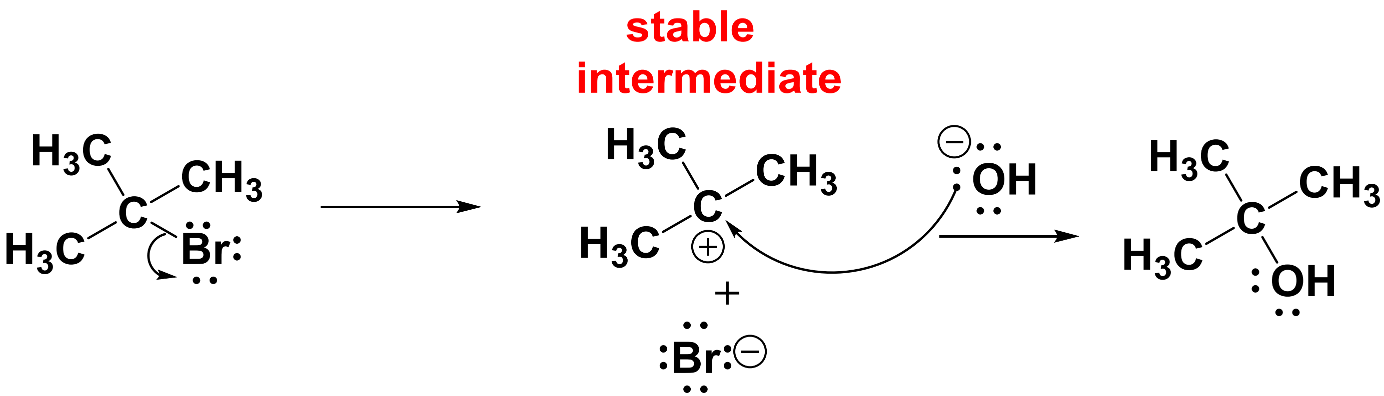
‡ = transistion state

Contd……

- Specific reaction (S_N1)

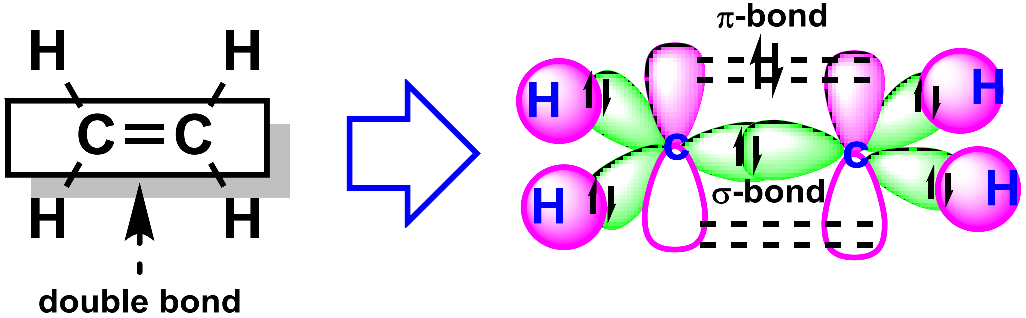


- Mechanism



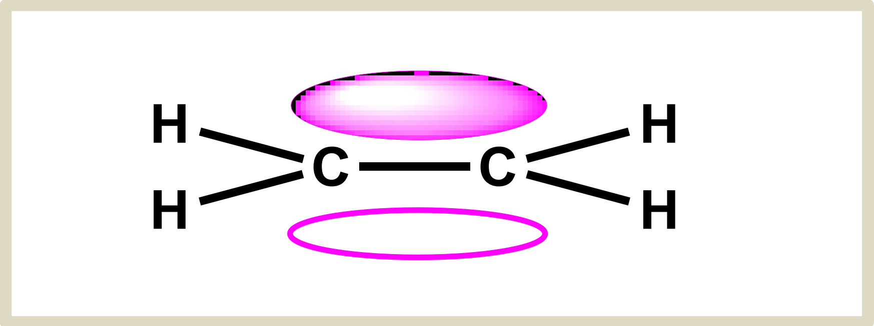
11.0 Alkenes

- Alkenes are unsaturated hydrocarbons whose molecular formula is C_nH_{2n}
- Recall; They contain atleast one double bond (σ and π) in their structures



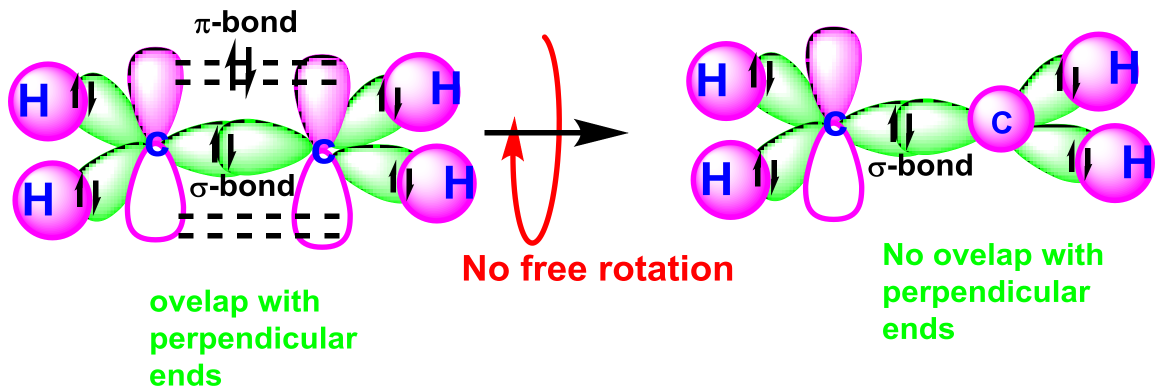
- The π-bond is weaker than the σ-bond
- Because of the side ways overlap of the π-bond in alkenes, this results in;

✓ The high density of electrons from above and below (susceptible to electrophiles)

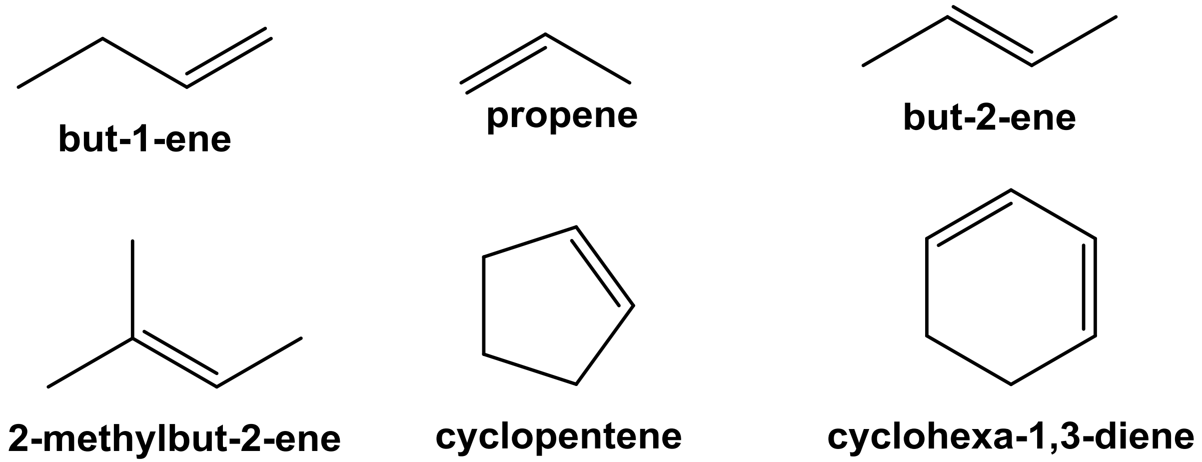


Contd……

✓ Lack of free rotation about the double bond



❖ Examples of alkenes



11.1 Stereoisomerism in Alkenes

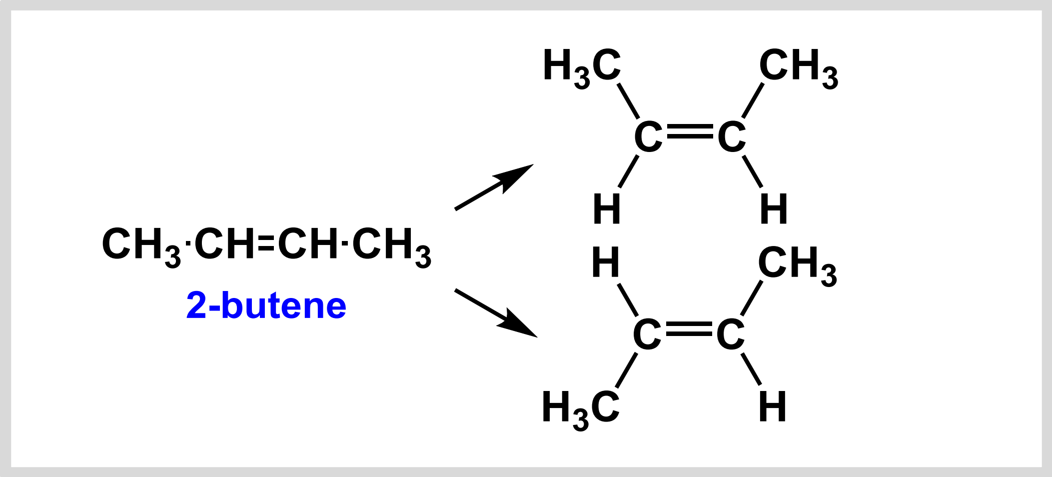
- Geometrical isomers are stereoisomers have the same molecular and structural formula but have different spatial arrangement of atoms

✓ Alkenes can exhibit a type of isomerism called E-Z Geometric isomerism

✓ E-Z Geometric isomerism can exist when:

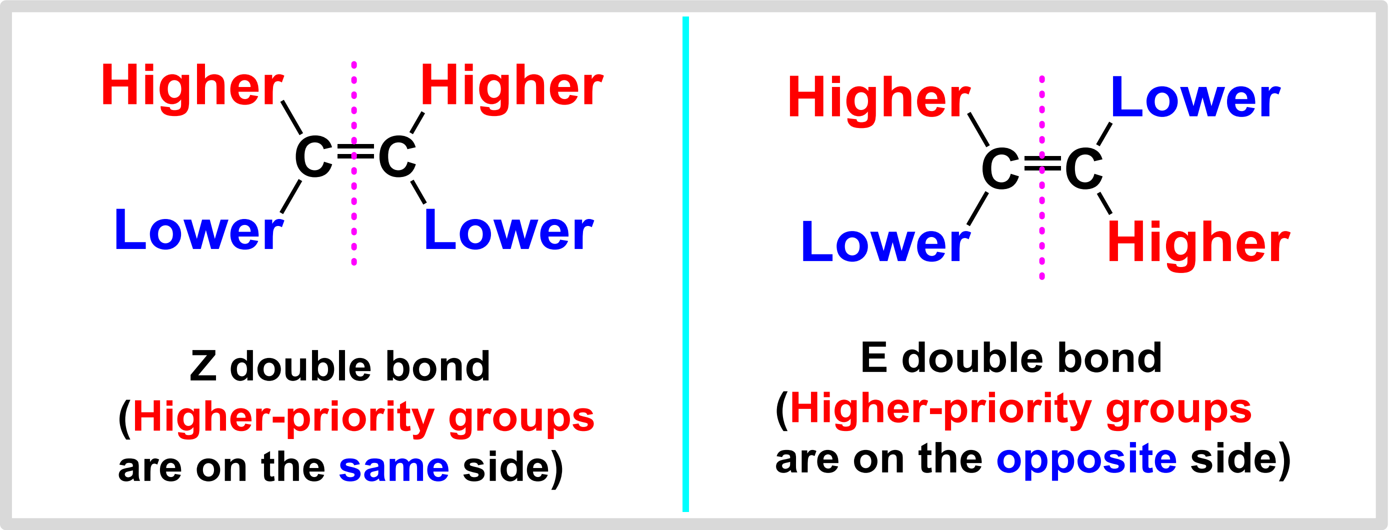
- There is restricted rotation around the C=C double bond.
- There are two different groups/atoms attached at both double bond carbons

- Example is 2-butene



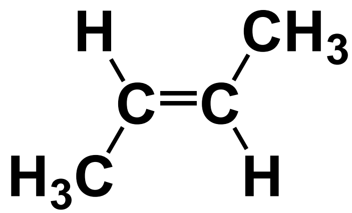
Contd……

- How do we assign the E/Z configuration?
- The two different groups/atoms attached at both double bond carbons must have different molecular weights
- The higher the molecular weight, the higher the priority; and the lower the molecular weight the lower the priority
- General Example

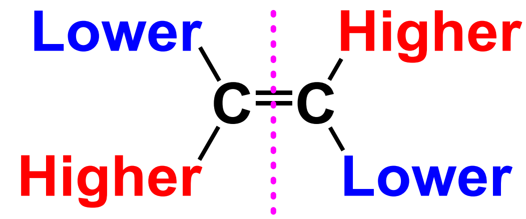


Contd……

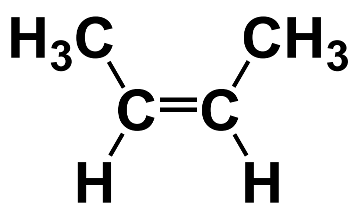
❖ **Specific Example**



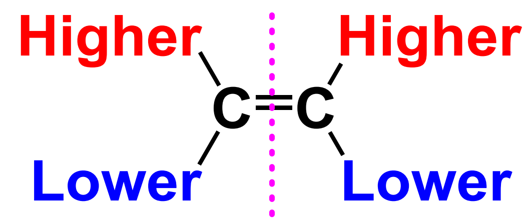
(*E*)-but-2-ene



E double bond
(Higher-priority groups are on the opposite side)



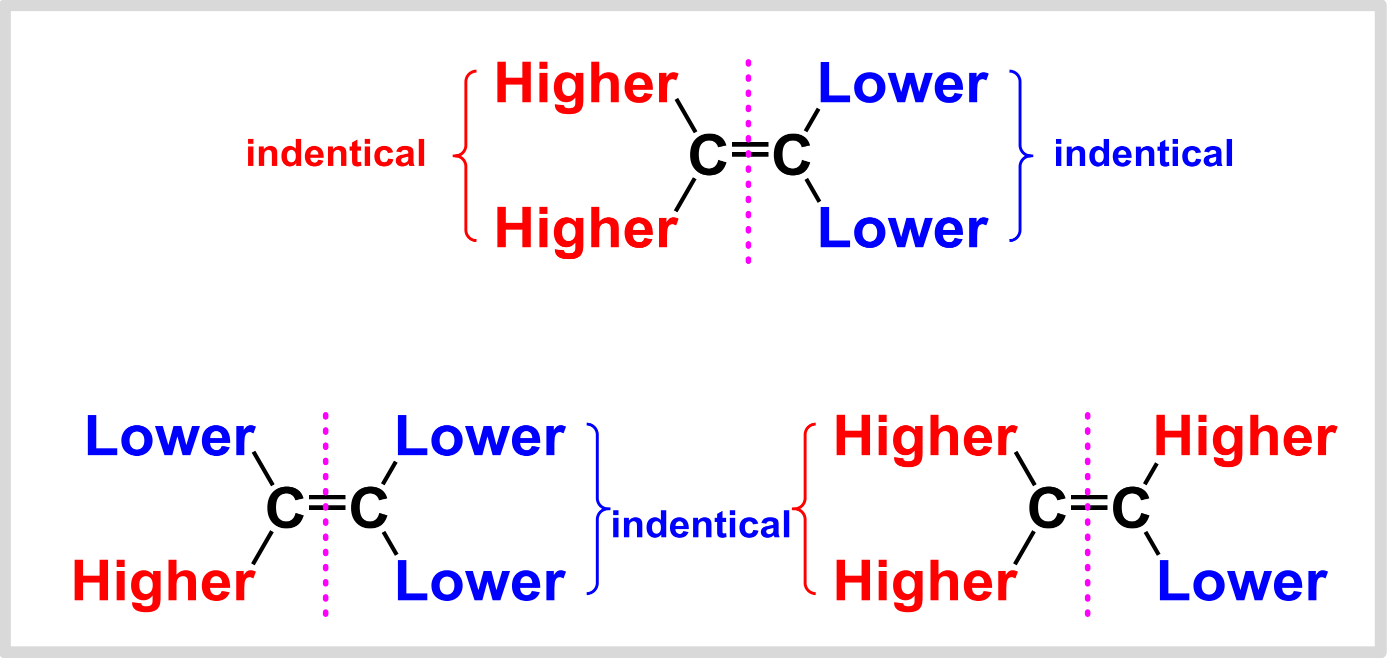
(*Z*)-but-2-ene



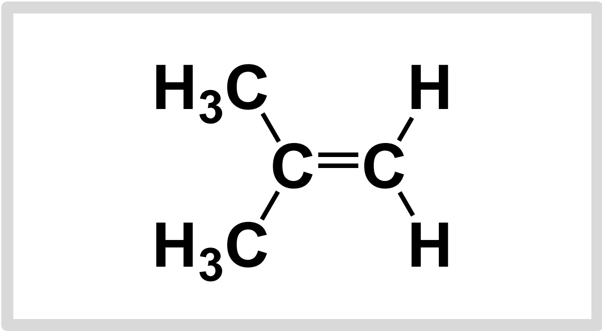
Z double bond
(Higher-priority groups are on the same side)

Contd……

- **Note;** Alkenes cannot be geometrical isomers or assigned E/Z configuration if the atoms attached on each of the end carbons are identical



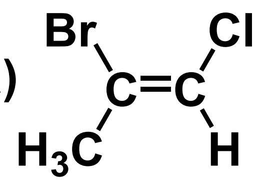
- Example



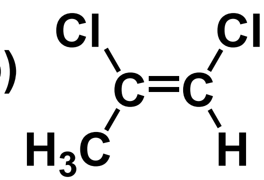
Practice Question(s)

❖ Determine whether the following compounds are geometrical isomers, and assign the E/Z configuration where possible;

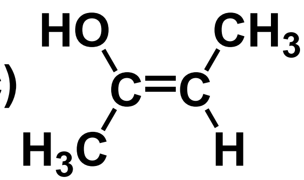
(a)



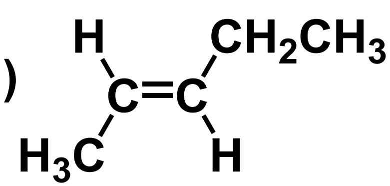
(b)



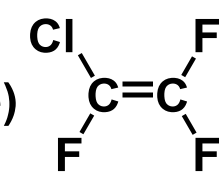
(c)



(d)



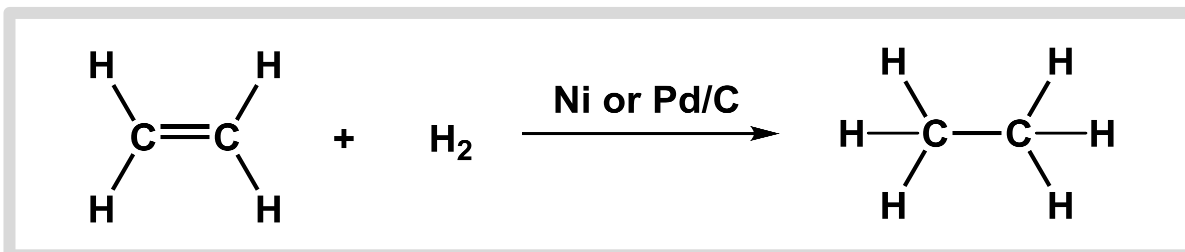
(e)



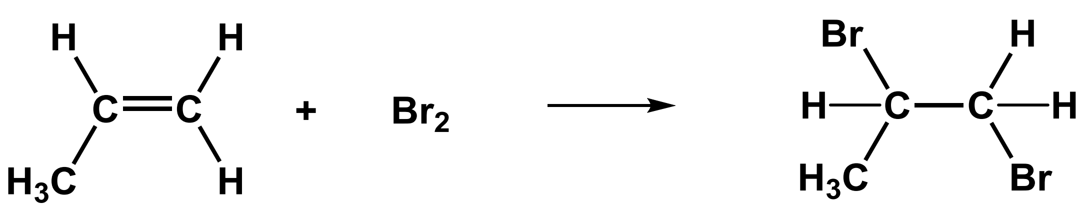
11.2 Reaction of Alkenes

- Alkenes undergo addition reactions with hydrogen, H_2, hologens, X_2 and HX (X=Cl, Br and I) acid

