

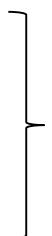
Welcome to CY1101 (general chemistry)



Scope and Objective

The course provides a comprehensive survey of the concepts involved in the study of the

- Electronic structure of atoms
- Chemical bonding
- Coordination chemistry



Inorganic Prof. V. Sivakumar

- Chemical kinetics



Physical Prof (Mrs). Usharani Subuddhi.

- Organic Chemistry (Stereochemistry).

Organic Prof (Mrs). Sabita Patel

CY1101 (Syllabus)

Schrodinger wave equation (origin of quantization), Interpretation of wave function (radial and angular), Hydrogen atom: concept of atomic orbitals. Chemical bonding: VBT, VSEPR, MO theory, Structure, bonding and energy levels of diatomic molecules. Examples N₂, O₂, CO and HF. Werner's coordination theory, Chelate Effect (Metal-EDTA complexes), CFT.

Rate equation, empirical chemical kinetics, methods of determination of order of a reaction, examples and rate equations, Complex reactions, opposing, consecutive and parallel reaction. Concept of steady state approximation, chain reaction (free radical), temperature dependence of rate constants, Arrhenius theory, concept of activation energy, Theories of reaction rates, Enzymatic catalysis, Michaelis-Menten equation, competitive, non-competitive and uncompetitive inhibition.

Chirality, Configuration and conformation, Geometrical isomerism, Optical isomerism, Enantiomers, Diastereomers, projection formulae, interconversion of projection formulas, D-L and R-S nomenclature (CIP rules), Erythro and threo nomenclature. dl- and meso compounds, Atropisomerism, Stereospecific and stereoselective reactions, Conformations vs reactivity of cycloalkanes.



Books:

1. *Inorganic Chemistry by Gary L. Miessler and Donald A. Tarr*
2. *Atkins' Physical Chemistry by Peter Atkins and Julio de Paula*
3. *Fundamentals of molecular spectroscopy, C. N. Banwell, E. N. McCash, 1994.*
4. *Organic Chemistry, Clayden, Greeves, Warren and Wothers, Oxford, 2001.*
5. *Principles of physical Chemistry, B. R. Puri, L. R. Sharma, M. S. Pathania, 2001.*

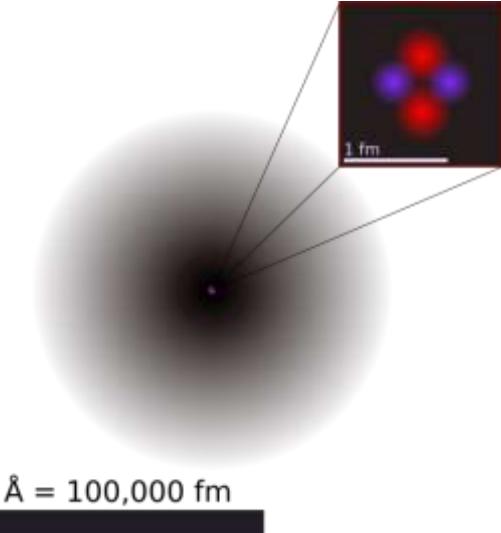
Atomic Structure

- Origin of quantization
 - Schrodinger wave equation
 - Hydrogen (like) atom
 - Interpretation of wave function (radial and angular)
 - Concept of atomic orbitals
- Books:**

1. *Atkins' Physical Chemistry by Peter Atkins and Julio de Paula*
2. *Inorganic Chemistry by Gary L. Miessler and Donald A. Tarr*
3. *Physical Chemistry (Volume 4) by K. L. Kapoor*

Atoms

- Two regions.
- Nucleus- protons and neutrons. (*Occupies very small space*)
- Electron cloud- region where you might find an electron. [*Occupies large (most of the) space*]



Subatomic particles

Name	Symbol	Discovered by, year
------	--------	---------------------

Electron	e^-	J. J. Thomson, 1897
----------	-------	---------------------

Nucleus	$n + p$	E. Rutherford, 1911
---------	---------	---------------------

Proton	p^+	H.G.J. Moseley, 1913
--------	-------	----------------------



Dalton (1805)



Thomson (1896) - Positive and negative charges



Rutherford (1909) - The Nucleus



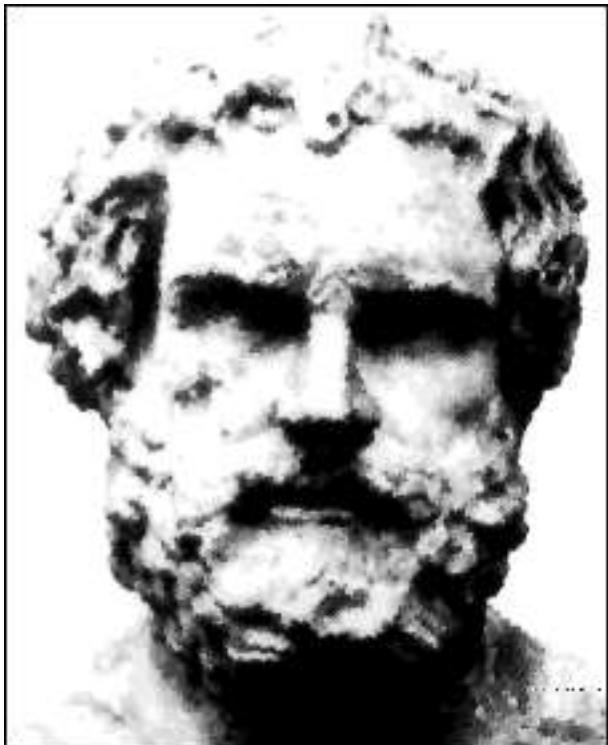
Bohr (1913) - Energy levels



Schrödinger (1926) - Electron cloud model

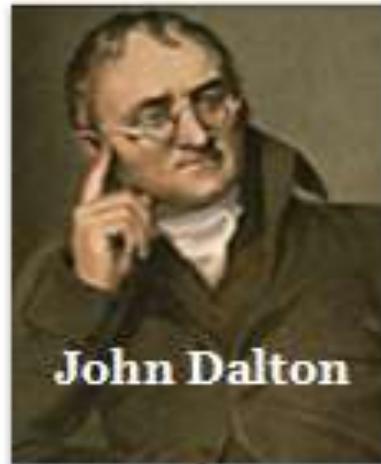
■ Atomic Model : Timeline

Democritus (400 BC)



- The smallest possible indivisible piece of matter is called “*atomos*,” meaning “*not to be cut*.”
- Atoms are small, hard particles that are all made of the same material but are of different shapes and sizes.
- Atoms are infinite in number, always moving and capable of joining together

Dalton's Model



John Dalton

Matter is made up of small indivisible particles, called atoms.

Atoms can neither be created nor destroyed.

Atom is the smallest particle of an element which takes part in a chemical reaction.

Atoms of the same element are identical in all respects especially, size, shape and mass.

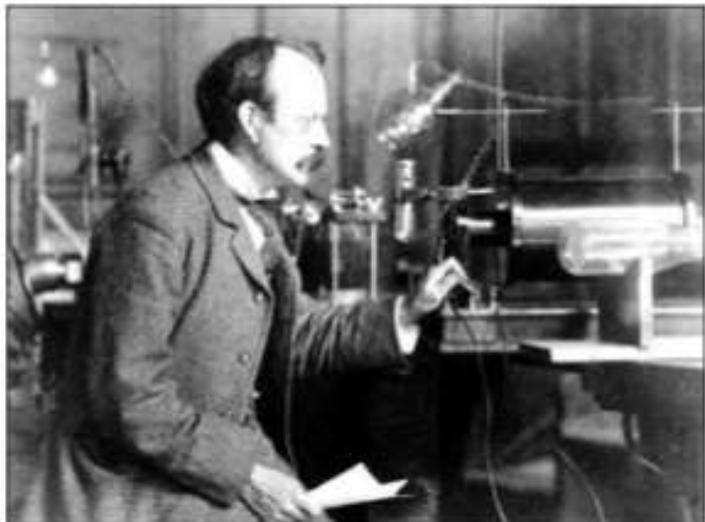
Atoms of different elements have different mass, shape and size.

Atoms of different elements combine in a fixed ratio of small whole numbers to, form molecules.

- *This theory became one of the foundations of modern chemistry.*

Dalton's theory states

1. matter is composed of indivisible particles called atoms. (Dalton visualized atoms as dense spheres – not unlike billiard balls)



However, the discovery of the electron by J.J. Thomson in the late 1800's introduced the idea that there might be something smaller than atoms.

Thomson's Plum Pudding Model



In 1897, the English scientist J.J. Thomson provided the first hint that an atom is made of even smaller particles.