- ✓ Alkenes reacts with hydrogen in the presence of a transition metal catalyst such as nickel or palladium to produce alkanes



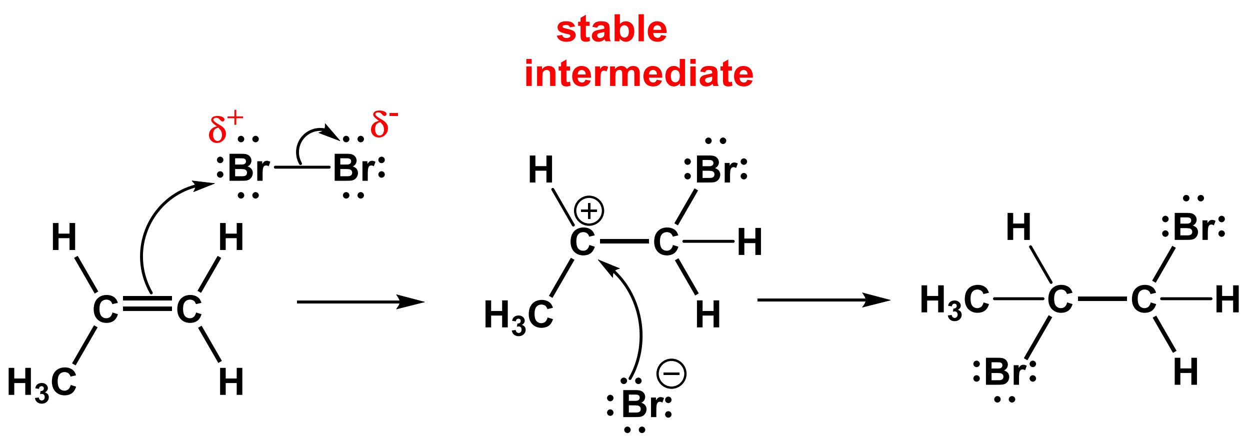
- ✓ Alkenes reacts with bromine to produce a dibromoalkane



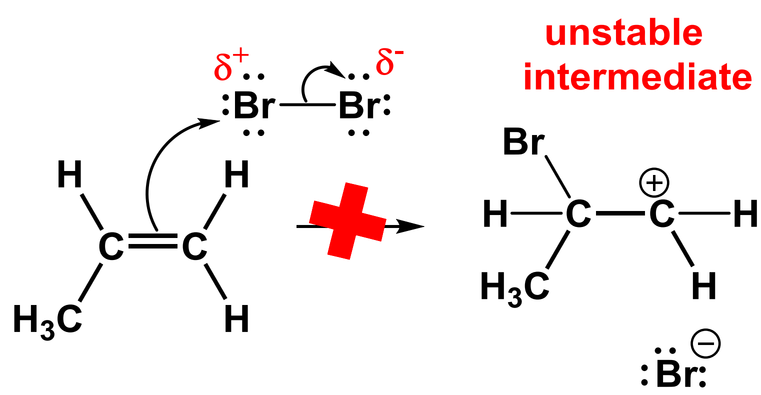
- Note; This is the test for unsaturation or the presence of a double bond in a given organic compound

11.2 Reaction of Alkenes

❖ Mechanism

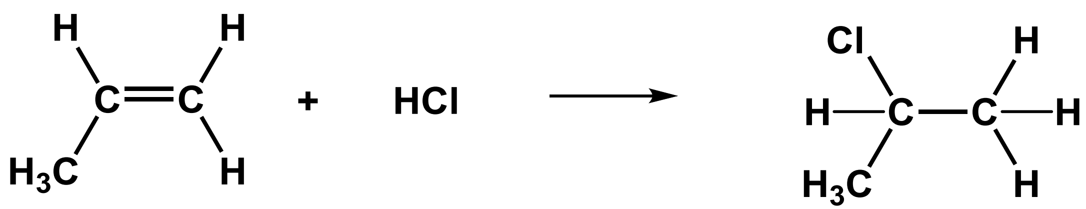


- **Note;**

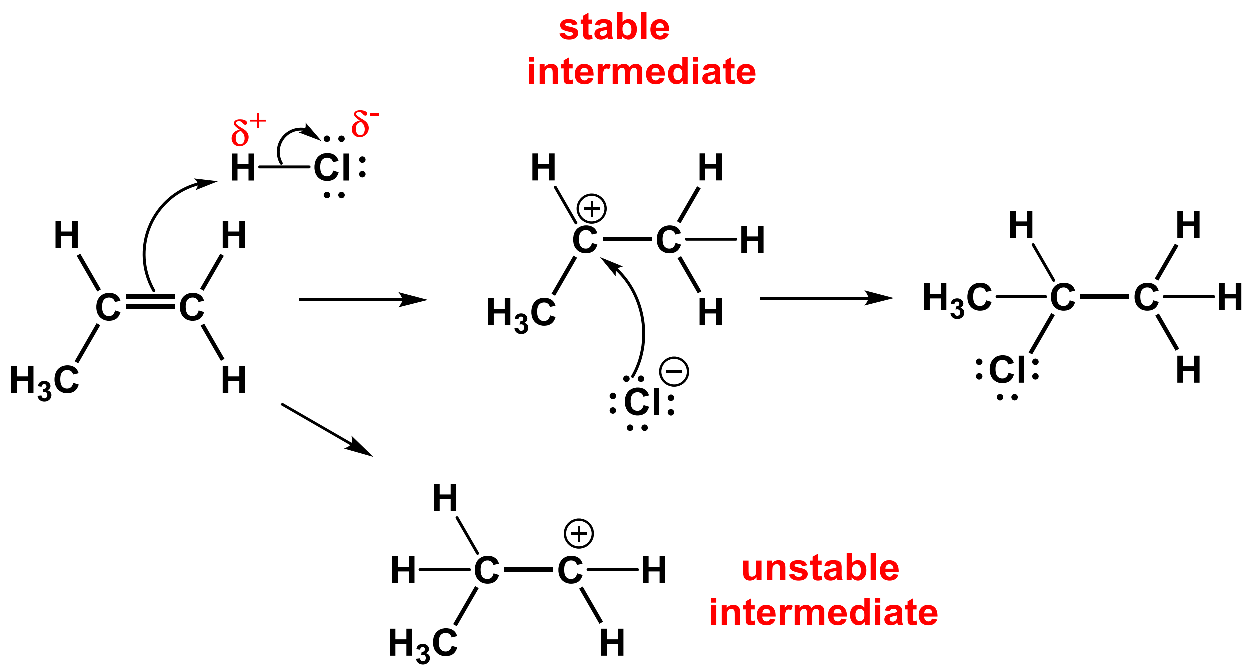


Contd……

❖ Alkenes reacts with hydrogen chloride to produce a chloroalkane

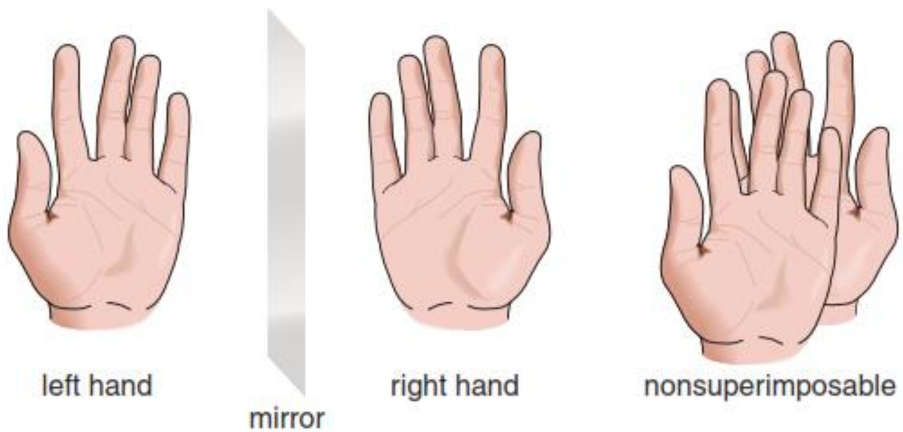


❖ Mechanism



12.0 Stereochemistry

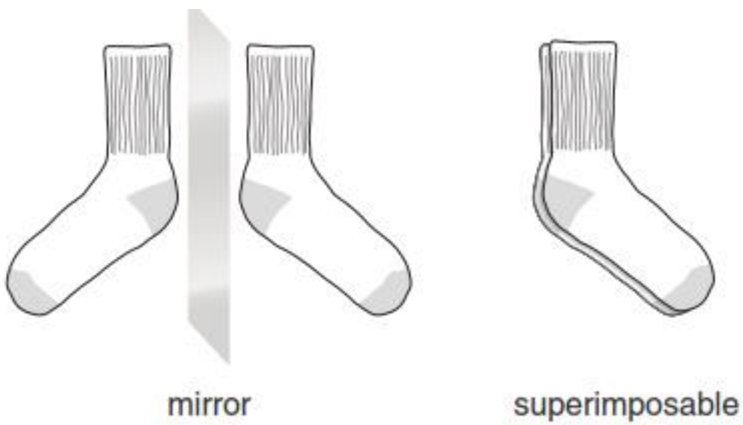
- Stereochemistry refers to the 3-dimensional properties and reactions of molecules
- It has its own language and terms that need to be learned in order to fully communicate and understand the concepts
- Some molecules are like hands. Left and right hands are mirror images, but they are not identical or superimposable



- A molecule (or object) that is not superimposable on its mirror image is said to be chiral

Contd……

- Other molecules are like socks. Two socks from a pair are mirror images that *are superimposable.*
- A sock and its mirror image are *identical*



- A molecule (or object) that is superimposable on its mirror image is said to be achiral

Contd……

- Let's determine whether three molecules—H_2O, CH_2BrCl, and CHBrClF—are superimposable on their mirror images; that is, are H_2O, CH_2BrCl, and CHBrClF chiral or achiral?
- To test chirality:

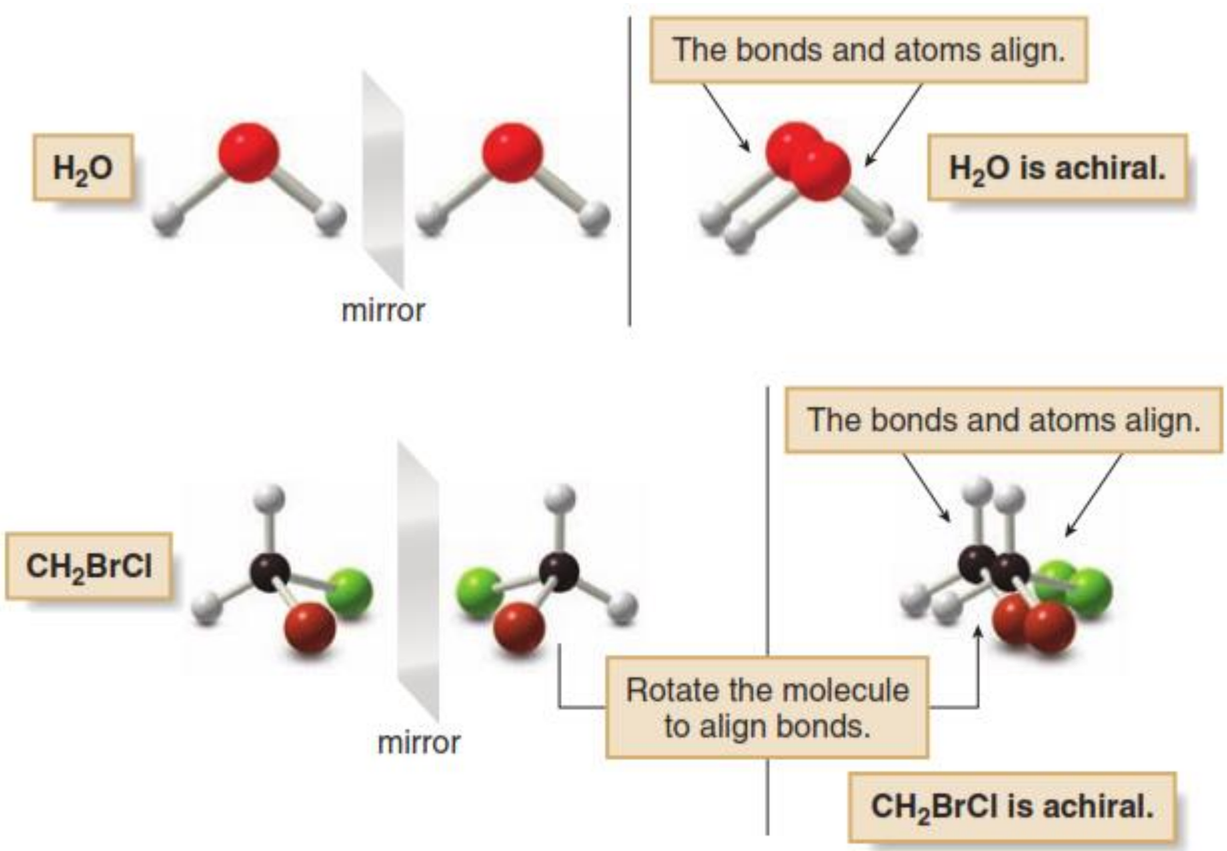
✓ Draw the molecule in three dimensions.

✓ Draw its mirror image.

✓ Try to align all bonds and atoms. To superimpose a molecule and its mirror image you can perform any rotation but you cannot break bonds

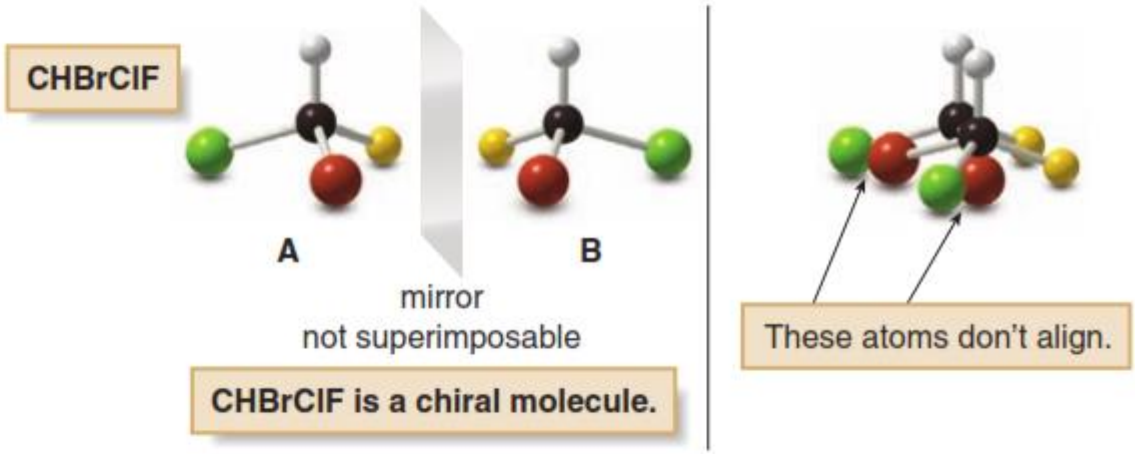
Contd……

❖ Following the procedure; we can see that H_2O and CH_2BrCl are achiral



Contd……

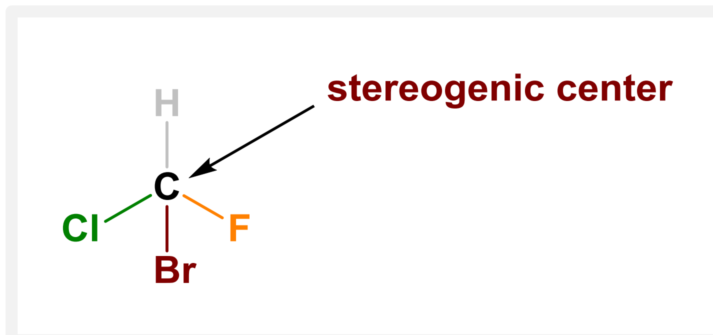
- And $CHBrClF$ is chiral



- Note: A and B are different compounds
- A and B are stereoisomers because they are isomers differing only in the three-dimensional arrangement of substituents. These stereoisomers are called enantiomers.

Contd……

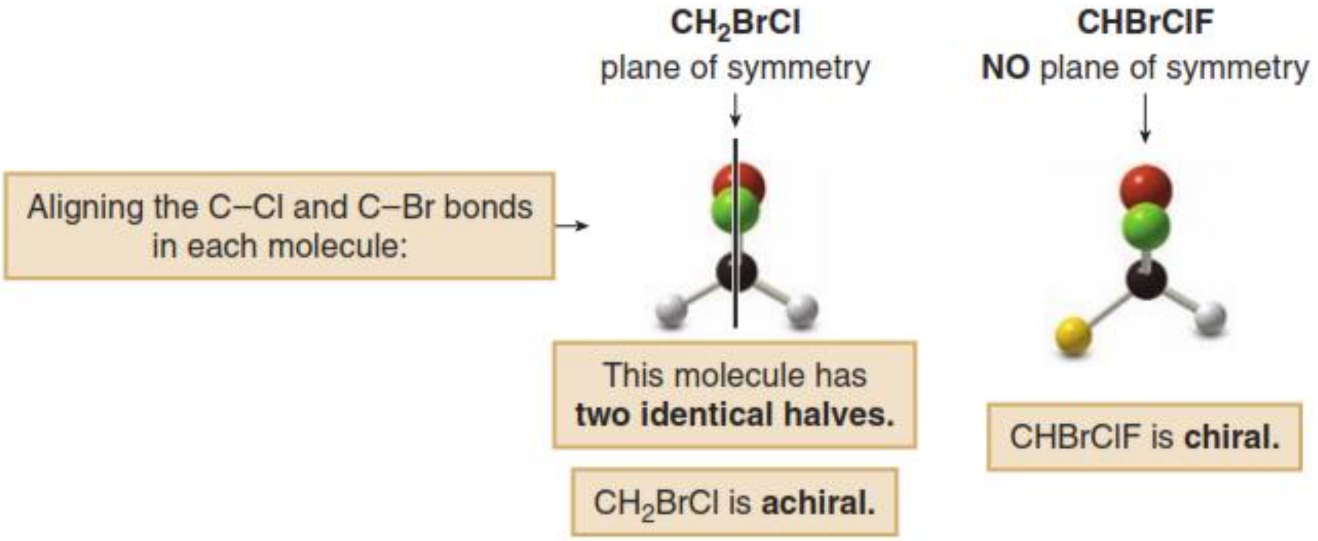
- CHBrClF contains a carbon atom bonded to four different groups
- A carbon atom bonded to four different groups is called a tetrahedral *stereogenic center (chiral center)*



- Note; always omit from consideration all C atoms that can’t be tetrahedral stereogenic centers. These include:
- ✓ CH_2 and CH_3 groups (more than one H bonded to C)
- ✓ Any *sp or sp²* hybridized C (less than four groups around C)