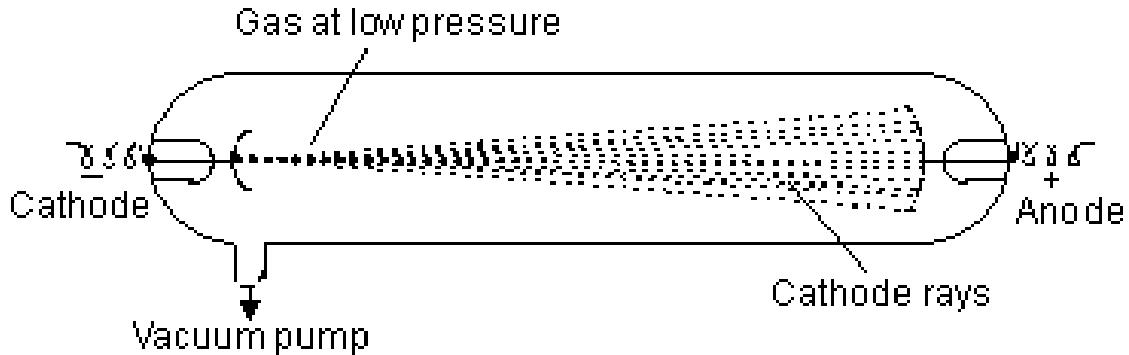
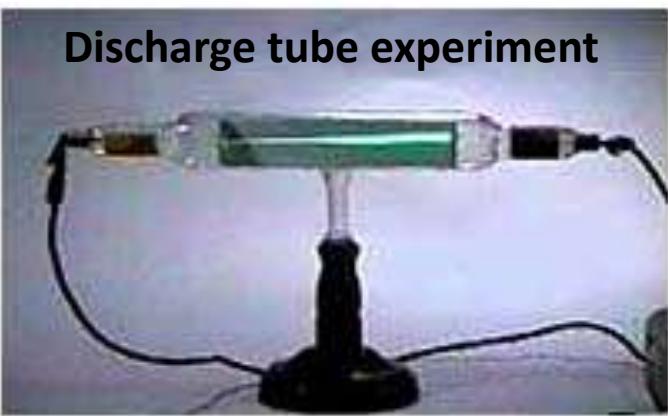


Fig. 1 Production of cathode rays

Discharge tube experiment



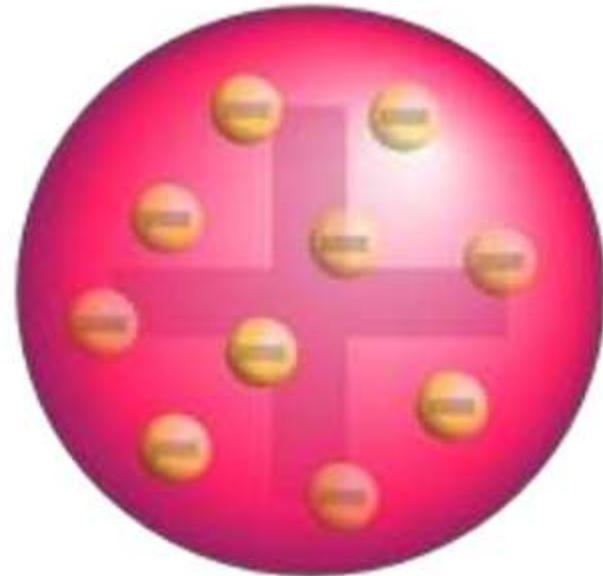
As the current passed through the gas, it gave off rays of negatively charged particles

Atoms were made from a positively charged substance with negatively charged electrons scattered about, like raisins in a pudding.

Thomson concluded that the negative charges came from within the atom.

A particle smaller than an atom had to exist. Thomson called the negatively charged “corpuscles,” today known as electrons.

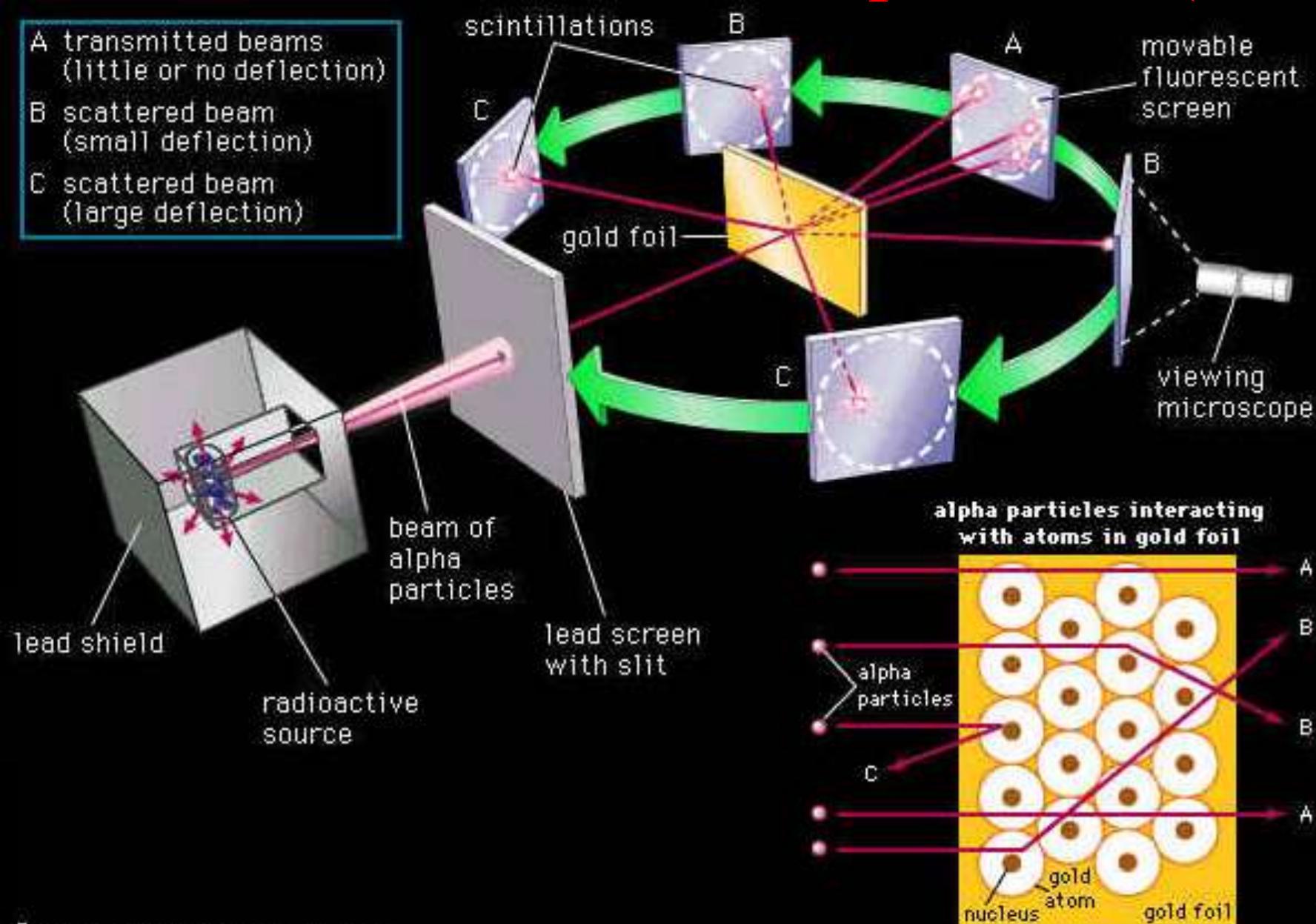
Since the gas was known to be neutral, having no charge, he reasoned that there must be positively charged particles in the atom.



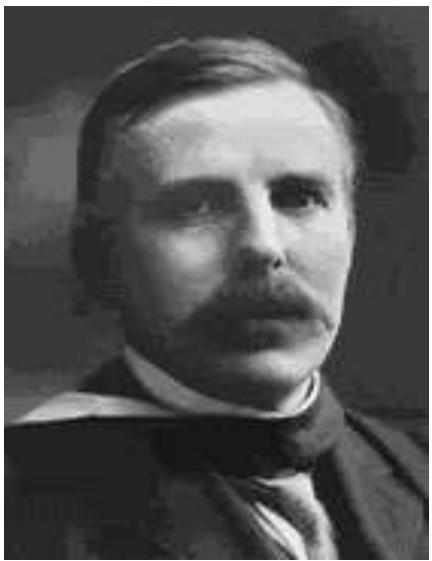
Atoms were made from a positively charged substance with negatively charged electrons scattered about, like raisins in a pudding.

Rutherford's Gold Foil Experiment (1911)

- A transmitted beams
(little or no deflection)
- B scattered beam
(small deflection)
- C scattered beam
(large deflection)



Rutherford's Gold Foil Experiment



- Rutherford concluded that an atom had a small, dense, positively charged center that repelled his positively charged “bullets”(α particles)
- He called the center of the atom the “nucleus”
- Rutherford reasoned that all of an atom’s positively charged particles are contained in the nucleus.

Electrons are in constant motion around the nucleus so that the Coulombic attraction of electron by nucleus is balanced by the centrifugal force that tends to pull the electron and nucleus apart.

A negative charge revolving around a positive charge without loss of energy!!

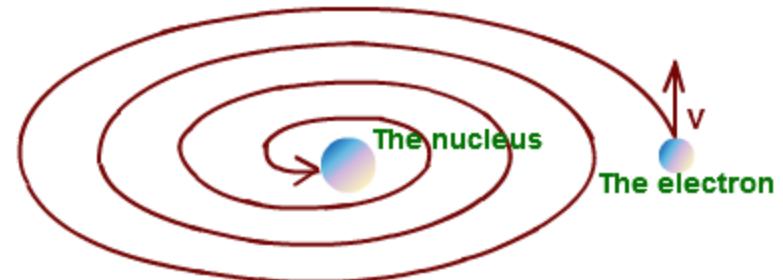
Such a model would give rise to continuous spectra instead of discrete line spectra!!

Drawbacks of Rutherford's Model

1. According to classic electromagnetic science which was known at the time, Rutherford's atomic model has an extremely short lifetime.

J.C. Maxwell had shown that whenever an electric charge is subjected to acceleration, it emits radiation and loses energy. This means, when an electron (negative charged particle) moves around the nucleus, it should be subjected to acceleration and should emit radiation with loss of energy. As a result, its orbit should become smaller and smaller and finally it should drop into the nucleus in a helical path instead of circular path. In other words, an atom is not a stable species.

On the contrary, the atom is stable and electrons and their energy in one of these orbits stay same.



In the planetary model of atom, the electron should emit energy and spirally fall on the nucleus.

- A number of experimental observations at that time were reported that could not be explained on the basis of the classical theory.
- Description of motion of physical objects (Classical Mechanics/Newtonian mechanics) is suitable only for macroscopic objects.

Problems that led to Quantum Concepts

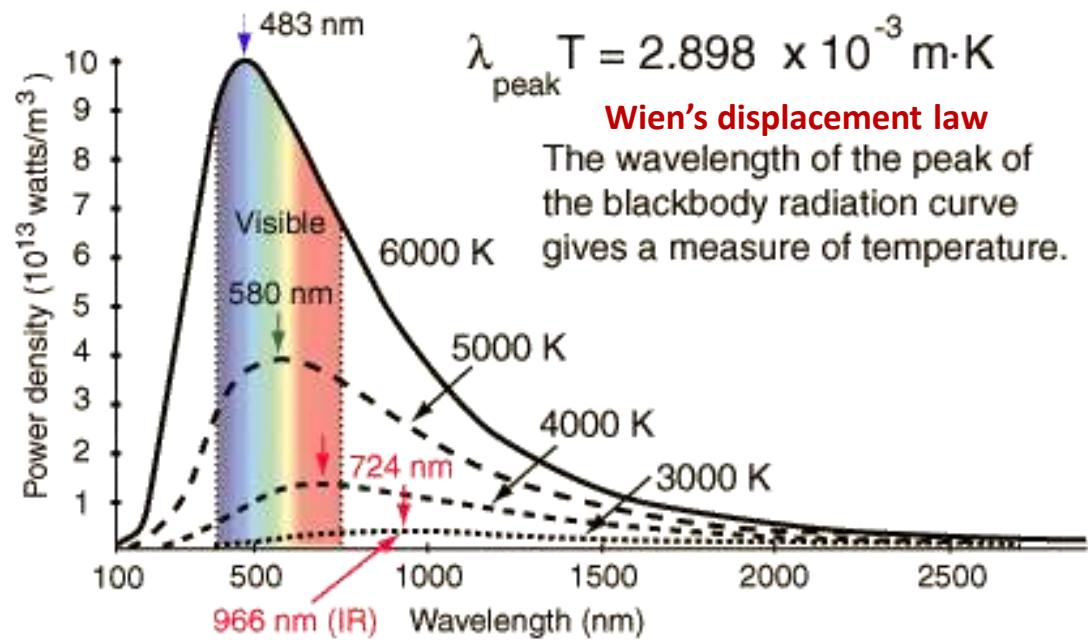
- Spectral energy distribution in black body radiation
- Photoelectric effect
- Discrete line spectra of atoms

Black-Body Radiation

A blackbody is defined as an object that

- completely absorbs all the incident radiations falling on it.
- A perfect absorber is also a perfect emitter of radiation and emits radiation at the maximum possible monochromatic intensity in all directions and at all wavelengths.
- Thus all bodies heated to a given temperature, maximum energy is radiated by a blackbody.

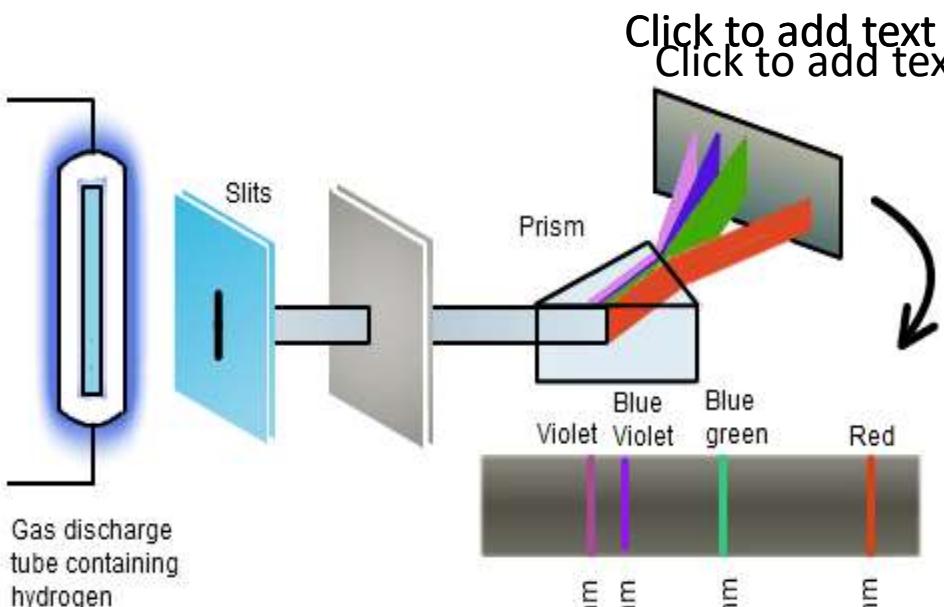
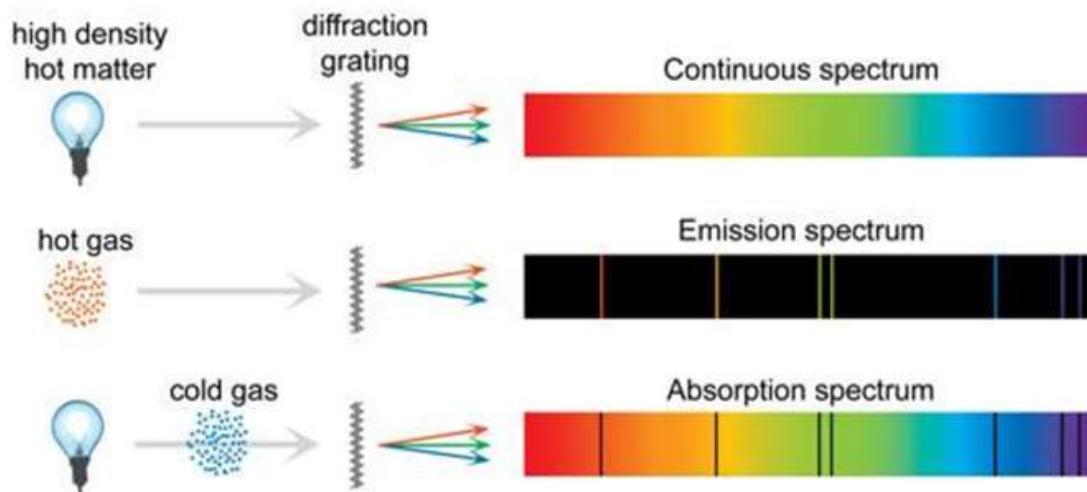
Black-body radiation curves showing peak wavelengths at various temperatures