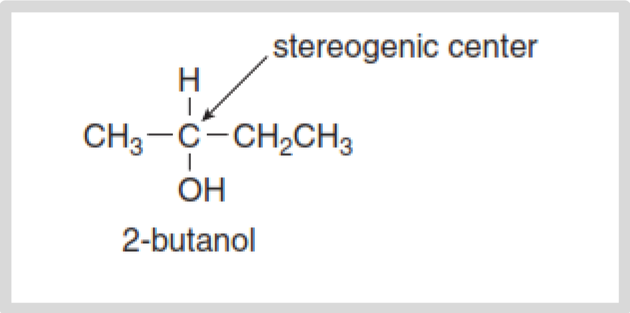
Contd……

- CH_2BrCl has a plane of symmetry, but the chiral molecule CHBrClF does not



Contd……

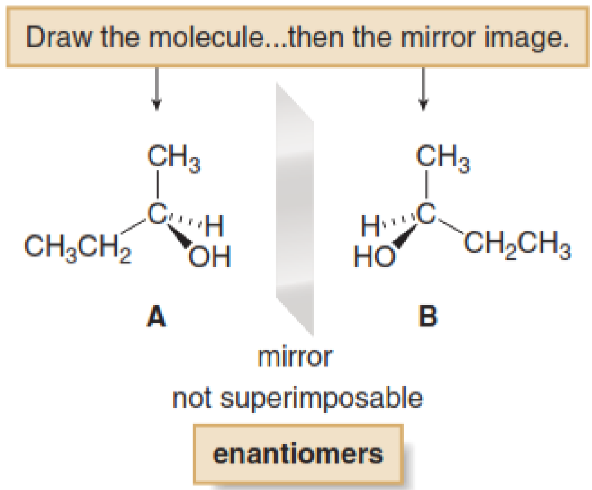
- In general any molecule with;
- ✓ No stereogenic center is not chiral e.g H_2O
- ✓ One tetrahedral stereogenic center is a chiral compound and exists as a pair of enantiomers
- 2-Butanol, for example, has one stereogenic center



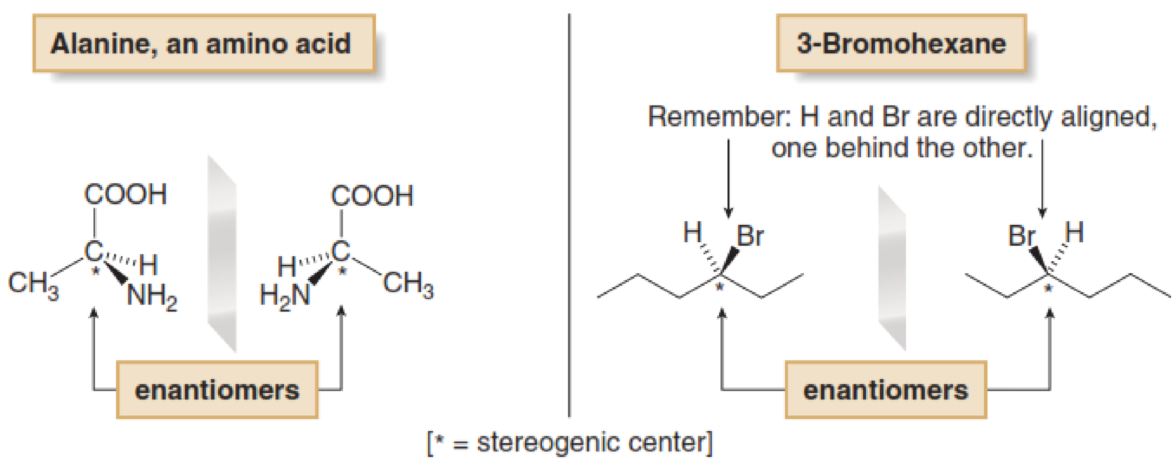
- To draw both enantiomers, use the typical convention for depicting a tetrahedron: place two bonds in the plane, one in front of the plane on a solid wedge, and one behind the plane on a dashed wedge

Contd……

- Then, to form the first enantiomer A, arbitrarily place the four groups—H, OH, CH_3 CH_2CH_3—on any bond to the stereogenic center

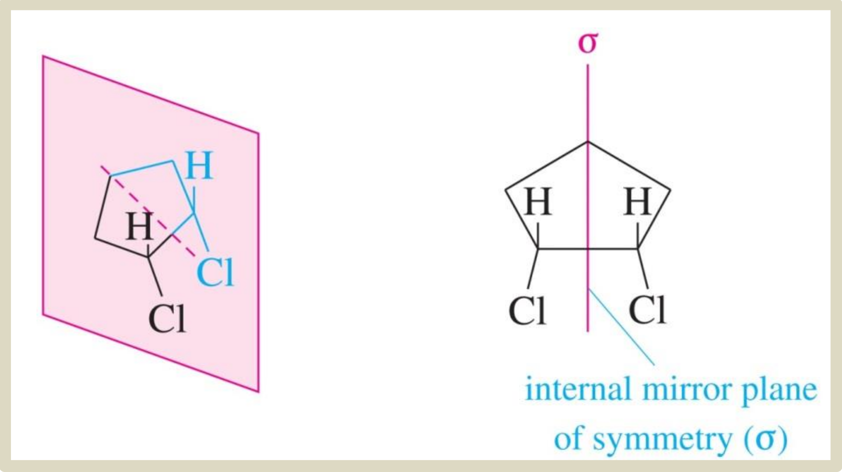


❖ Other examples



Contd……

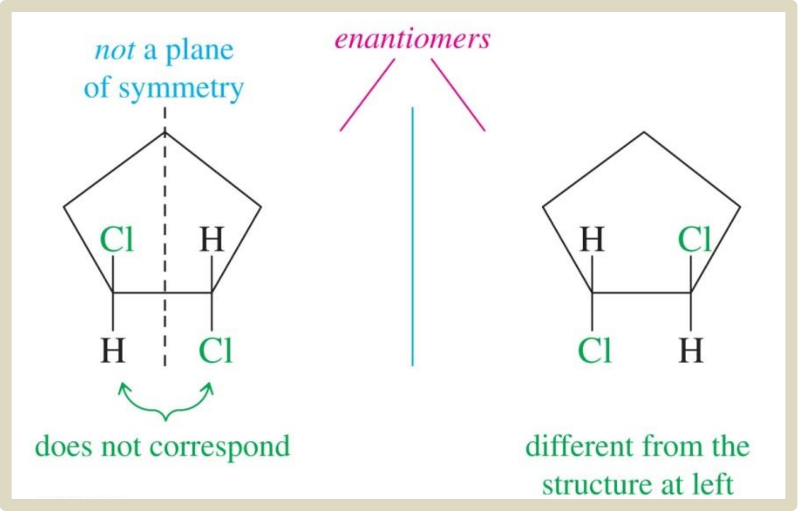
- ✓ **Two or more stereogenic centers, a molecule *may or may not be chiral***
- ➢ **E.g Cyclic Compounds**
- ***Cis*-1,2-dichlorocyclopetane**



- **The molecule is achiral because the molecule has an internal plane of symmetry**
- **Both structures above can be superimposed (they are identical to their mirror images)**

Contd……

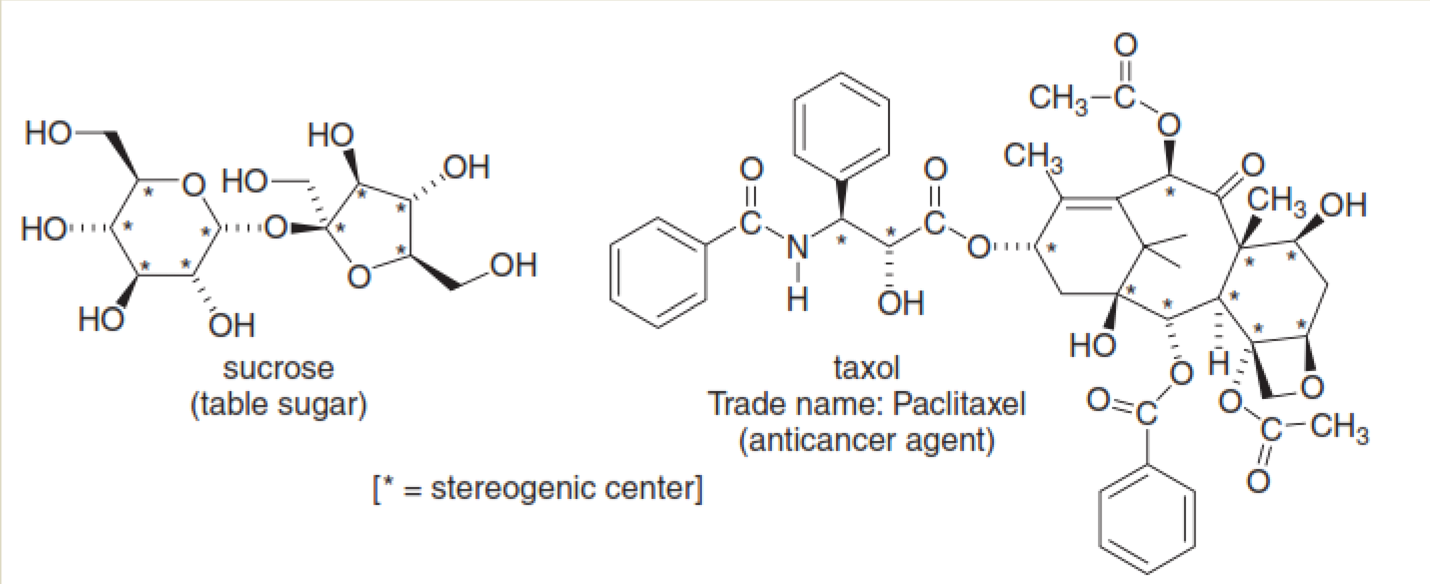
- *Trans*-1,2-dichlorocyclopentane



- The molecule does not have a plane of symmetry so the images are nonsuperimposable and the molecule has two enantiomers

Contd……

- ❖ Examples of biological molecules with stereogenic centers
- ✓ Sucrose, with nine stereogenic centers on two rings, is the carbohydrate used as table sugar
- ✓ Taxol, with 11 stereogenic centers, is an anticancer agent active against ovarian, breast, and some lung tumors



sucrose
(table sugar)

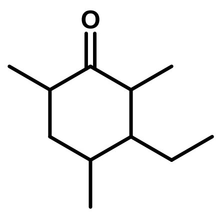
taxol
Trade name: Paclitaxel
(anticancer agent)

[* = stereogenic center]

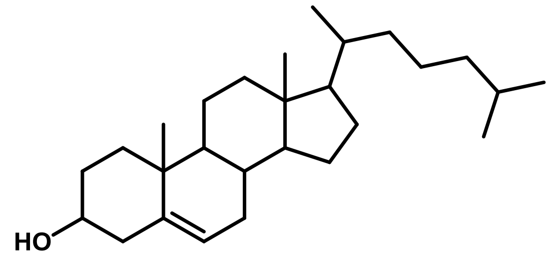
Practice Question(s)

❖ Locate the stereogenic centers in each compound

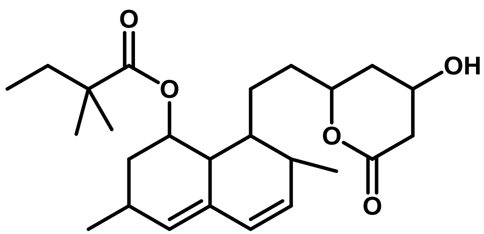
(a)



(b)



(c)



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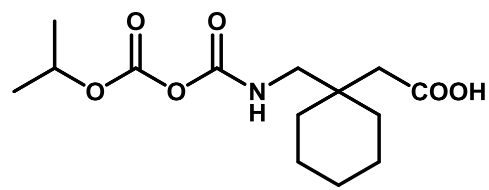


❖ Locate the stereogenic center in each compound and draw both enantiomers

(a) $CH_3CH(Cl)CH_2CH_3$ (b) $CH_3CH_2CH(OH)CH_2OH$

12.1 Absolute Configuration R or S

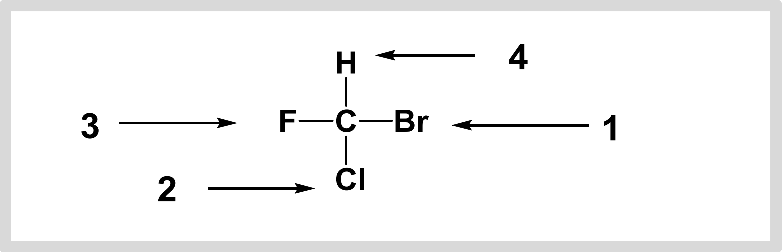
- Enantiomers have different spatial arrangements of the four groups attached to the asymmetric carbon
- The two possible spatial arrangements are called configurations
- Each asymmetric carbon atom is assigned a letter (*R*) or (*S*) based on its three-dimensional configuration
- Cahn–Ingold–Prelog convention is the most widely accepted system for naming the configurations of chirality centers

Contd……

- **Rules Needed to Assign Priority**

- Assign priorities (1, 2, 3, or 4) to the atoms directly bonded to the stereogenic center in order of decreasing atomic number. The atom of highest atomic number gets the highest priority (1)

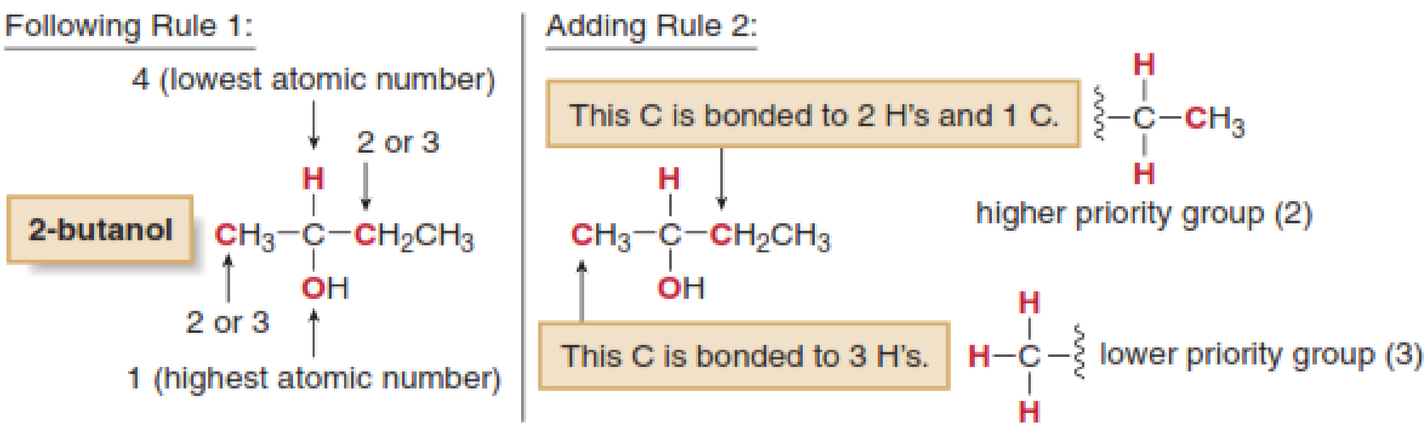
- In CHBrClF, priorities are assigned as follows: Br (1, highest) → Cl (2) → F (3) → H (4, lowest). In many molecules the lowest priority group will be H



Contd……

- If two atoms on a stereogenic center are the same, assign priority based on the atomic number of the atoms bonded to these atoms. One atom of higher atomic number determines a higher priority and if priority still cannot be assigned, continue along a chain until a point of difference is reached

✓ **Example 2-butanol**



✓ The order of priority of groups in 2-butanol is: –OH (1), $–CH_2CH_3$ (2), $–CH_3$ (3) and –H (4)

Contd……

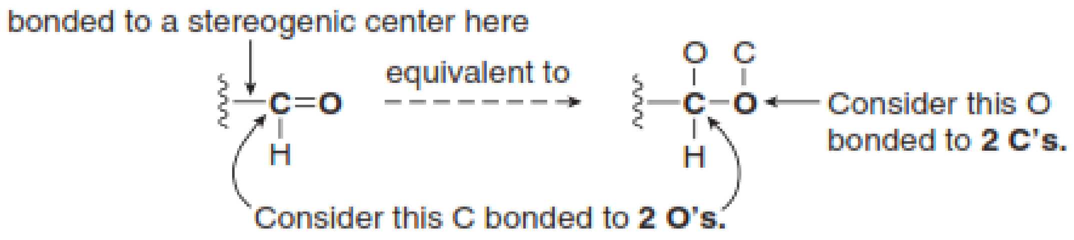
- If two isotopes are bonded to the stereogenic center, assign priorities in order of **decreasing mass number**

- ✓ **In comparing the three isotopes of hydrogen, the order of priorities is;**

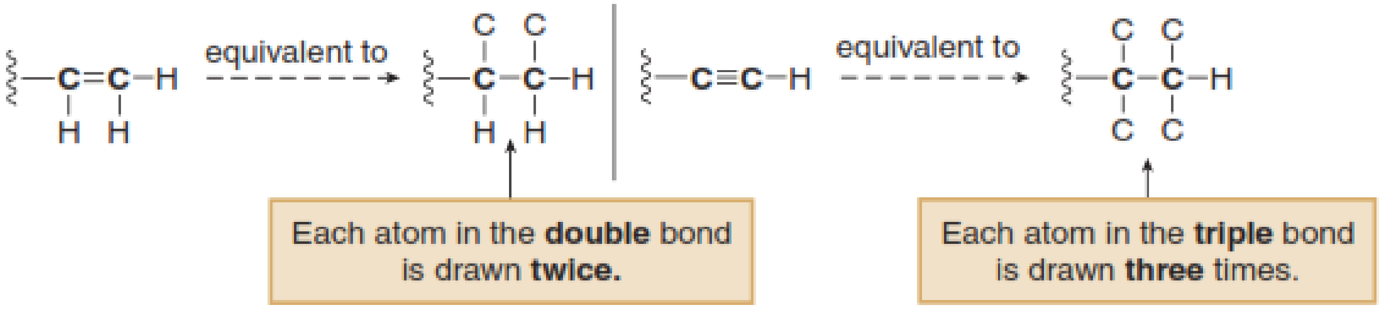
	Mass number	Priority
T (tritium)	3 (1 proton + 2 neutrons)	1
D (deuterium)	2 (1 proton + 1 neutron)	2
H (hydrogen)	1 (1 proton)	3

Contd……

- To assign a priority to an atom that is part of a multiple bond, treat a multiply bonded atom as an equivalent number of singly bonded atoms
- ✓ For example, the C of a C=O is considered to be bonded to two O atoms



- ✓ Other common multiple bonds are drawn below



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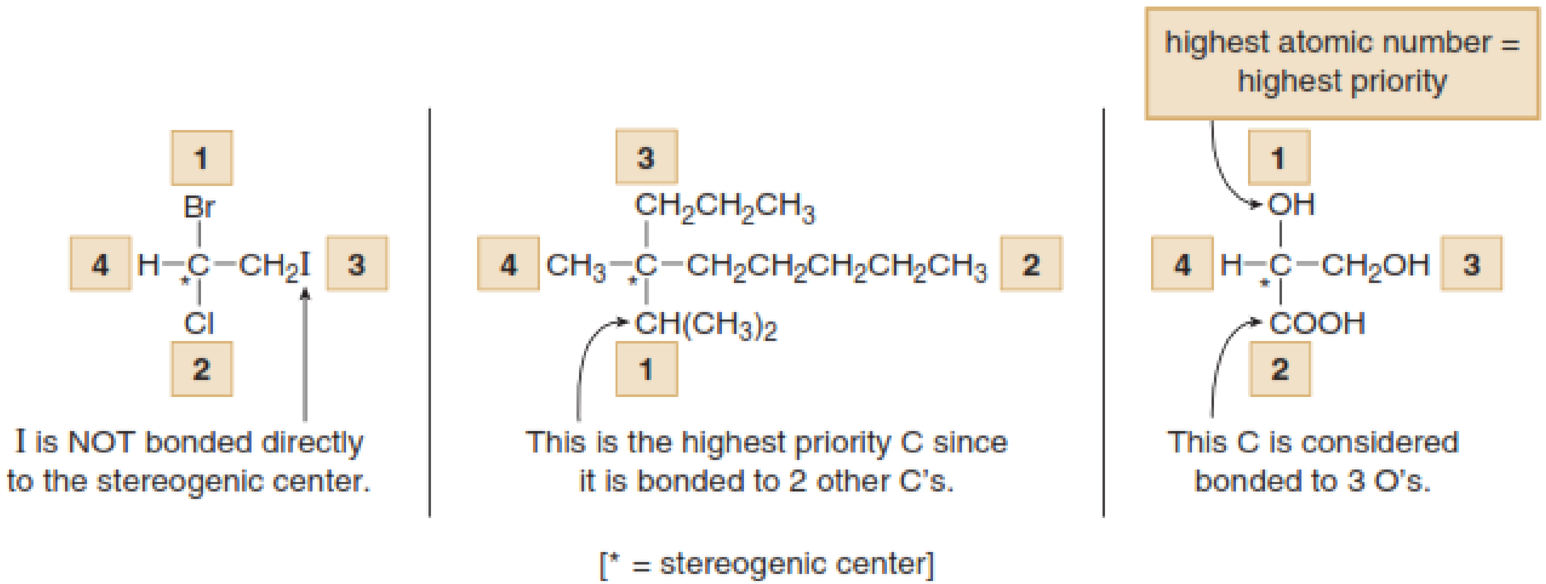
❑ **Examples of assigning priorities to stereogenic centers**



Practice Question(s)

1. Which group in each pair is assigned the higher priority?

(a) $-CH_3$, $-CH_2CH_3$ (b) -H, -D (c) $-CH_2CH_2Cl$, $-CH_2CH(CH_3)_2$

(d) $-CH_2Cl$, $-CH_2CH_2Cl$ (e) $-CH_2OH$, -CHO

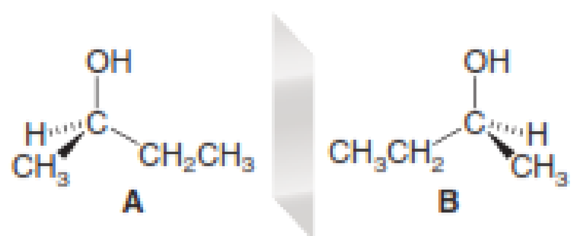
2. Rank the following groups in order of decreasing priority.

(a) -COOH, -H, $-NH_2$, -OH (b) $-CH_2CH_3$, -H, $-CH_3$, $-CH(CH_3)_2$

(c) $-CH_3$, -H, -Cl, $-CH_2Cl$

Contd……

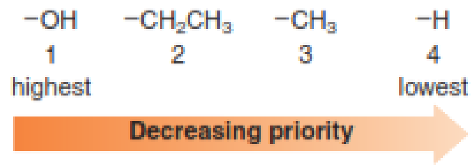
- Once priorities are assigned to the four groups around a stereogenic center, we can use three steps to designate the center as either *R or S*
- Note: R is derived from the Latin word rectus meaning "right" and S is from the Latin word sinister meaning "left"
- HOW TO assign *R or S to a Stereogenic Center*
- ✓ Example; Label each enantiomer as R or S



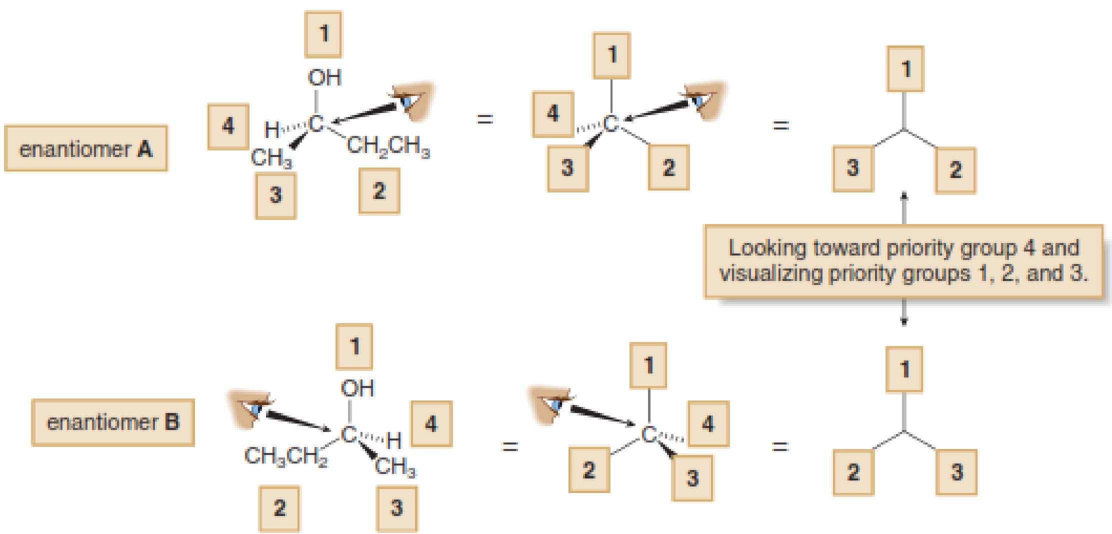
two enantiomers of 2-butanol

Contd……

- **Step [1]: Assign priorities from 1 to 4 to each group bonded to the stereogenic center**



- **Step [2]: Orient the molecule with the lowest priority group (4) back (on a dash), and visualize the relative positions of the remaining three groups (priorities 1, 2, and 3)**

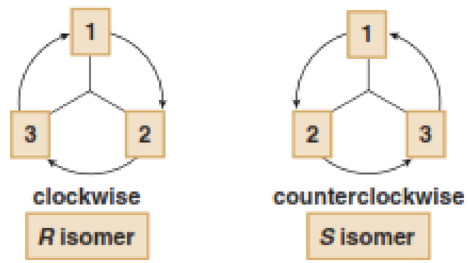


Contd……

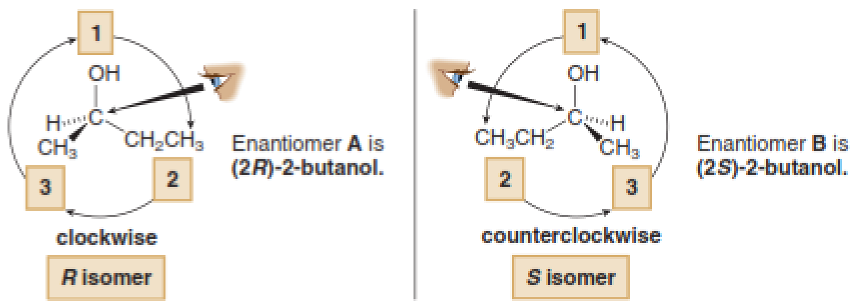
- **Step [3]:** Trace a circle from priority group 1 → 2 →3

- If tracing the circle goes in the clockwise direction—to the right from the noon position—the isomer is named R

- If tracing the circle goes in the counterclockwise direction—to the left from the noon position—the isomer is named S

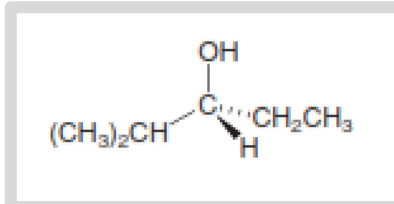


- The letters R or S precede the IUPAC name of the molecule. For the enantiomers of 2-butanol

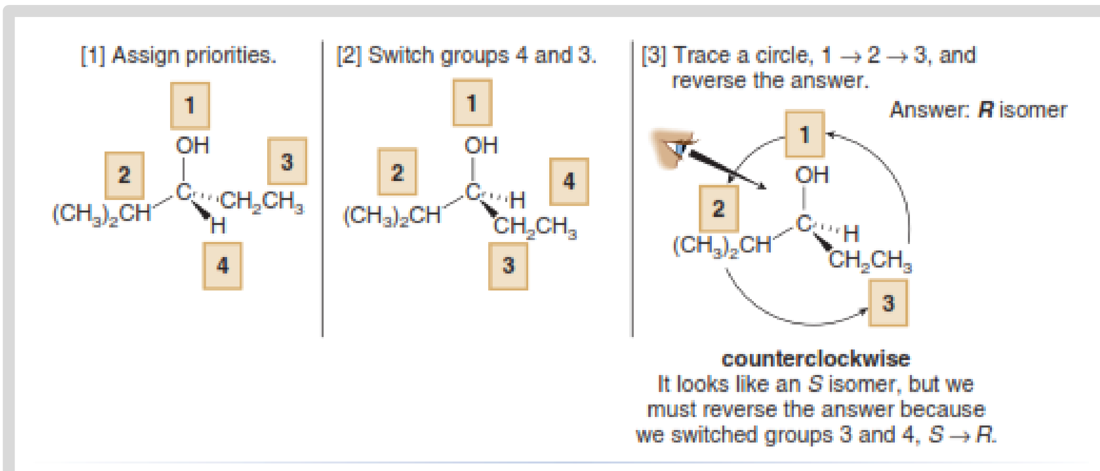


Contd……

2. Label the following compounds as R or S

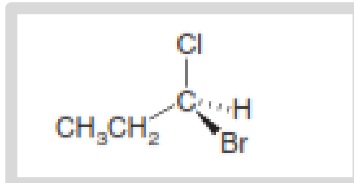


❖ **Solution**

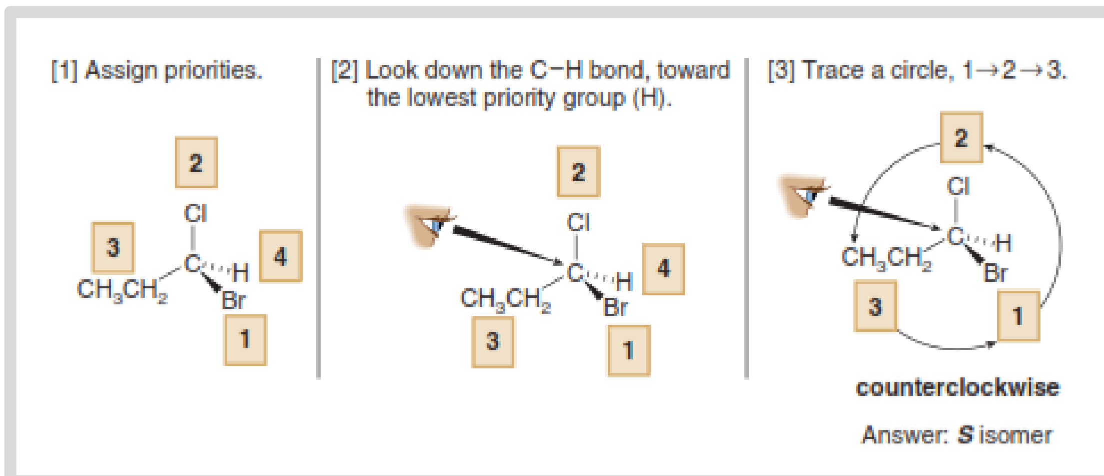


Contd……

1. Label the following compounds as R or S

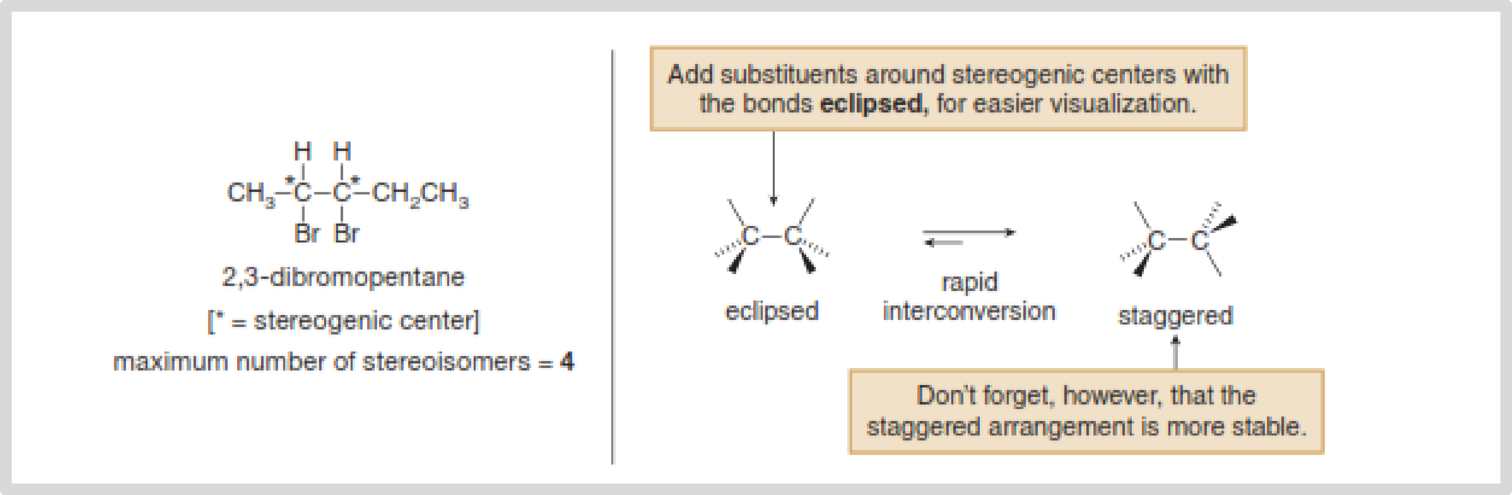


❖ Solution



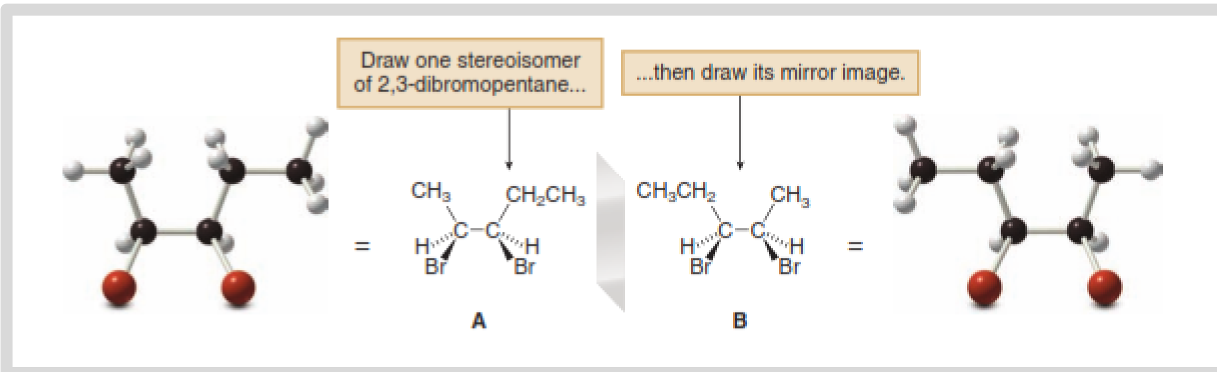
Contd……

- **Note: A molecule with two stereogenic centers *may or may not be* chiral**
- **For n stereogenic centers, the maximum number of stereoisomers is 2^n**
- **When n = 2, $2^n = 2^2 = 4$. With two stereogenic centers, the maximum number of stereoisomers is four, although sometimes there are *fewer than four***
- **Let's illustrate a stepwise procedure for finding all possible stereoisomers using 2,3-dibromopentane**

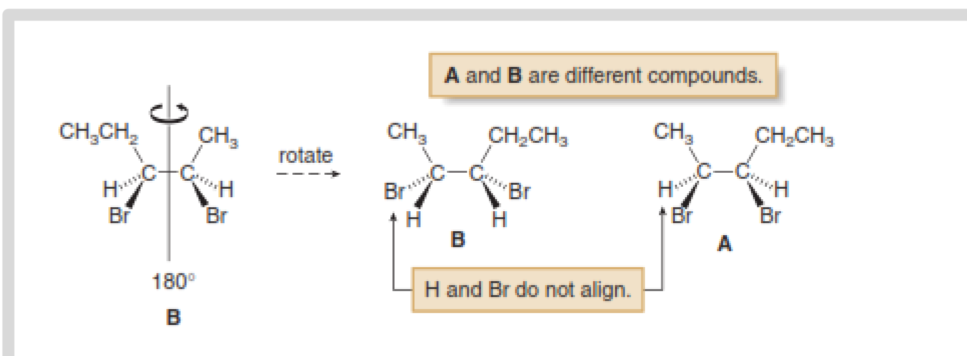


Contd……

✓ **Step [1]: Draw one stereoisomer by arbitrarily arranging substituents around the stereogenic centers. Then draw its mirror image**



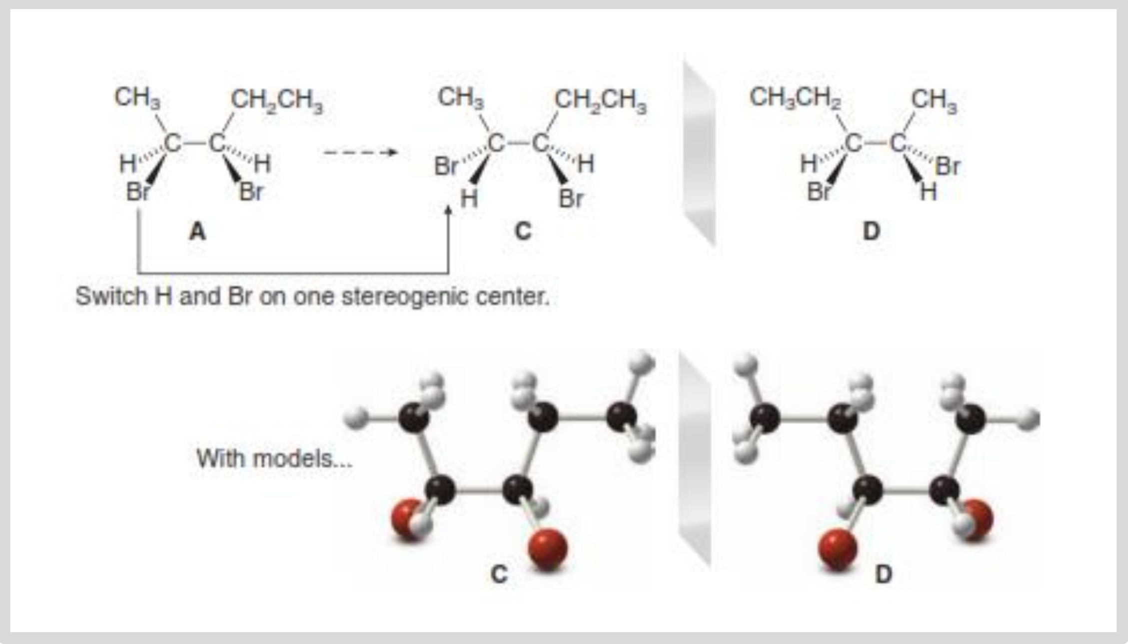
- **Determine whether A and B are superimposable by flipping or rotating one molecule to see if all the atoms align**



- **In this case, the atoms of A and B do not align, making A and B nonsuperimposable mirror images—enantiomer**

Contd……

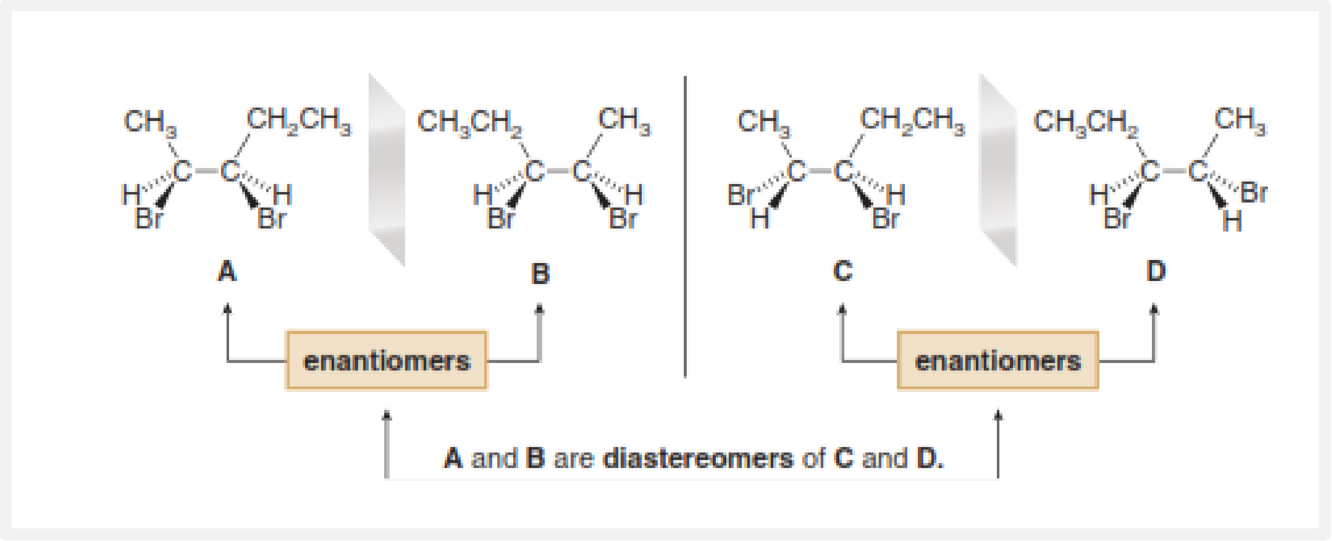
Step [2]: Draw a third possible stereoisomer by switching the positions of any two groups on one stereogenic center