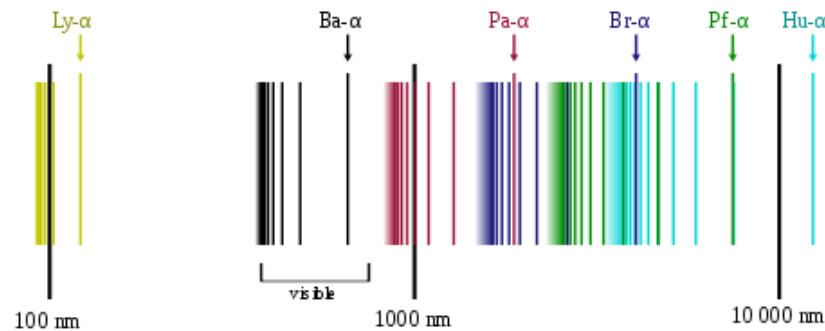
These curves show:

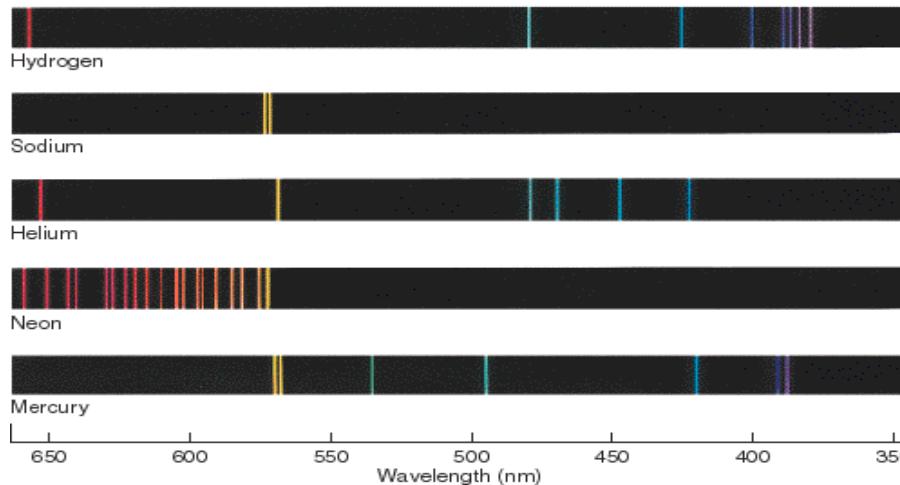
- For each temperature, there is a particular wavelength at which the energy radiated is maximum.
- The position of the maximum shifts towards lower wavelengths with increase in temperature.
- The higher the temp. the more pronounced in the maximum.
- As temperature increases, the total energy emitted increases, because total area under the curves increases

2. Discrete line spectrum of atoms



Hydrogen Spectrum





As per the Rutherford planetary model of atom, If an electron continually emits radiation, the atomic spectrum must be continuous. It means that there must be no line for fixed frequency. But the atomic spectrum is not a continuous spectrum. There are many lines with fixed frequency. Hence the Rutherford atomic model failed to explain the line spectrum of atoms.

In order to explain the first objection concerning why electrons do not fall into the nucleus on account of mutual electrostatic attraction, Rutherford proposed that the electrons are revolving at an extremely high speed and at great distance from the center. So, the centrifugal force arising from this motion balances the force of electrostatic attraction.

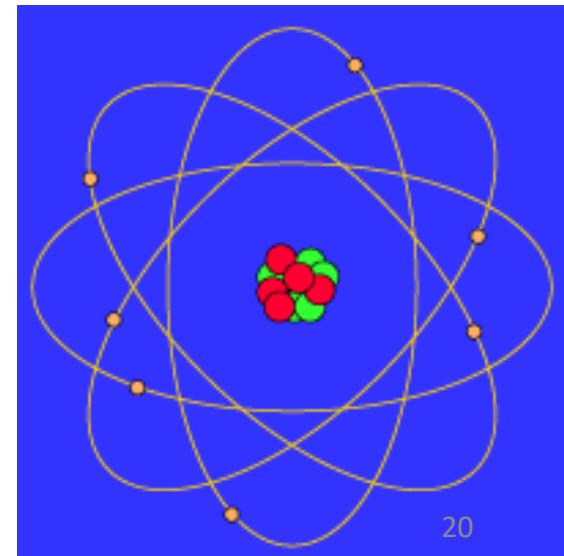
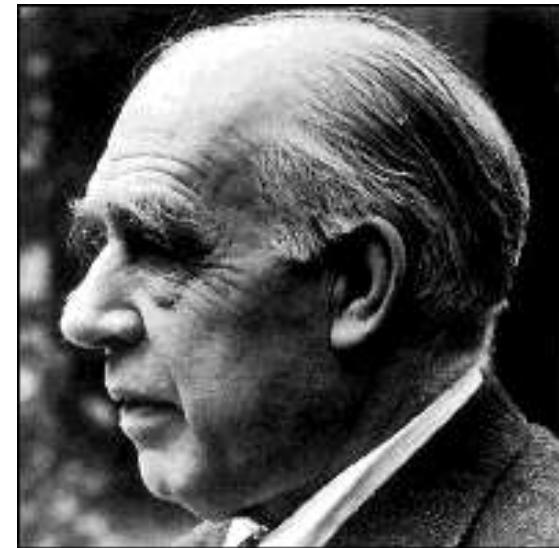
The electrons, therefore, do not fall in to the nucleus and the atom will be stable. But there was no clarification for atomic spectrum pattern. Bohr supplied the solution of this difficulty on the basis of quantum theory of radiation.

Bohr's Model

Got Nobel Prize in 1922 for foundational contribution to understand atomic structure.

- Electrons move in definite orbits around the nucleus, much like planets circle the sun.
- Each orbit is associated with a certain amount of energy (quantized)
- Not every orbit is possible but only certain specific ones
- The allowed orbits depend on quantized (discrete) values of *orbital angular momentum* according to the equation
$$mv_r = nh/2\pi = nh$$

Where $n = 1, 2, 3, \dots$ and is called the *principal quantum no.*, and h is Planck's constant

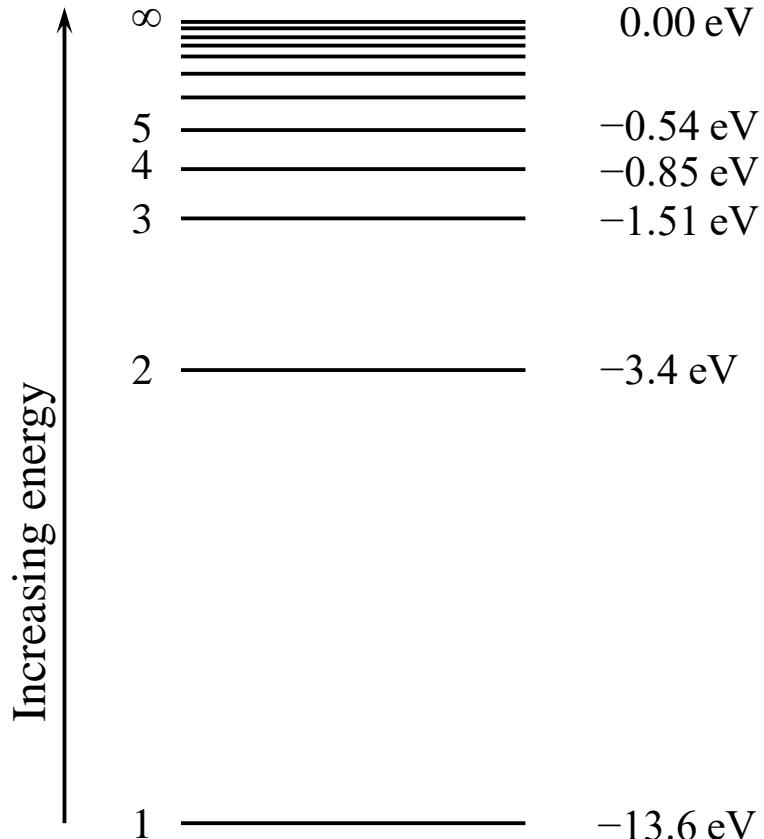


Bohr's Model

$$r = \frac{4\pi\varepsilon_0 n^2 \hbar^2}{\mu Ze^2} = \frac{\varepsilon_0 n^2 h^2}{\pi\mu Ze^2}$$

$$E = -\frac{Z^2 e^4 \mu}{8\varepsilon_0^2 n^2 h^2} = -\frac{Ze^2}{8\pi\varepsilon_0 r}$$