- There are four stereoisomers for **2,3-dibromopentane**: enantiomers A and B, and enantiomers C and D
- **What is the relationship between two stereoisomers like A and C?**

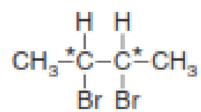
Contd……

- A and C represent the second broad class of stereoisomers, called diastereomers
- *Diastereomers are stereoisomers* that are not mirror images of each other. A and B are diastereomers of C and D, and vice versa



Contd……

- Lets consider another molecule 2,3-dibromobutane



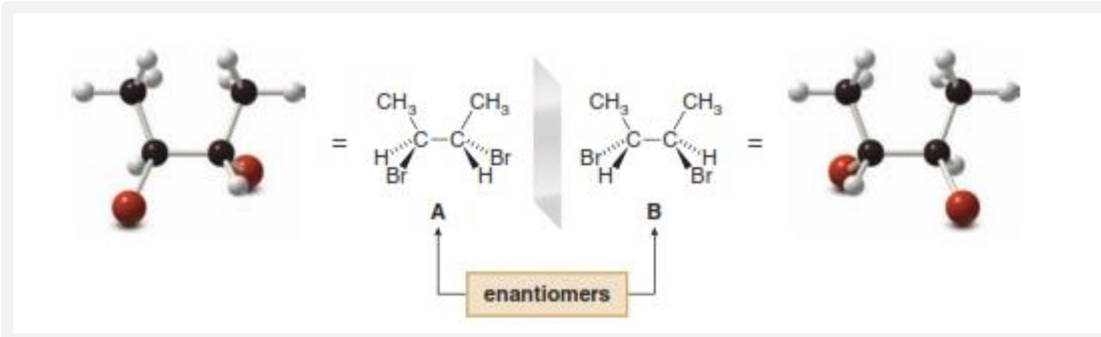
2,3-dibromobutane
[* = stereogenic center]

With two stereogenic centers, the **maximum** number of stereoisomers = **4.**

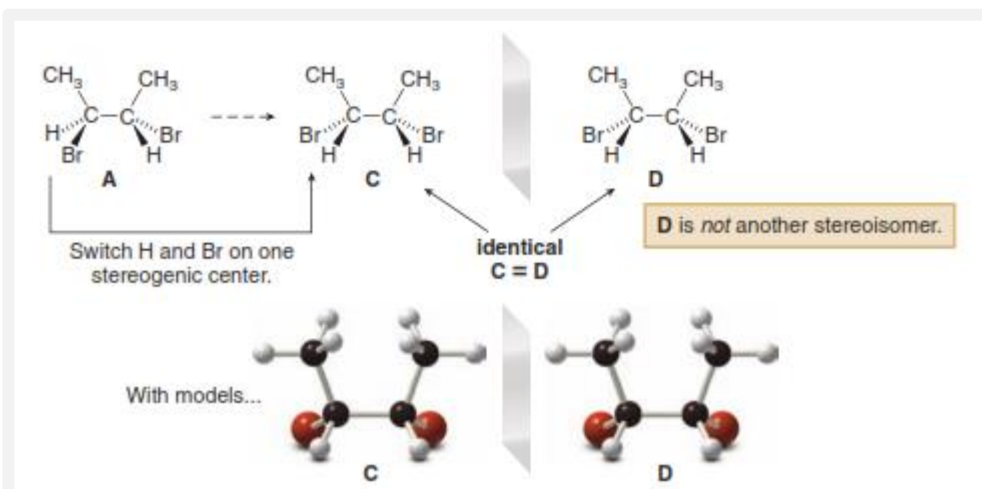
- 2,3-dibromobutane has two stereogenic centers but fewer than the maximum number of stereoisomers
- How?
- To find and draw all the stereoisomers of 2,3-dibromobutane, follow the same stepwise procedure outlined earlier

Contd……

- **Arbitrarily add the H, Br and CH_3 groups to the stereogenic centers forming one stereoisomer A, and then draw its mirror image B**

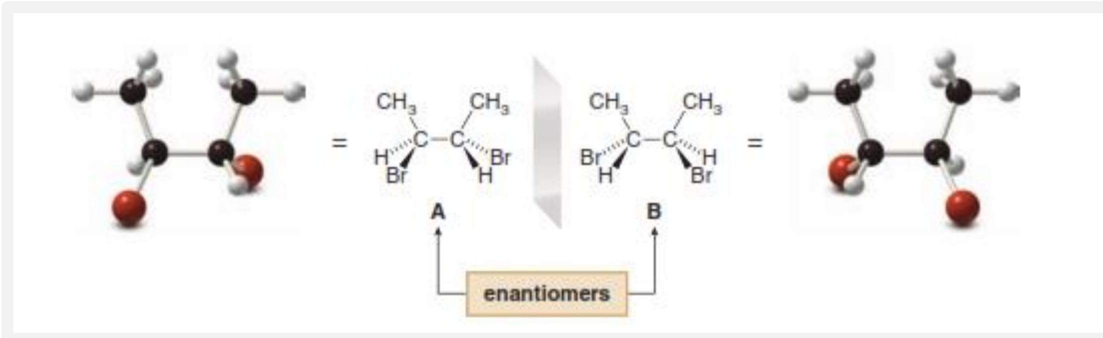


- **To find the other two stereoisomers (if they exist), switch the position of two groups on *one* stereogenic center of *one enantiomer only***

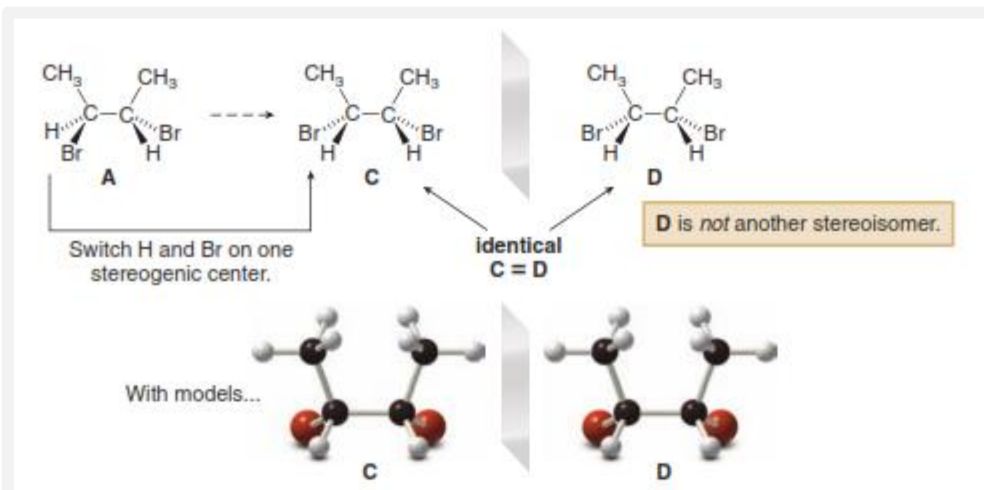


Contd……

- **Arbitrarily add the H, Br and CH_3 groups to the stereogenic centers forming one stereoisomer A, and then draw its mirror image B**

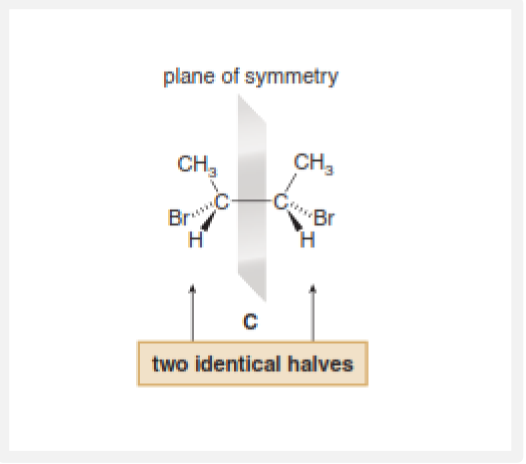


- **To find the other two stereoisomers (if they exist), switch the position of two groups on *one* stereogenic center of *one enantiomer only***



Contd……

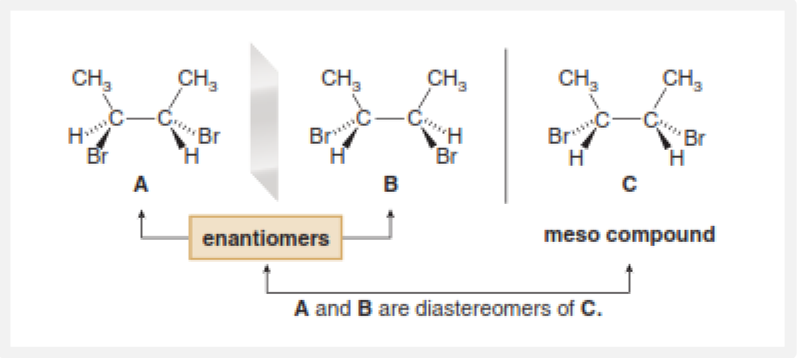
- The mirror image of C, labeled D, is superimposable on C, so C and D are identical
- Thus, C is achiral, even though it has two stereogenic centers
- C is a meso compound
- Meso compounds generally have a plane of symmetry, so they possess two identical halves



- A meso compound is an achiral compound that contains tetrahedral stereogenic centers

Contd……

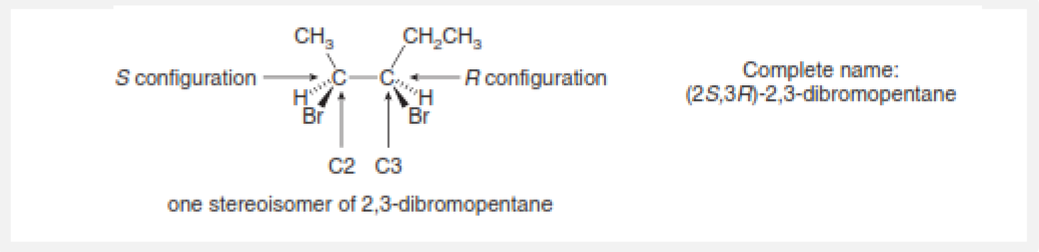
- Because one stereoisomer of 2,3-dibromobutane is superimposable on its mirror image, there are only three stereoisomers and not four
- Summary: The three stereoisomers of 2,3-dibromobutane



- When a compound has more than one stereogenic center, the *R or S configuration must be assigned* to each of them

Contd……

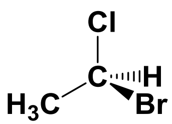
- Consider the stereoisomer of 2,3-dibromopentane drawn here as an example

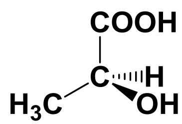


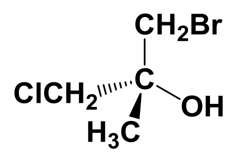
- The R,S configurations can be used to determine whether two compounds are identical, enantiomers, or diastereomers
- Note:
- ✓ Identical compounds have the same R,S designations at every tetrahedral stereogenic center
- ✓ Enantiomers have exactly opposite R,S designations
- ✓ Diastereomers have the same R,S designation for at least one stereogenic center andthe opposite for at least one of the other stereogenic centers

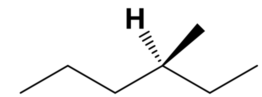
Practice Question(s)

❖ Label each compound as R or S

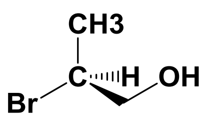
(a) 

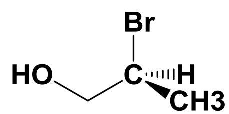
(b) 

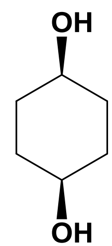
(c) 

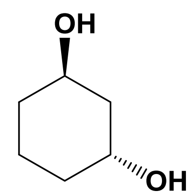
(d) 

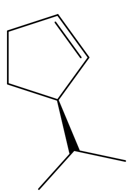
❖ State how each pair of compounds is related. Are they enantiomers, diastereomers, constitutional isomers, or identical?

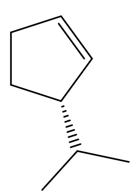
(a) 

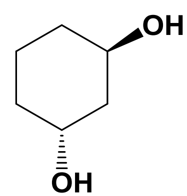
and 

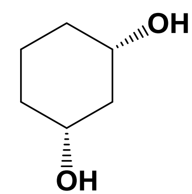
(b) 

and 

(c) 

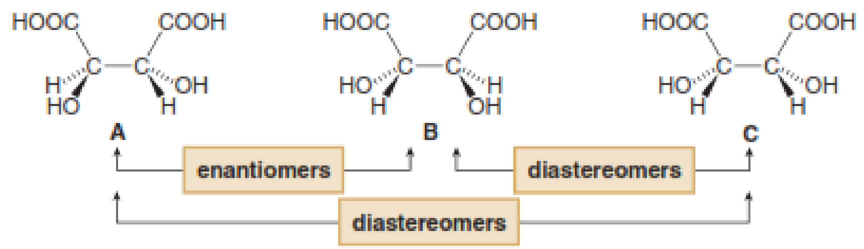
and 

(d) 

and 

12.2 Physical properties of Enantiomers and Diastereomers

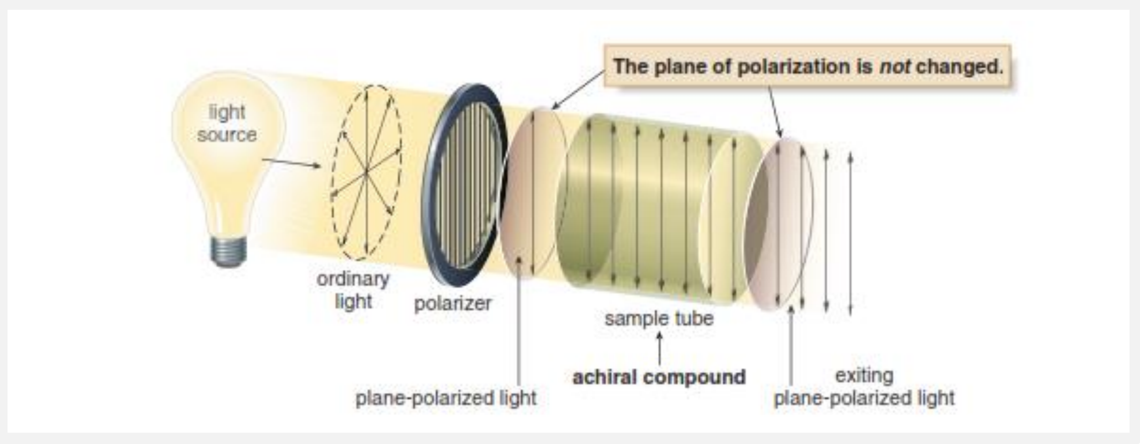
- Two enantiomers have identical physical properties—melting point, boiling point, solubility—except for how they interact with plane-polarized light (optical rotation)
- Diastereomers are not mirror images of each other, and as such, their physical properties are different, including optical rotation



Property	A	B	C	A + B (1:1)
melting point (°C)	171	171	146	206
solubility (g/100 mL H_2O)	139	139	125	139
[α]	+13	−13	0	0
R,S designation	*R,R*	*S,S*	*R,S*	–
d,l designation	*d*	*l*	none	*d,l*

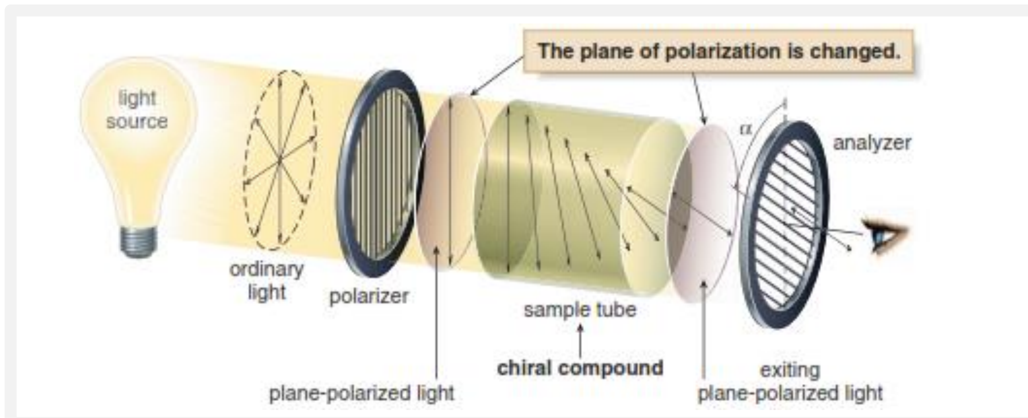
12.3 Optical Activity

- A polarimeter is an instrument that allows plane-polarized light to travel through a sample tube containing an organic compound
- After the light exits the sample tube, an analyzer slit is rotated to determine the direction of the plane of the polarized light exiting the sample tube
- There are two possible results
- ✓ With achiral compounds, the light exits the sample tube *unchanged, and the plane of the polarized* light is in the same position it was before entering the sample tube
- ✓ A compound that does not change the plane of polarized light is said to be *optically inactive*



Contd……

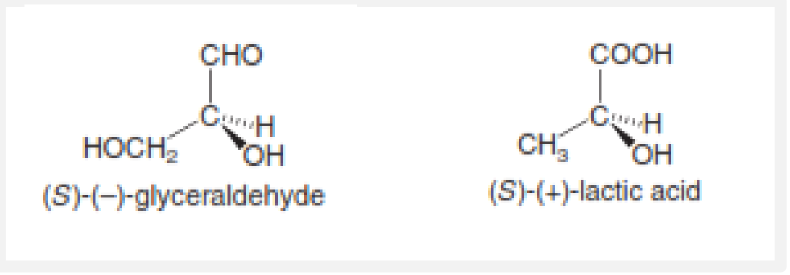
- With chiral compounds, the plane of the polarized light is rotated through an angle α. The angle α, measured in degrees (°), is called the observed rotation
- A compound that rotates the plane of polarized light is said to be *optically active*



- The rotation of polarized light can be in the clockwise or counterclockwise direction
- If the rotation is clockwise (to the right from the noon position), the compound is called dextrorotatory. The rotation is labeled d or (+)
- If the rotation is counterclockwise (to the left from noon), the compound is called levorotatory. The rotation is labeled *l or (–)*

Contd……

- No relationship exists between the *R and S prefixes that designate configuration and the (+) and* (–) designations indicating optical rotation
- For example, the *S enantiomer of lactic acid is dextrorotatory* (+), whereas the *S* enantiomer of glyceraldehyde is levorotatory (–)



- How does the rotation of two enantiomers compare?
- ✓ Two enantiomers rotate plane-polarized light to an equal extent but in the opposite direction
- Thus, if enantiomer A rotates polarized light +5°, then the same concentration of enantiomer B rotates it –5°

Contd……

- What is the observed rotation of an equal amount of two enantiomers?
- Because two enantiomers rotate plane-polarized light to an equal extent but in opposite directions, the rotations cancel, and no rotation is observed
- An equal amount of two enantiomers is called a racemic mixture or a racemate. A racemic mixture is optically inactive
- To standardize optical rotation data, the quantity observed specific rotation ($[\alpha]$) is defined using a specific sample tube length (usually 1 dm), concentration (g/ml), temperature (25 °C), and wavelength (589 nm, the D line emitted by a sodium lamp)

$$\text{specific rotation} = [\alpha] = \frac{\alpha}{l \times c}$$

α = observed rotation (°)
l = length of sample tube (dm)
c = concentration (g/mL)

[dm = decimeter
1 dm = 10 cm]

Contd……

- A natural product was isolated in the laboratory, and its observed rotation was +1.00° when measured in a 1 dm sample tube containing 1.0 g of compound in 10 mL of water. **What is the specific rotation of this compound?**

$$\text{specific rotation} = \frac{\alpha}{l \, X \, C} = \frac{+1.00^{o}}{1\text{ dm } X \, 0.1\text{g/ml}} = +10$$

- The enantiomeric excess (*ee*), also called the optical purity, tells how much one enantiomer is present in excess of the racemic mixture

Enantiomeric excess = ee = % of one enantiomer – % of the other enantiomer

- For example, if a mixture contains 75% of one enantiomer and 25% of the other, the enantiomeric excess is 75% – 25% = 50%. There is a 50% excess of one enantiomer over the racemic mixture

Contd……

- ❖ **Examples;**
- ✓ **If the enantiomeric excess is 95%, how much of each enantiomer is present?**
- ❖ **Solution**
- ✓ **Label the two enantiomers A and B and assume that A is in excess. A 95% ee means that the solution contains an excess of 95% of A, and 5% of the racemic mixture of A and B. Because a racemic mixture is an equal amount of both enantiomers, it has 2.5% of A and 2.5% of B**

Total amount of A = 95% + 2.5% = 97.5%

Total amount of B = 2.5% (or 100% – 97.5%)

- ❖ **The enantiomeric excess can also be calculated if two quantities are known—the specific rotation $[\alpha]$ of a mixture and the specific rotation $[\alpha]$ of a pure enantiomer**

$$ee = \frac{[\alpha]\text{ mixture}}{[\alpha]\text{ pure enantiomer}} \times 100\%$$

Contd……

❖ **Example;**

✓ Pure cholesterol has a specific rotation of –32. A sample of cholesterol prepared in the lab had a specific rotation of –16. What is the enantiomeric excess of this sample of cholesterol?

❖ **Solution**

$$\text{ee} = \frac{[\alpha]\ \text{mixture}}{[\alpha]\ \text{pure}} \times 100\% = \frac{-16}{-32} \times 100\% = 50\ \%$$

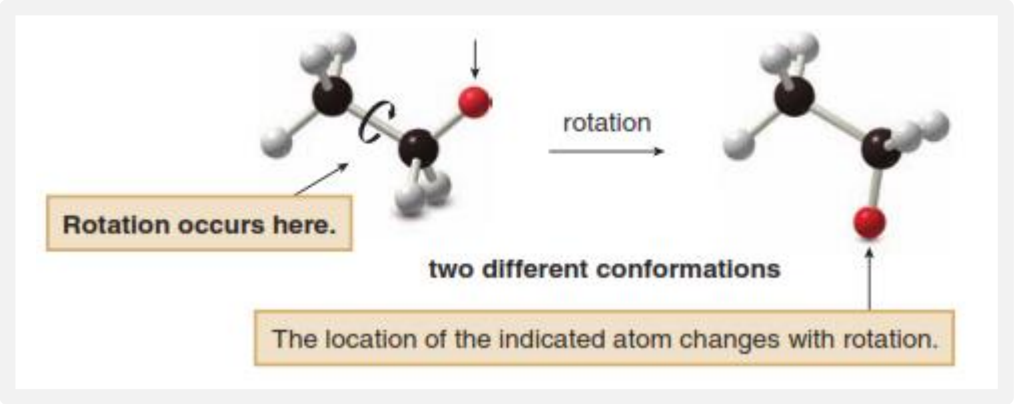
Practice Questions

1. Pure (R)-mandelic acid has a specific rotation of –154. If a sample contains 60% of the R isomer and 40% of its enantiomer, what is $[\alpha]$ of this solution?

Calculate the ee of a solution of mandelic acid having $[\alpha]$ = +50. What is the percentage of each enantiomer present?

13.0 Conformational Analysis

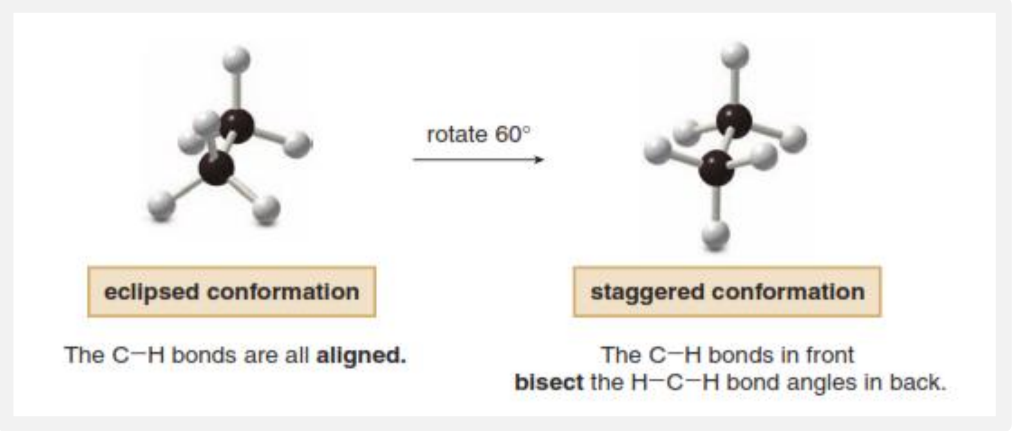
- **Conformations** are different arrangements of atoms that are interconverted by rotation about single bonds



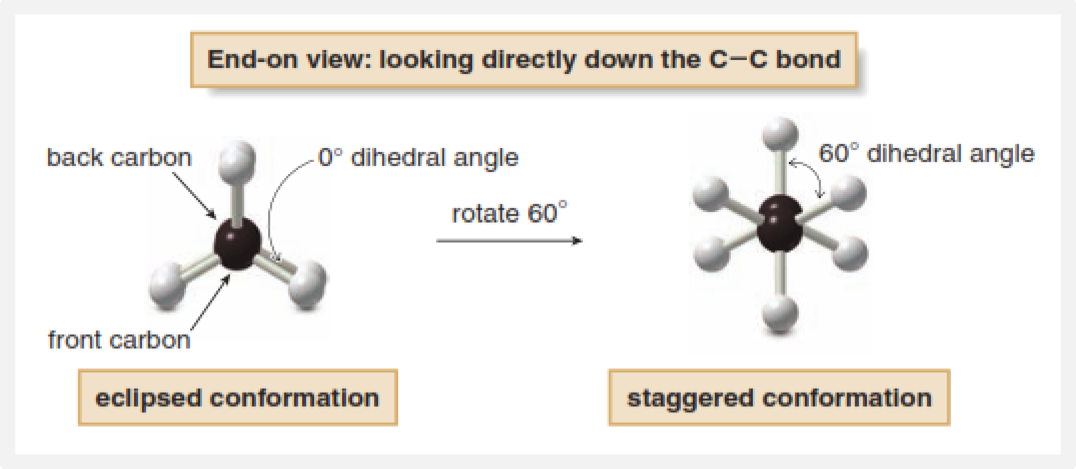
- Names are given to two different arrangements
- In the eclipsed conformation, the C–H bonds on one carbon are directly aligned with the C–H bonds on the adjacent carbon
- In the staggered conformation, the C–H bonds on one carbon bisect the H–C–H bond angle on the adjacent carbon

Contd……

- Rotating the atoms on one carbon by 60° converts an eclipsed conformation into a staggered conformation, and vice versa



- The angle that separates a bond on one atom from a bond on an adjacent atom is called a dihedral angle



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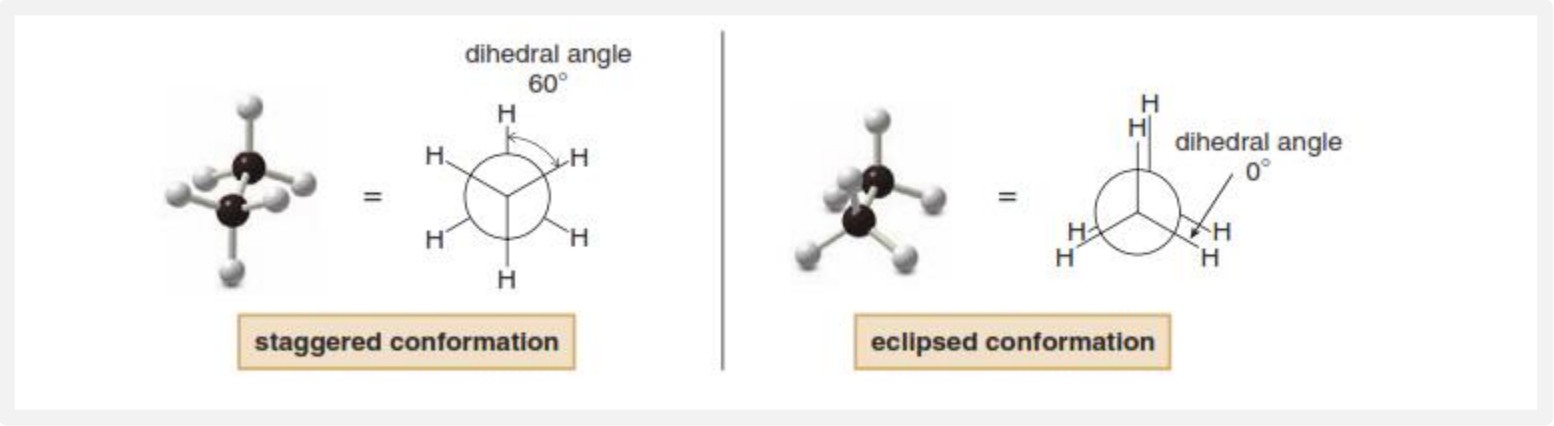
- For example, ethane in the staggered conformation, the dihedral angle for the C–H bonds is 60°. For eclipsed ethane, it is 0°
- End-on representations for conformations are commonly drawn using a convention called a Newman projection
- A Newman projection is a graphic that shows the three groups bonded to each carbon atom in a particular C–C bond, as well as the dihedral angle that separates them
- Newman projections for the staggered and eclipsed conformations of ethane



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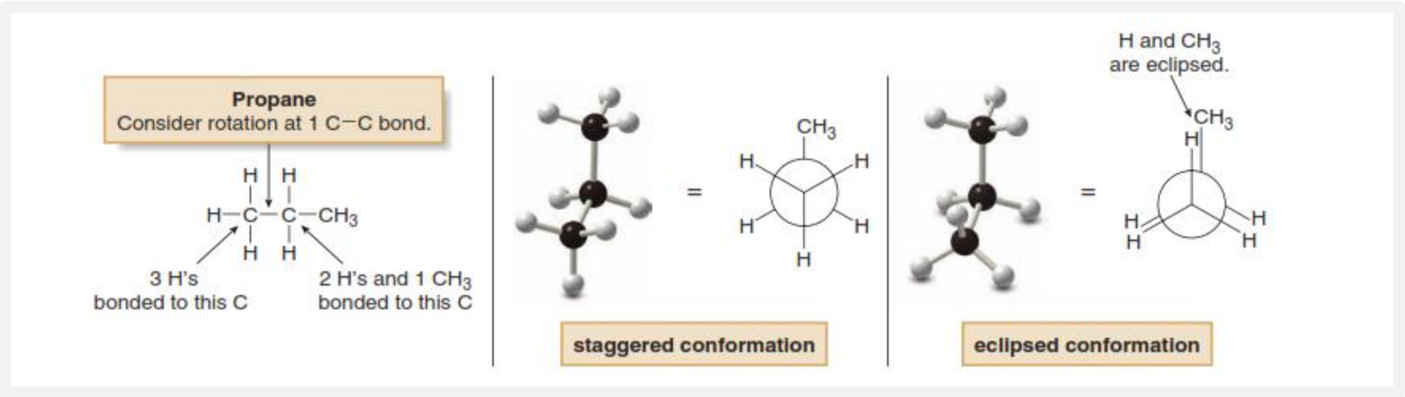
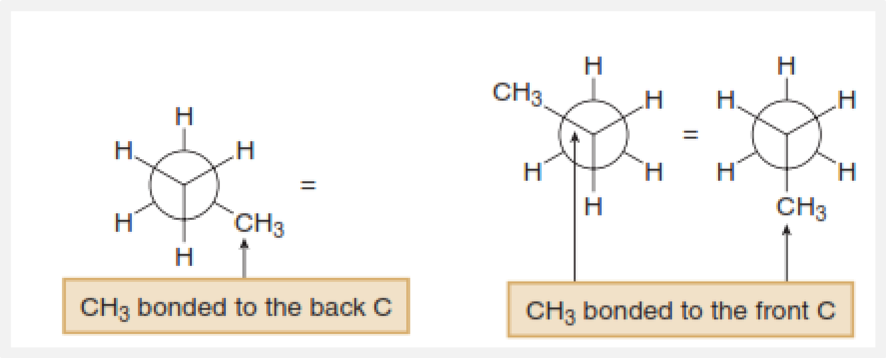
- Newman projections for the **staggered** and **eclipsed conformations of** propane



- In a Newman projection it doesn't matter which C you pick to be in the front or the back

- All of the Newman projections shown here represent the staggered conformation of propane



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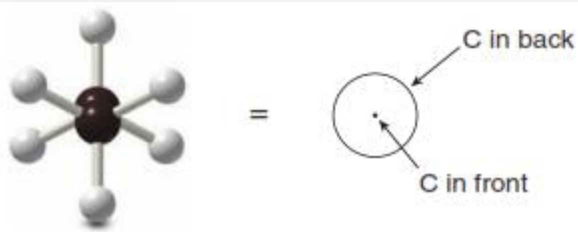
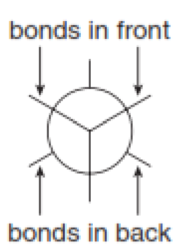
❖ HOW TO Draw a Newman Projection for ethane

✓ Step [1]: Look directly down the C–C bond (end-on), and draw a circle with a dot in the center to represent the carbons of the C–C bond



- The circle represents the back carbon and the dot represents the front carbon.

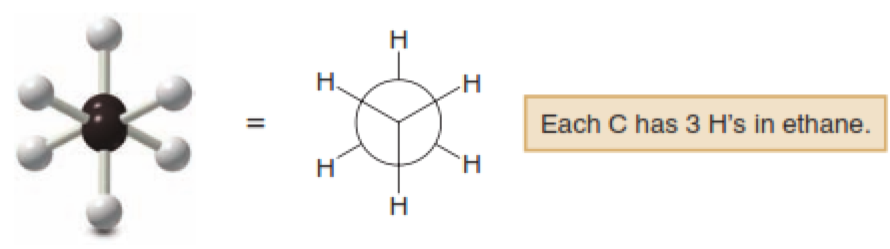
✓ Step [2]: Draw in the bonds



- Draw the bonds on the **front** C as three lines **meeting at the center** of the circle.
- Draw the bonds on the **back** C as three lines coming **out of the edge** of the circle.

Contd……

✓ Step [3]: Add the atoms on each bond

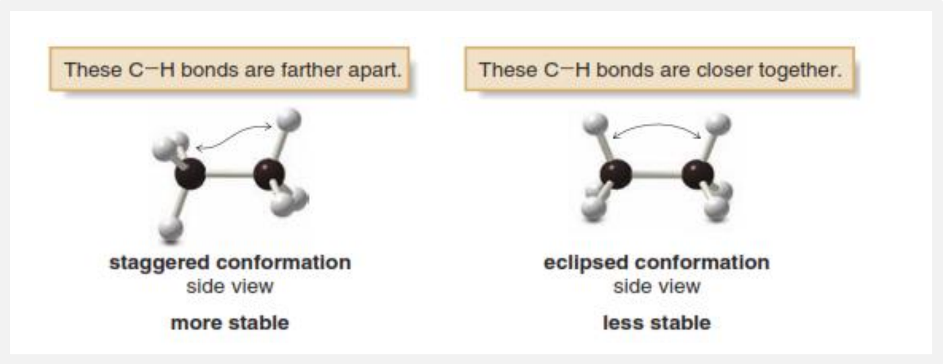


❖ The staggered conformations are more stable (lower in energy) than the eclipsed conformations

❖ Why?

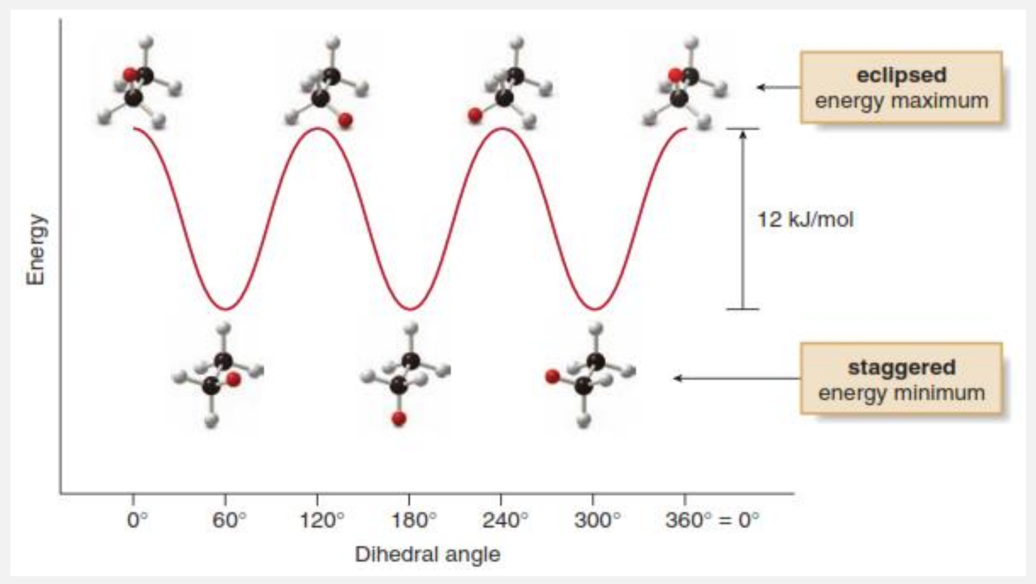
✓ Electron–electron repulsion between the bonds in the eclipsed conformation increases its energy compared to the staggered conformation, where the bonding electrons are farther apart

Contd……



- Thus, eclipsing introduces **torsional strain** into a molecule
- Torsional strain is an increase in energy caused by eclipsing interactions

Graph: Energy versus dihedral angle for ethane



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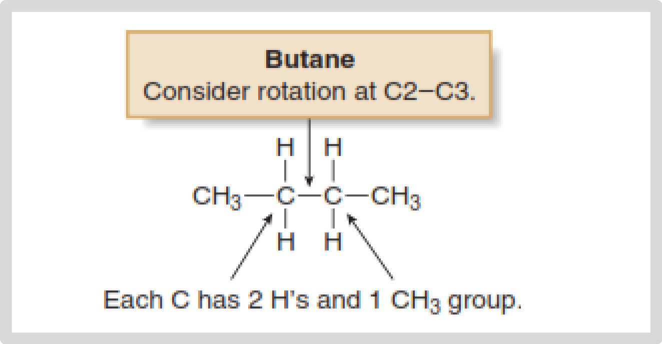
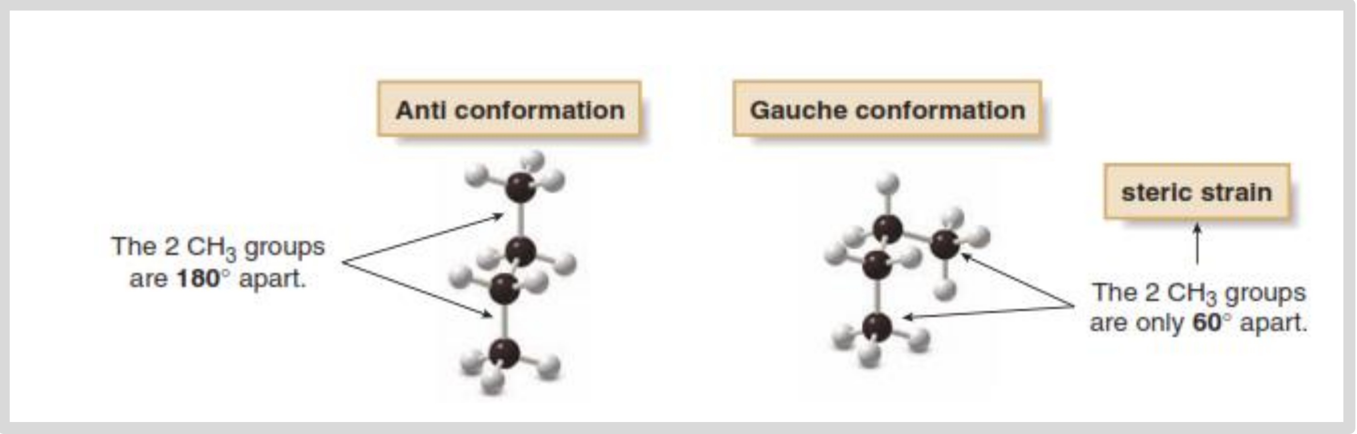
- Butane and higher molecular weight alkanes have several carbon–carbon bonds, all capable of rotation