$$E = \frac{-13.6}{n^2} \text{ eV}$$



μ = reduced mass of electron-nucleus combination = $mm_N/(m+m_N)$

Z = Charge of nucleus or atomic number

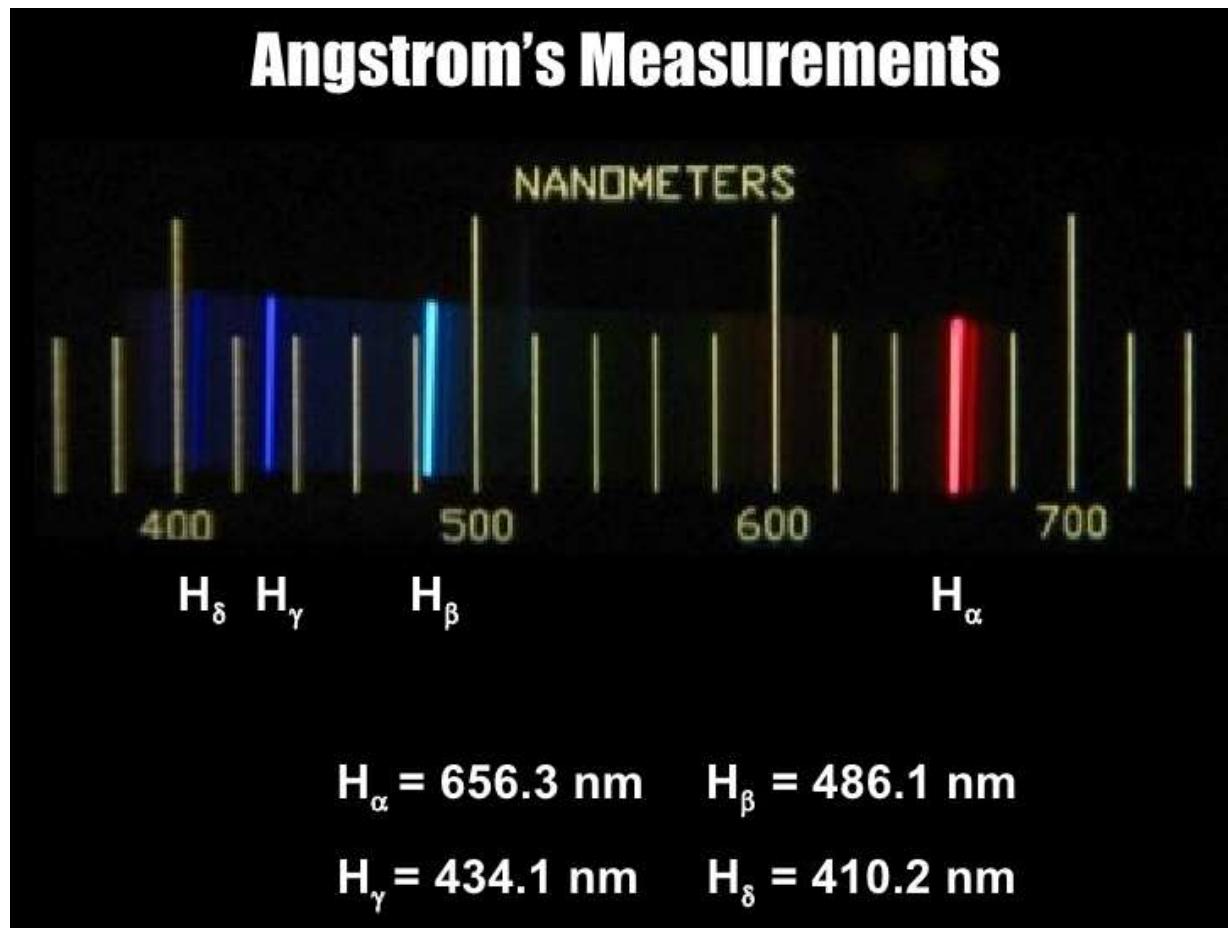
e = electronic charge

h = Planck's constant

n = principal quantum number

The spectrum of the Hydrogen atom

Accurate measurements of four visible emission lines of hydrogen had been measured by Anders Angstrom.



Balmer Series

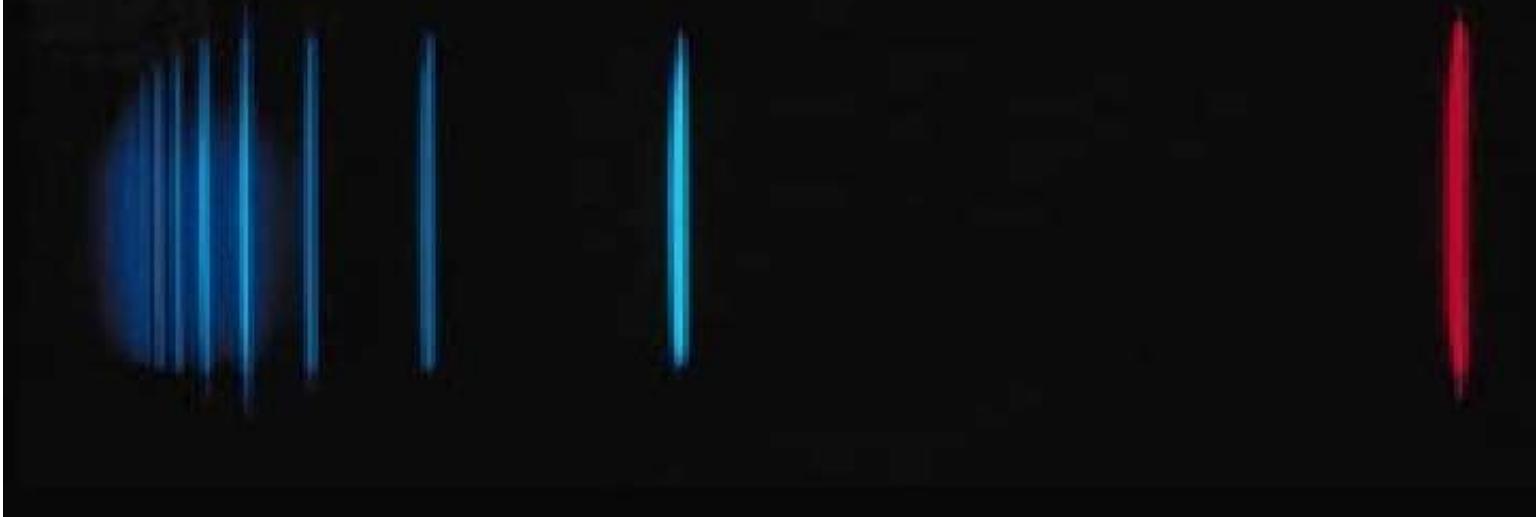
- By trial and error a Swiss school teacher, Johann Balmer, found a formula which correctly predicted the wavelengths of Angstrom's four visible lines.
- Balmer gave his formula in the form:



$$\lambda \text{ (cm)} = C_2 \left(\frac{n^2}{n^2 - 2^2} \right) \quad n = 3, 4, 5, \dots$$

- Where $C_2 = 3645.6 \times 10^8 \text{ cm}$ and is known as the convergence limit.

- Only four lines were known to Balmer when he started his investigation of the spectral series.
- By the time he finished, ten more lines in the violet and ultraviolet range had been measured.
- These newly measured lines agreed to the empirical formula to within 0.1%!



Encouraged by his success, Balmer speculated that other hydrogen series might exist of the form:

$$\lambda \text{ (cm)} = C_2 \left(\frac{n^2}{n^2 - 3^2} \right)$$

$$\lambda \text{ (cm)} = C_2 \left(\frac{n^2}{n^2 - 4^2} \right)$$

Rydberg Formula

- Balmer was correct.
- The Rydberg formula combines all of these series into the single formula:

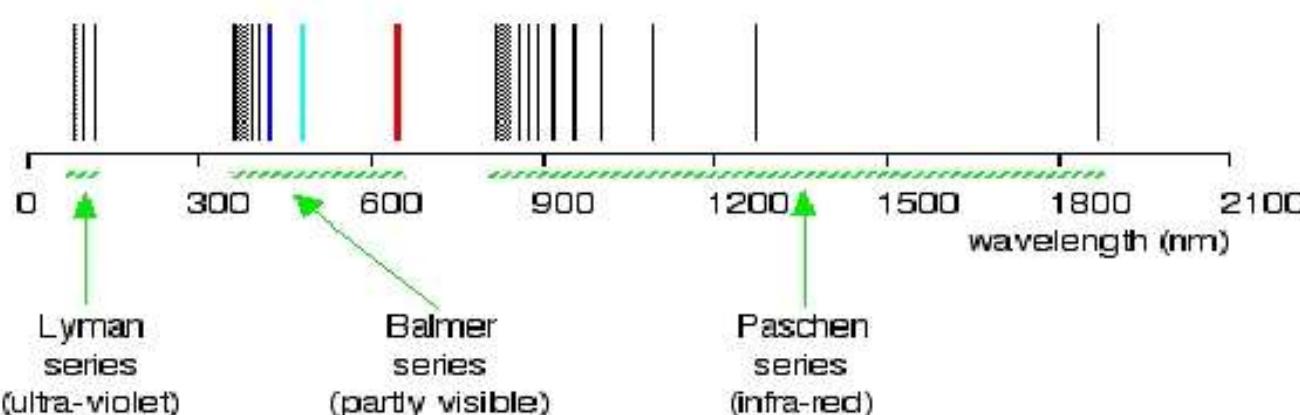
$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$



- Where n_f and n_i are integers.
- $n_i = n_f + 1$
- The Rydberg constant (R) = $1.0973 \times 10^7 \text{ m}^{-1}$

Spectral series for Hydrogen

Name	Wavelength Range	Series Expression
Lyman	Ultraviolet	$\frac{1}{\lambda} = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right), n \geq 2$
Balmer	Near UV & Visible	$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right), n \geq 3$
Paschen	Infrared	$\frac{1}{\lambda} = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right), n \geq 4$
Brackett	Infrared	$\frac{1}{\lambda} = R \left(\frac{1}{4^2} - \frac{1}{n^2} \right), n \geq 5$
Pfund	Infrared	$\frac{1}{\lambda} = R \left(\frac{1}{5^2} - \frac{1}{n^2} \right), n \geq 6$



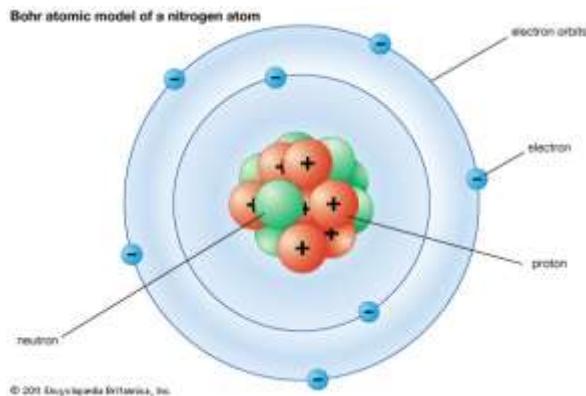


Atomic Structure

Bohr's Model (planetary model)-1914

Assumes electron as particle

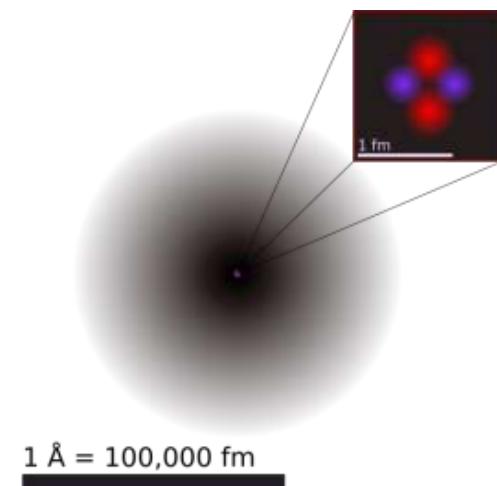
Got Nobel Prize in 1922 for foundational contribution to understand atomic structure.



Schrödinger Model (electron cloud model)- 1926

Assumes electron as wave

Got Nobel Prize in 1933 for his Schrödinger wave equation for H-like atoms.



Bohr's explanation

- When an electron makes a jump from one orbit to another the energy difference is carried off (or supplied) by a *photon* which has an energy equal to the energy difference between the two orbitals. **This accounts for the discrete line spectrum.**
- Bohr applied Planck's idea of quantization of energy to explain hydrogen spectra

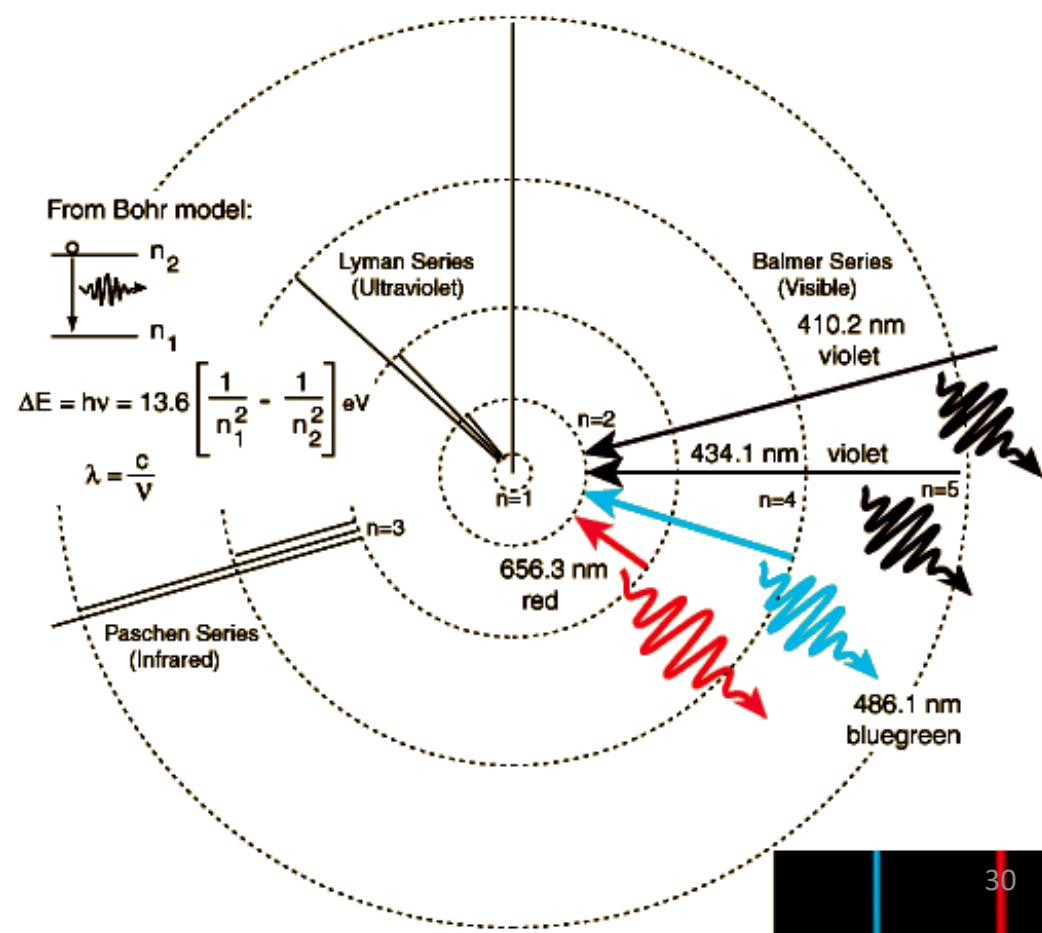
For hydrogen atom

$$\Delta E = h\nu = 13.6 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ eV}$$

Similar to **Ritz equation**

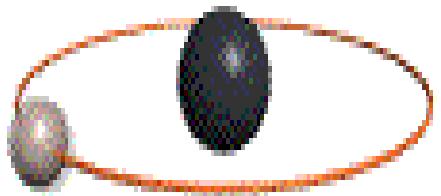
$$\nu = \frac{\Delta E}{h} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$R_H = \text{Rydberg Constant} \\ = 1.0974 \times 10^7 \text{ m}^{-1}$$



Bohr model of hydrogen-like atom

1. The electrons moves around the nucleus in a well defined circular orbits, which are distinctly separated from each other. The centipetal force that curves the path of the electron is provided by the columbic force of attraction between them



$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$





Bohr model of hydrogen-like atom

2. The total energy of the electron remains constant as long as it remains in the orbit

$$E_{total} = K.E. + P.E.$$

$$= \frac{1}{2}mv^2 + \left(-\frac{Ze^2}{4\pi\epsilon_0 r} \right)$$

3. Only certain orbits are allowed. Each orbit having a quantized value of angular momentum

$$mv r = nh/2\pi \quad (n = 1, 2, 3, \dots)$$

$$mv r = n\hbar$$



Bohr model of hydrogen-like atom

The orbits are discrete, so the energy of an electron in an orbit is quantized.

$$mv\mathbf{r} = nh/2\pi$$

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \quad \dots\dots \quad (1)$$

The electrostatic attraction between electron and nucleus must be equal to centrifugal force.