- In butane we have,
- ✓ A staggered conformation with two larger groups 180° from each other is called anti
- ✓ A staggered conformation with two larger groups 60° from each other is called gauche

Contd……

- The anti and gauche representations



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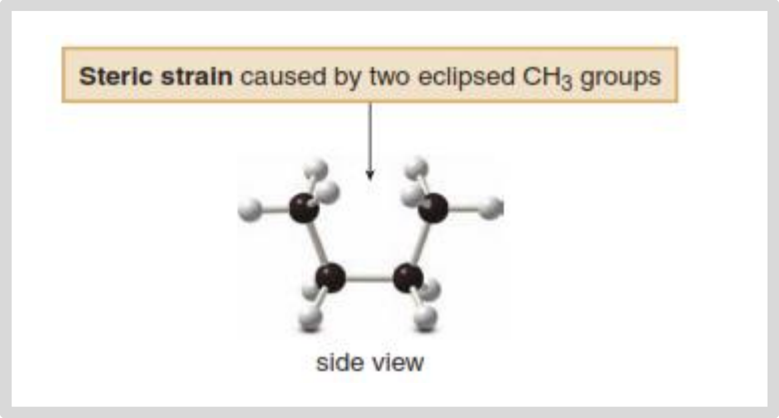
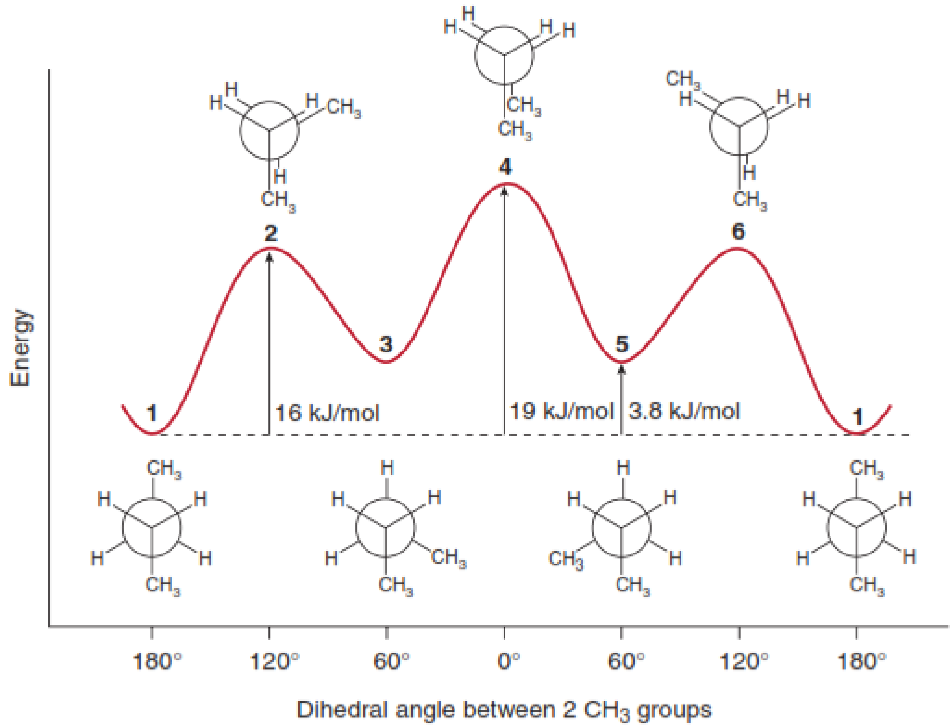
- The relative energies of the individual staggered conformations (or the individual eclipsed conformations) depend on their steric strain
- Steric strain is an increase in energy resulting when atoms are forced too close to one another



- To graph energy versus dihedral angle, keep in mind two considerations:
- ✓ Staggered conformations are at energy minima and eclipsed conformations are at energy maxima
- ✓ Unfavorable steric interactions increase energy

Contd……

Graph: Energy versus dihedral angle for butane



- Staggered conformations **1, 3,** and **5** are at energy minima.
- Anti conformation **1** is lower in energy than gauche conformations **3** and **5,** which possess steric strain.
- Eclipsed conformations **2, 4,** and **6** are at energy maxima.
- Eclipsed conformation **4,** which has additional steric strain due to two eclipsed CH_3 groups, is highest in energy.

Contd……

Torsional and Steric Strain Energies in Acyclic Alkanes

Type of interaction	Energy increase kJ/mol	kcal/mol
H,H eclipsing	4.0	1.0
H,CH_3 eclipsing	6.0	1.4
CH_3,CH_3 eclipsing	11	2.6
gauche CH_3 groups	3.8	0.9

- **We can use these values to calculate the energies of each conformation plotted graphically**
- **For examples;**

Total energy for conformation 2 = 1 x H,H eclipsing + 2 x H,CH_3 eclipsing

= (1 x 4.0 + 2 x 6.0) kJ/mol

= 16.0 kJ/mol

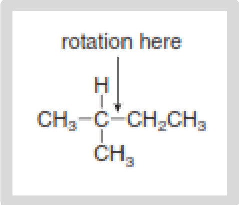
Total energy for conformation 4 = 2 x H,H eclipsing + 1 x CH_3,CH_3 eclipsing

= (2 x 4.0 + 1 x 11) kJ/mol

= 19 kJ/mol

Practice Question(s)

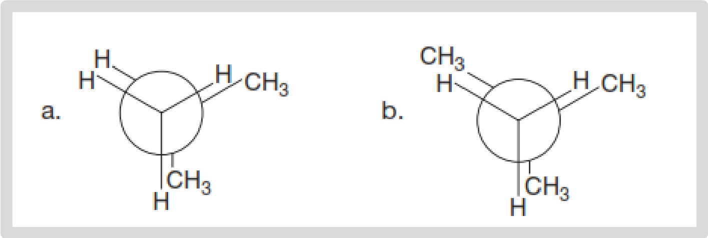
1. **Consider the molecule give below.**



a. Draw the three staggered and three eclipsed conformations that result from rotation around the designated bond using Newman projections.

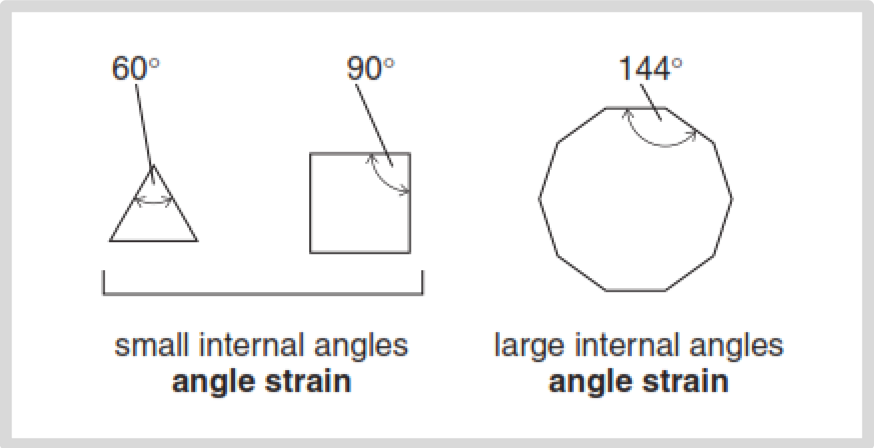
b. Label the most stable and least stable conformation

2. **Calculate the destabilization energy present in each eclipsed conformation**



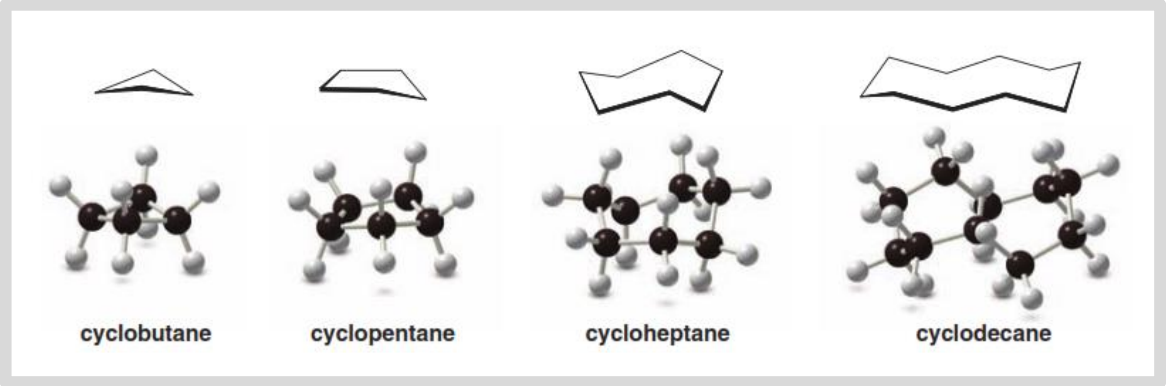
Contd……

- Besides torsional strain and steric strain, the conformations of cycloalkanes are also affected by angle strain
- Angle strain is an increase in energy when tetrahedral bond angles deviate from the optimum angle of 109.5°
- For example, a flat cyclopropane ring would have 60° internal bond angles, a flat cyclobutane ring would have 90° angles, and large flat rings would have very large angles
- It was assumed that rings with bond angles so different from the tetrahedral bond angle would be very strained and highly reactive
- This is called the Baeyer strain theory



Contd……

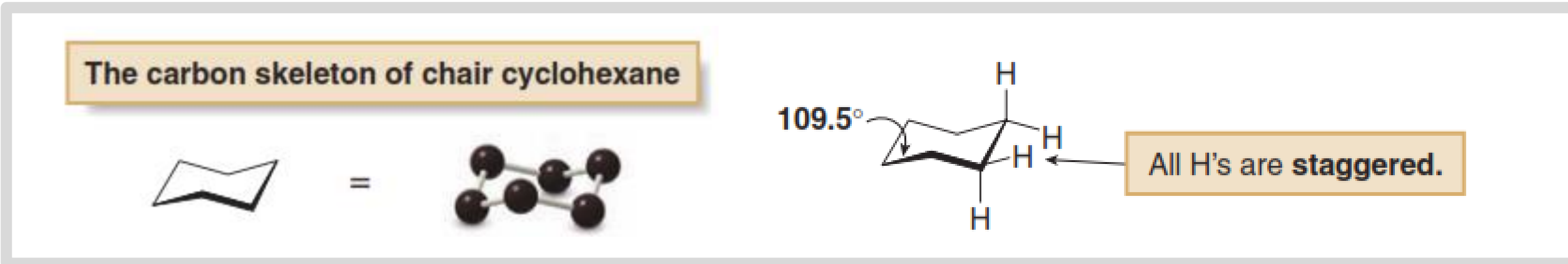
- Cycloalkanes with more than three C atoms in the ring are not flat molecules. They are puckered to reduce strain, both angle strain and torsional strain



- Let's now examine in detail the conformation of cyclohexane, the most common ring size in naturally occurring compounds
- Cyclohexane adopts a puckered conformation, called the chair form, which is more stable than any other possible conformation

Contd……

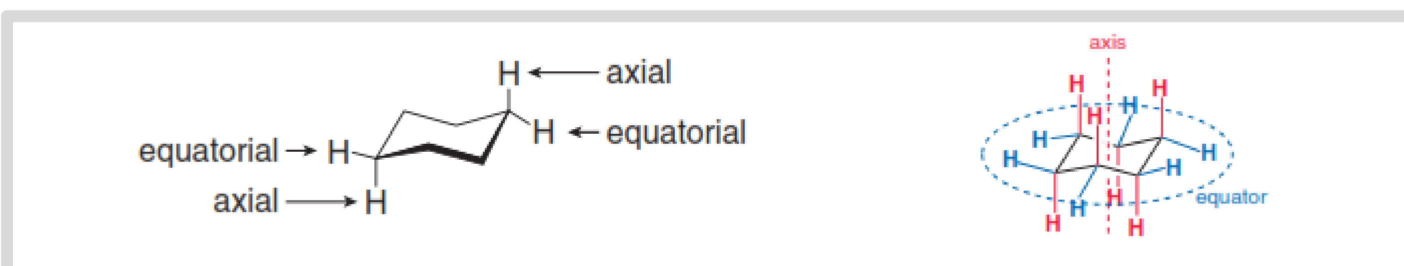
❖ The chair conformation is stable because it eliminates angle strain (all C-C-C bonds are 109°) and torsional strain (all hydrogens on adjacent carbon atoms are staggered, not eclipsed)



❖ Each carbon in cyclohexane has two different kinds of hydrogens

✓ Axial hydrogens are located above and below the ring (along a perpendicular axis)

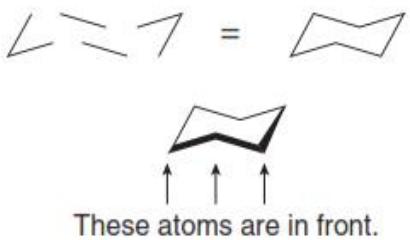
✓ Equatorial hydrogens are located in the plane of the ring (around the equator)



Contd……

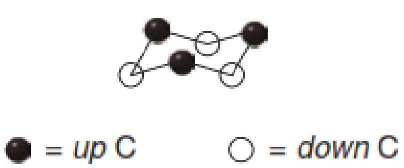
❖ **HOW TO Draw the Chair Form of Cyclohexane**

✓ **Step [1]: Draw the carbon skeleton**



- Draw three parts of the chair: **a wedge, a set of parallel lines,** and **another wedge.**
- Then, join them together.
- The bottom 3 C's come out of the page, and for this reason, bonds to them are often highlighted in bold.

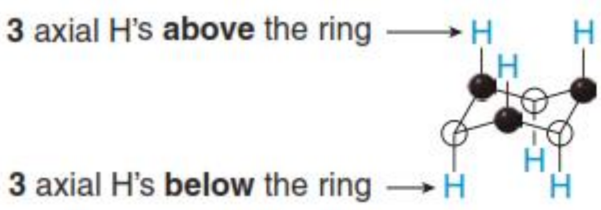
✓ **Step [2]: Label the up C's and down C's on the ring**



- There are 3 *up* and 3 *down* C's, and they alternate around the ring.

Contd……

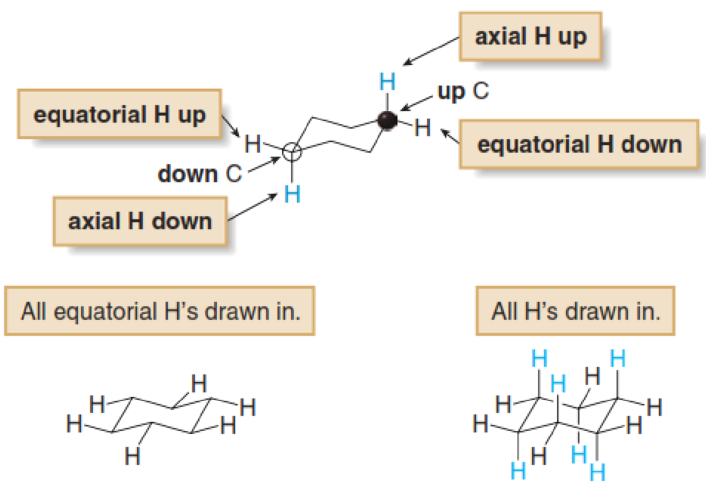
- ✓ **Step [3]:** Draw in the axial H atoms



- On an *up* C the axial H is *up*.
- On a *down* C the axial H is *down*.

- ✓ **Step [4]:** Draw in the equatorial H atoms

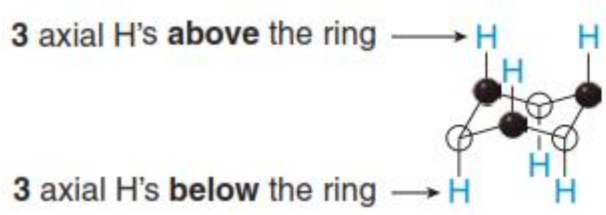
- The axial H is **down** on a down C, so the equatorial H must be up.
- The axial H is **up** on an up C, so the equatorial H must be down.



Axial H's are drawn in blue.

Contd……

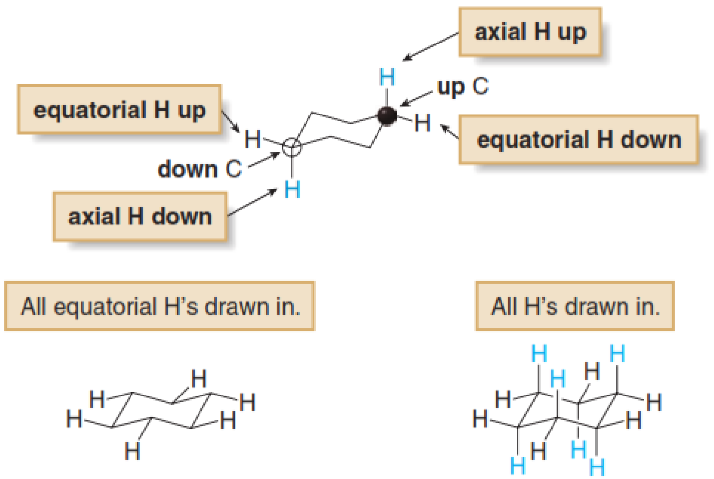
✓ **Step [3]: Draw in the axial H atoms**



- On an *up* C the axial H is *up*.
- On a *down* C the axial H is *down*.

✓ **Step [4]: Draw in the equatorial H atoms**

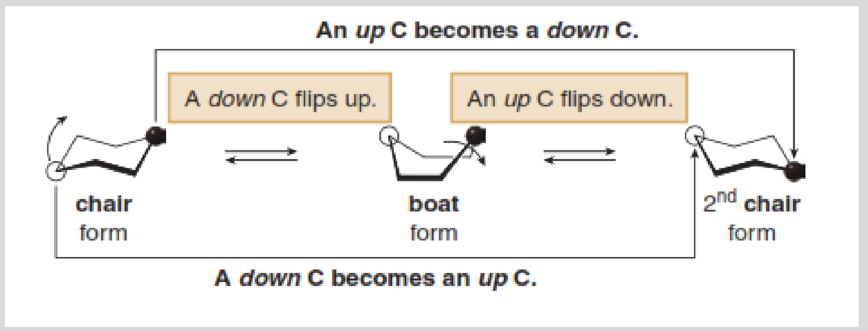
- The axial H is **down** on a down C, so the equatorial H must be up.
- The axial H is **up** on an up C, so the equatorial H must be down.



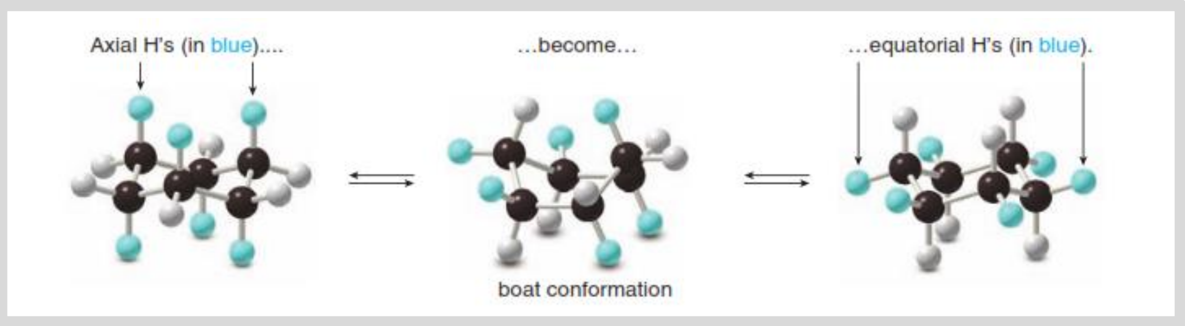
Axial H's are drawn in blue.

Contd……

- Cyclohexane does not remain in a single conformation
- It undergoes **ring-flipping** in which bonds twist and bend, resulting in new arrangements, but the movement is more restricted
- **Because of ring-flipping,** the *up carbons become down carbons and the down carbons become up carbons*



- **Axial and equatorial H atoms** are interconverted during a ring flip
- Axial H atoms become equatorial H atoms, and equatorial H atoms become axial H atoms



Contd……

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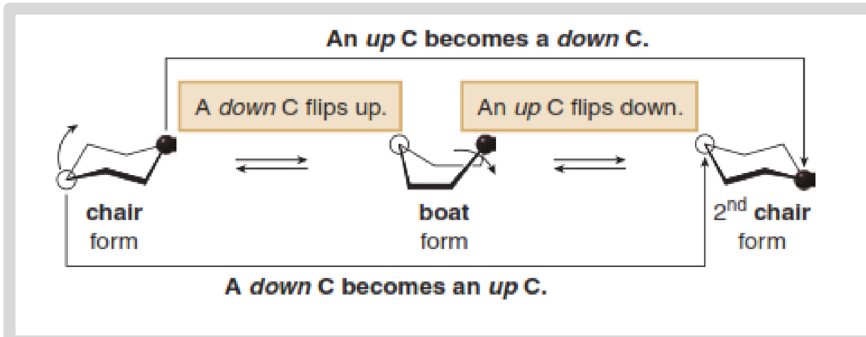

- Axial and equatorial H atoms are interconverted during a ring flip
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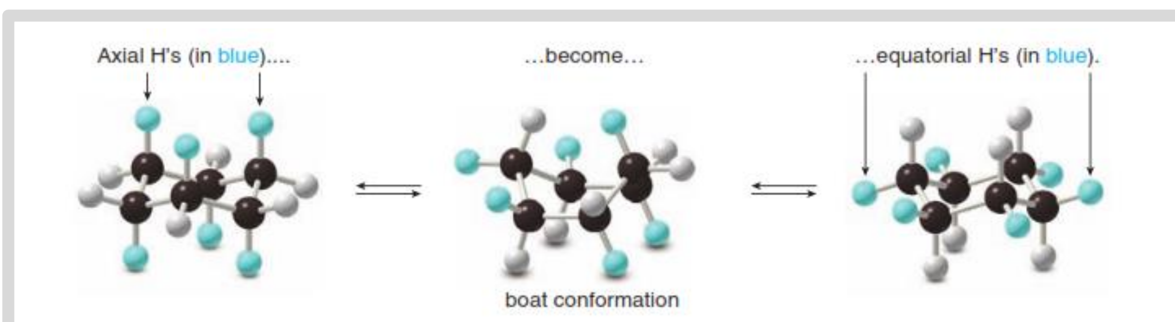
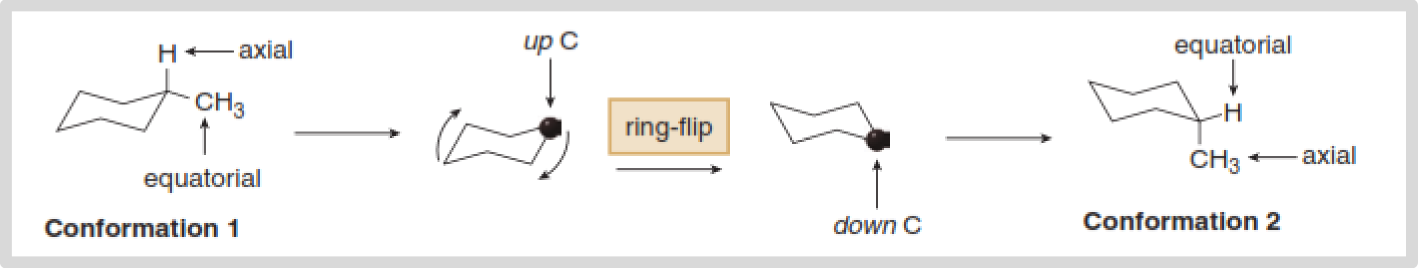
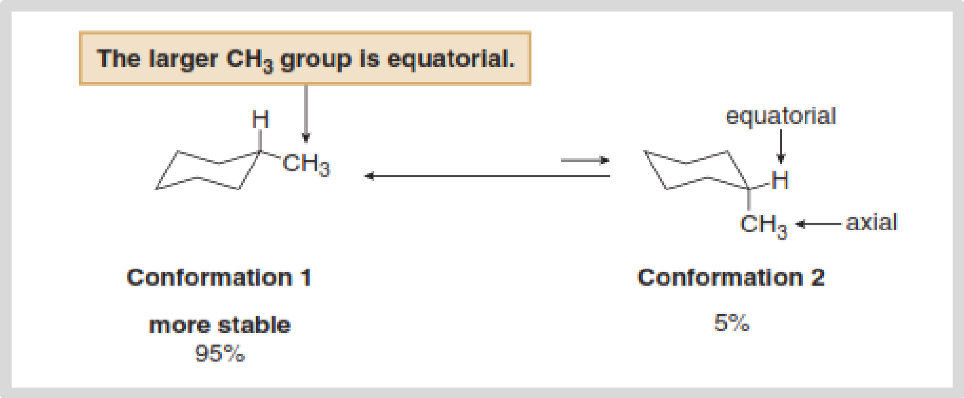


Contd......

- **Cyclohexane with One Substituent, such as methylcyclohexane forms two possible chair conformations**



- **The two conformations of methylcyclohexane are different, so they are not equally stable**

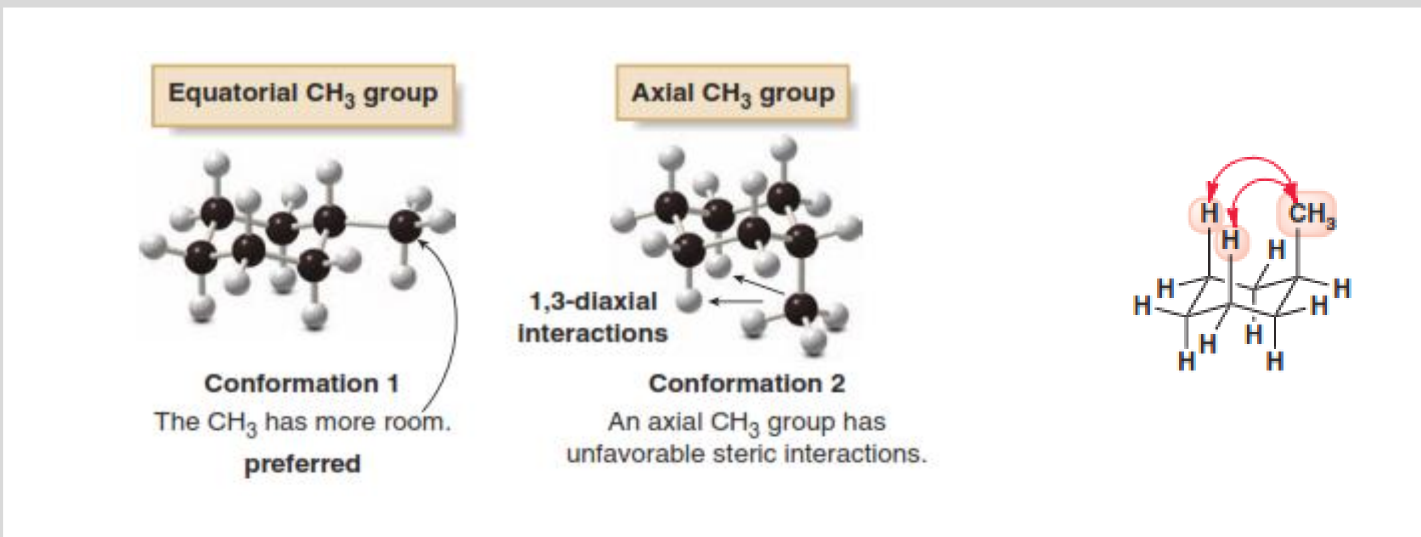


- **Why?**

✓ **The equatorial position has more room than the axial position, so larger substituents are more stable in the equatorial position**

Contd……

- ✓ Larger axial substituents create unfavorable 1,3-diaxial interactions, destabilizing a cyclohexane conformation
- 1,3-diaxial interactions are experienced when CH_3 group is close to two other axial H atoms, creating two destabilizing steric interactions



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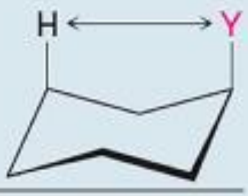
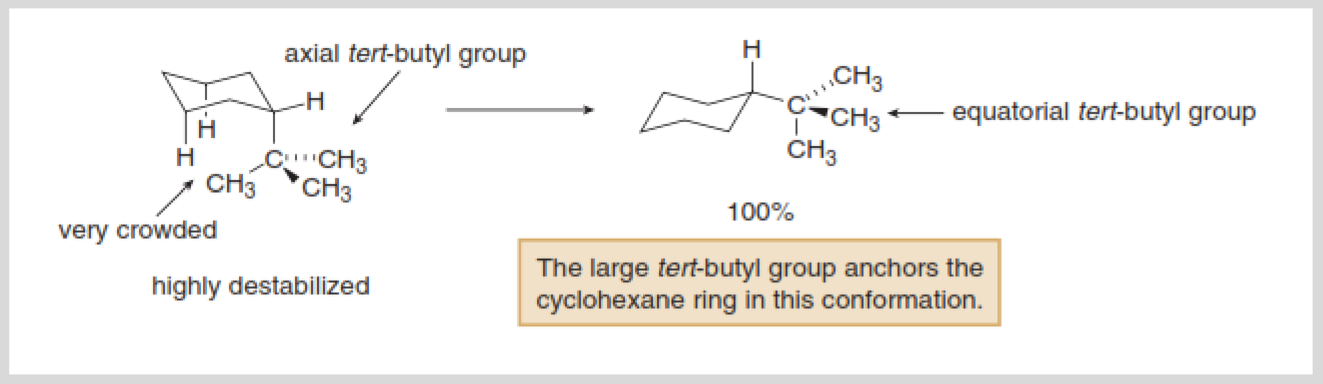
Steric Strain in Monosustituted Cyclohexanes



Y	1,3-Diaxial strain (kJ/mol)	1,3-Diaxial strain (kcal/mol)
F	0.5	0.12
Cl, Br	1.0	0.25
OH	2.1	0.5
CH_3	3.8	0.9
CH_2CH_3	4.0	0.95
$CH(CH_3)_2$	4.6	1.1
$C(CH_3)_3$	11.4	2.7
C_6H_5	6.3	1.5
CO_2H	2.9	0.7
CN	0.4	0.1

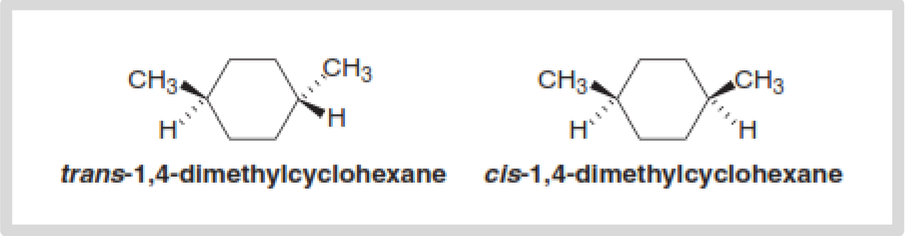
Contd……

- In fact, with a very large substituent like *tert-butyl* [$(CH_3)_3C$–], essentially none of the conformation containing an axial *tert-butyl group* is present at room temperature, so the ring is essentially anchored in a single conformation having an equatorial *tert-butyl group*



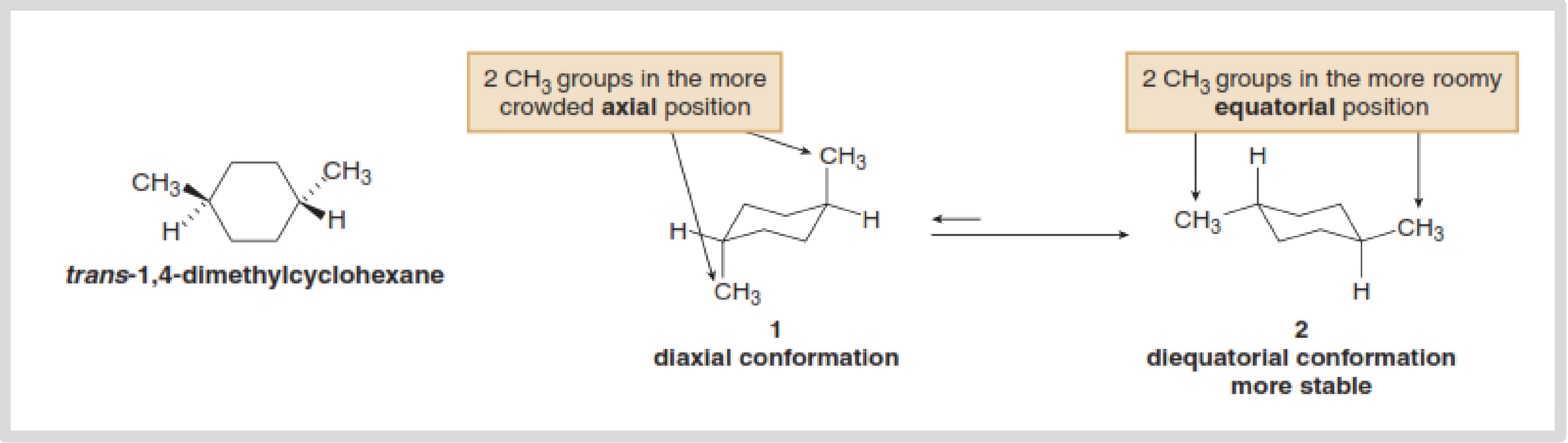
Contd……

- A disubstituted cyclohexane like 1,4-dimethylcyclohexane also has cis and trans stereoisomers



- In addition, each of these stereoisomers has two possible chair conformations

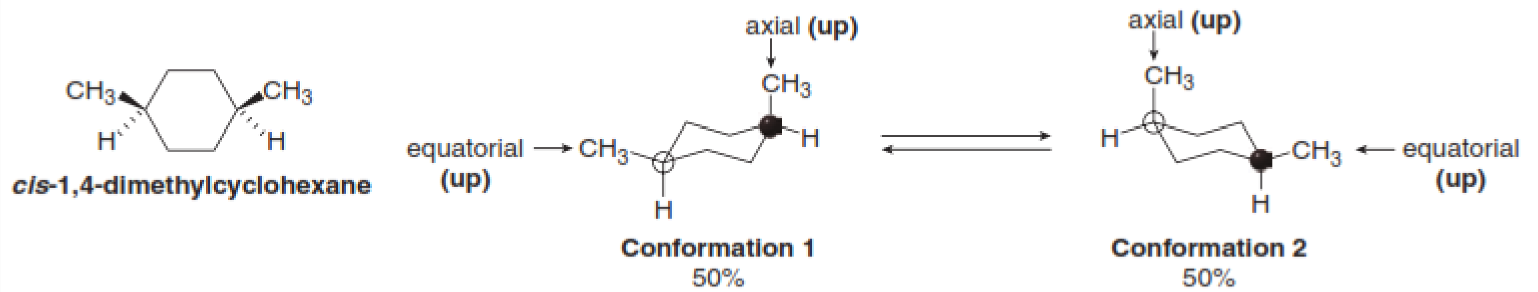
✓ For trans isomer



- Note; solid wedge represent the bond facing up, and dashed wedge represent the bond facing down

Contd……

❖ For the cis-isomer

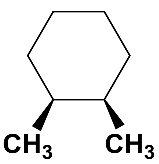


❖ Note; solid wedge represent the bond facing up, and dashed wedge represent the bond facing down

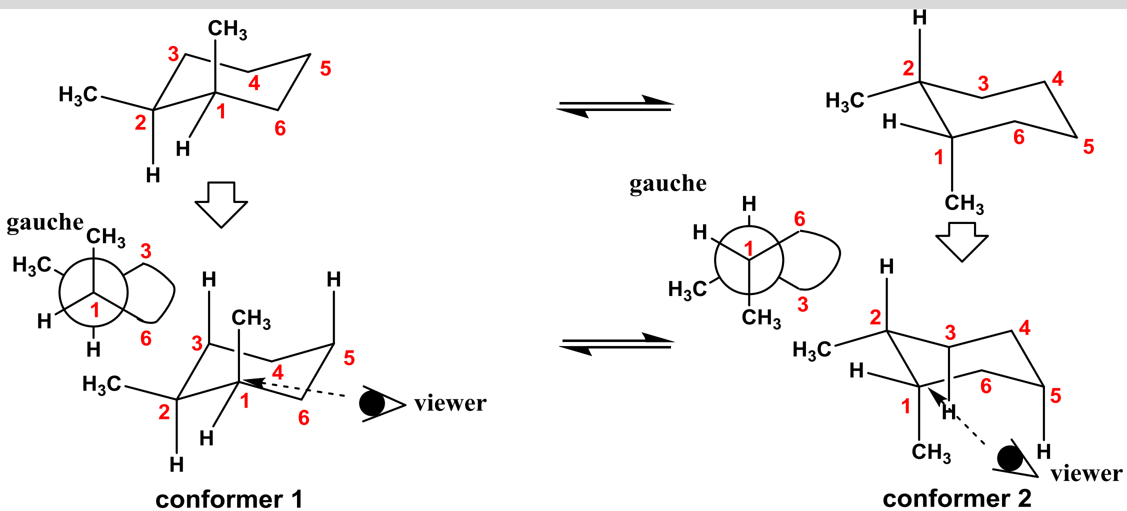
Contd……

❖ **HOW TO Calculate the Strain Energy in Disubstituted Cyclohexane**

✓ **Example trans-1,2- dimethyl Cyclohexane**



Cis-1,2-dimethylcyclohexane



$S_T = S_G + S_{1,3\text{-}DA}$

$= 0.9$ kcal/mol $+ 2 \times 0.9$ kcal/mol

$= 2.7$ kcal/mol

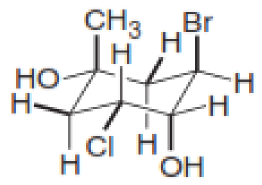
$S_T = S_G + S_{1,3\text{-}DA}$

$= 0.9$ kcal/mol $+ 2 \times 0.9$ kcal/mol

$= 2.7$ kcal/mol

Practice Question(s)

1. Identify the bonds highlighted in bold as axial or equatorial



2. Consider 1,2-dimethylcyclohexane.

a) Draw structures for the cis and trans isomers using a hexagon for the six-membered ring.

b) Draw the two possible chair conformations for the cis isomer. Which conformation, if either, is more stable?

c) Draw the two possible chair conformations for the trans isomer. Which conformation, if either, is more stable?

d) Which isomer, cis or trans, is more stable and why?

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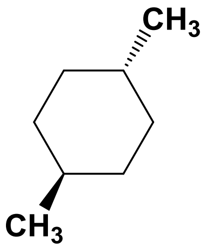
3. Draw the two conformers for Trans-1,4-dimethylcyclohexane and calculate the energy strain for each chair. Which one is more stable?



Tran-1,4-dimethylcyclohexane

END!!!!!!!