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad \Rightarrow \quad v^2 = \frac{Ze^2}{4\pi\epsilon_0 mr} \quad \dots\dots\dots \quad (2)$$

Combining (1) and (2)

$$r = \epsilon_0 n^2 h^2 / \pi m e^2 Z \quad \dots\dots \quad (3)$$

$$r = 0.529 \text{ \AA} = \text{First Bohr's radius for H-atom}$$

Bohr's Model

The energy of an electron when it jumps from one orbit to other is

$$E = -1/2mv^2, \quad E = -Ze^2/8\pi\epsilon_0 r$$

By putting the value of r in the above equation,

$$E = -Z^2e^4m/8\epsilon_0^2n^2h^2 \dots\dots (4)$$

$$\text{Or, } E = -Z^213.6/n^2 \text{ eV} \dots\dots (5)$$

m = mass of electron

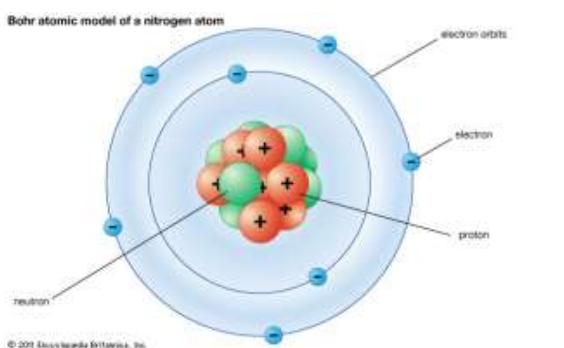
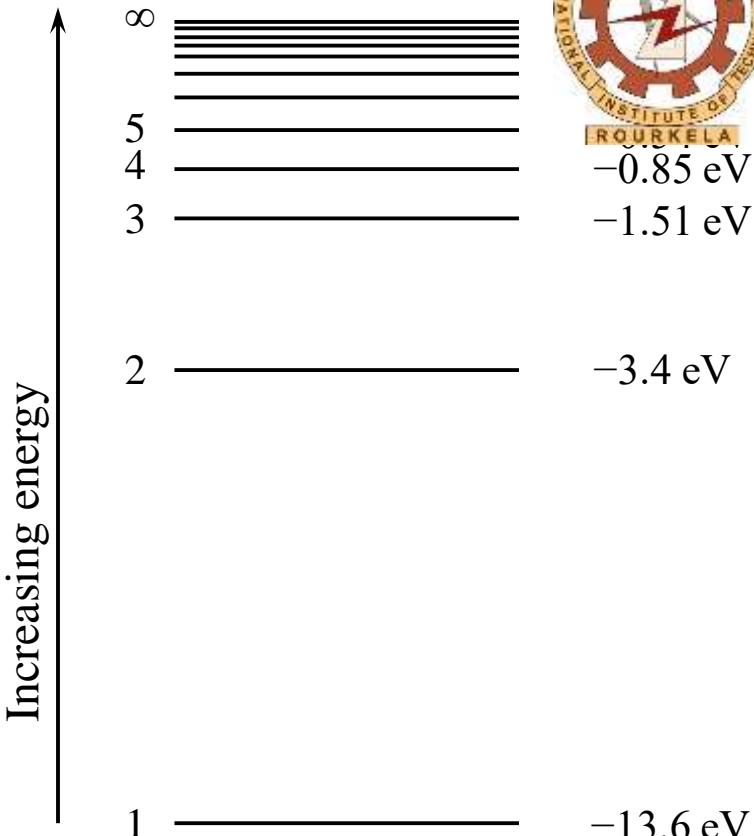
Z = Charge of nucleus or atomic number

e = electronic charge

h = Planck's constant

n = principal quantum number

Q1. What is the ratio of the energy of a ground state He^+ ion to that of Be^{3+} ion?



- Explains Line spectra of hydrogen atom

$$h\nu = E_f - E_i$$

$$h\nu = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0 n_f^2} + \frac{Z^2 e^2}{8\pi\epsilon_0 a_0 n_i^2}$$

$$\frac{hc}{\lambda} = \frac{Z^2 e^2}{8\pi\epsilon_0 a_0} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

- Calculated the Value of Rydberg Constant (R).

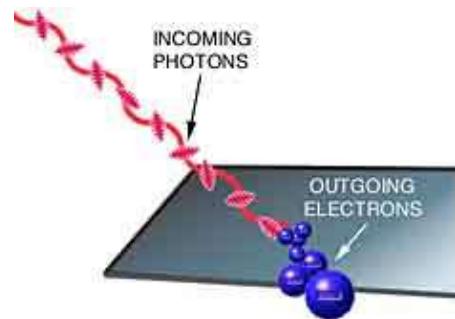
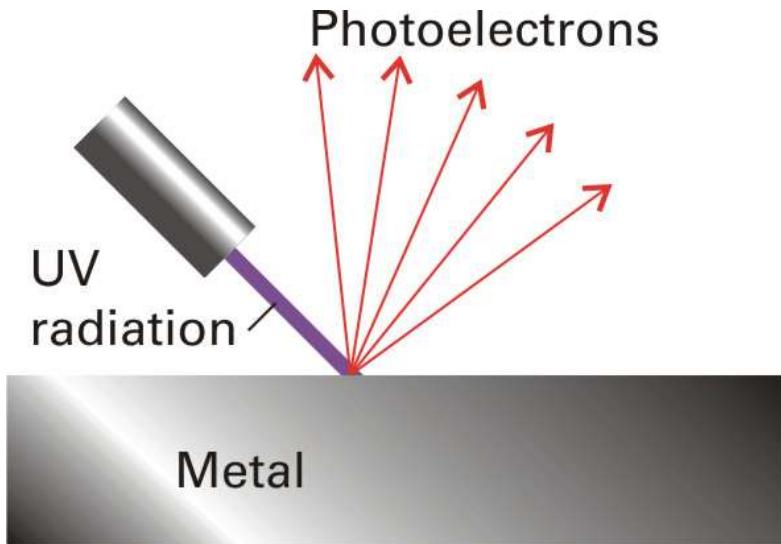
Drawbacks of Bohr's model

- The model only worked for hydrogen-like atoms.
- Failed to explain the spectra of larger atoms. At best, it can make some approximate predictions about the emission spectra for atoms with a single outer-shell electron
- Could not explain the relative intensities of spectral lines
- The existence of fine and hyperfine structure in spectral lines.
- The Zeeman effect - changes in spectral lines due to external magnetic fields.

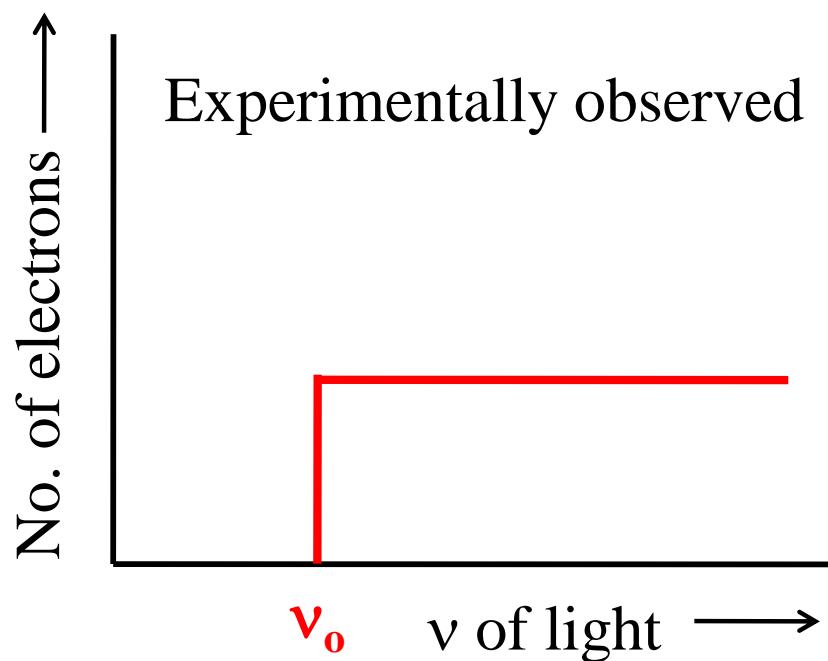
Bohr's model considered electrons as particles

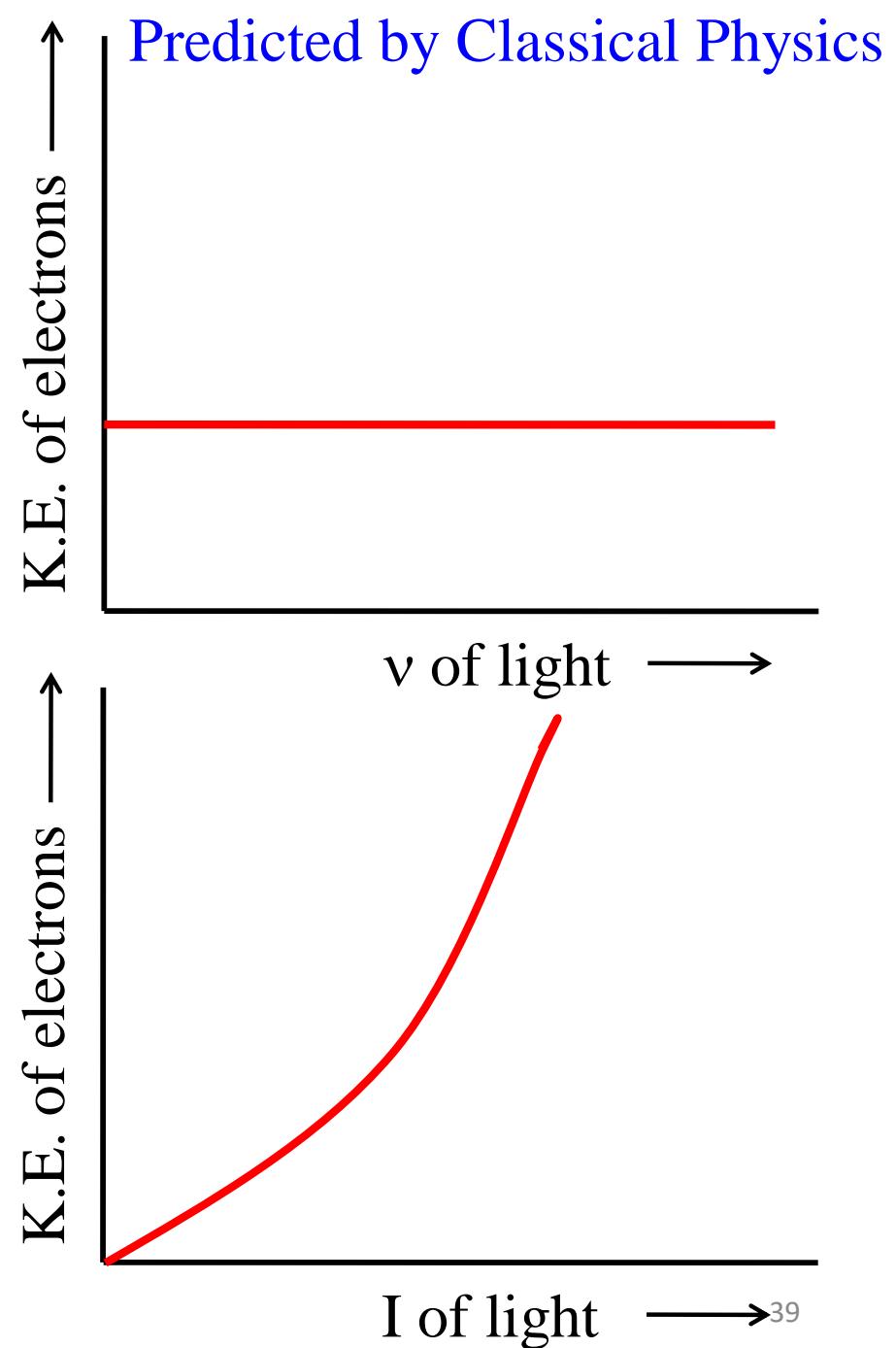
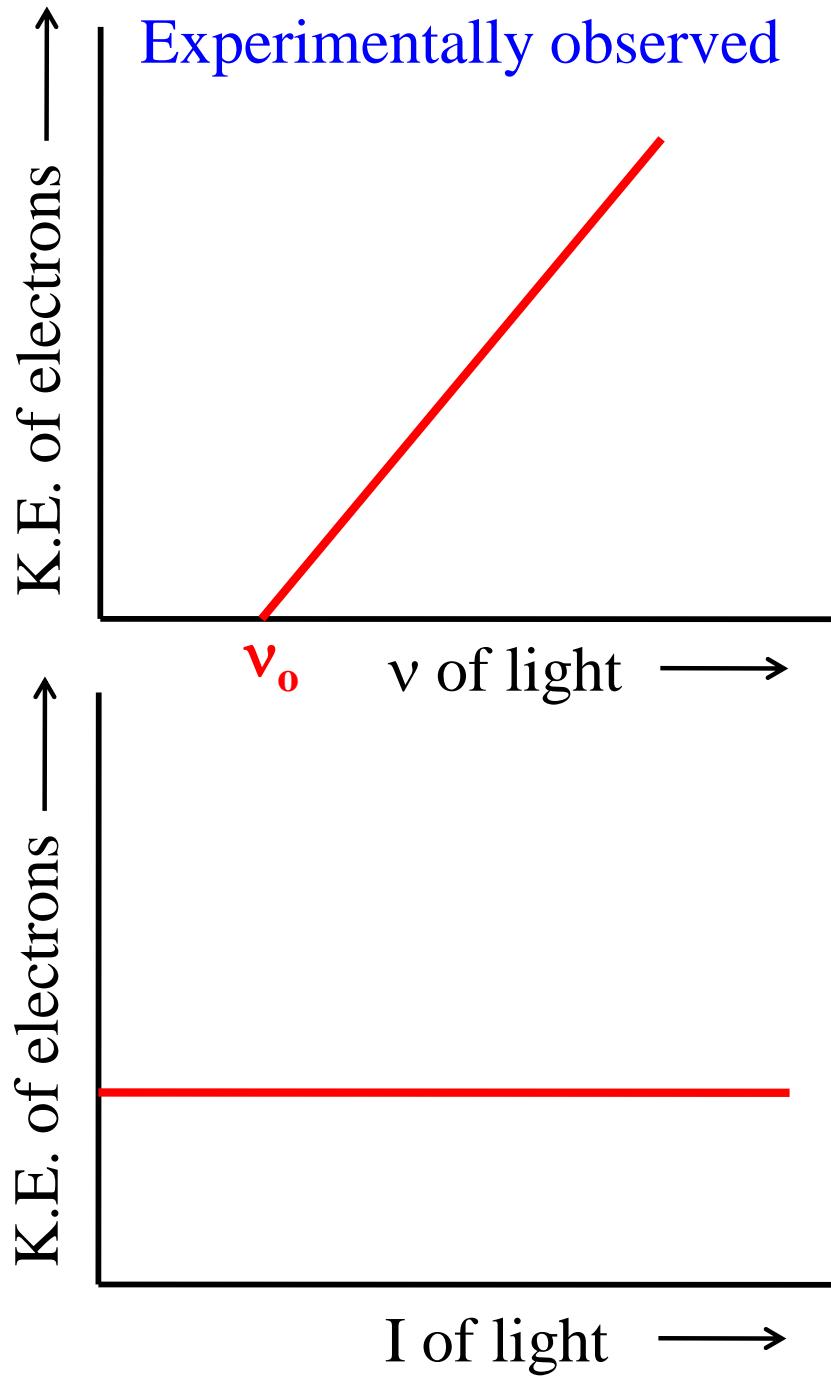
A semiclassical model

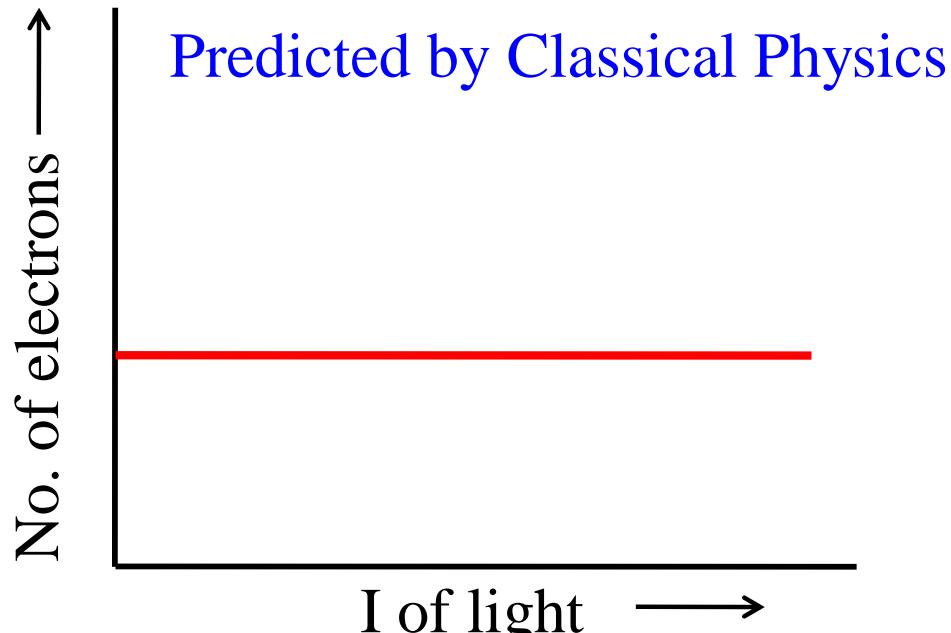
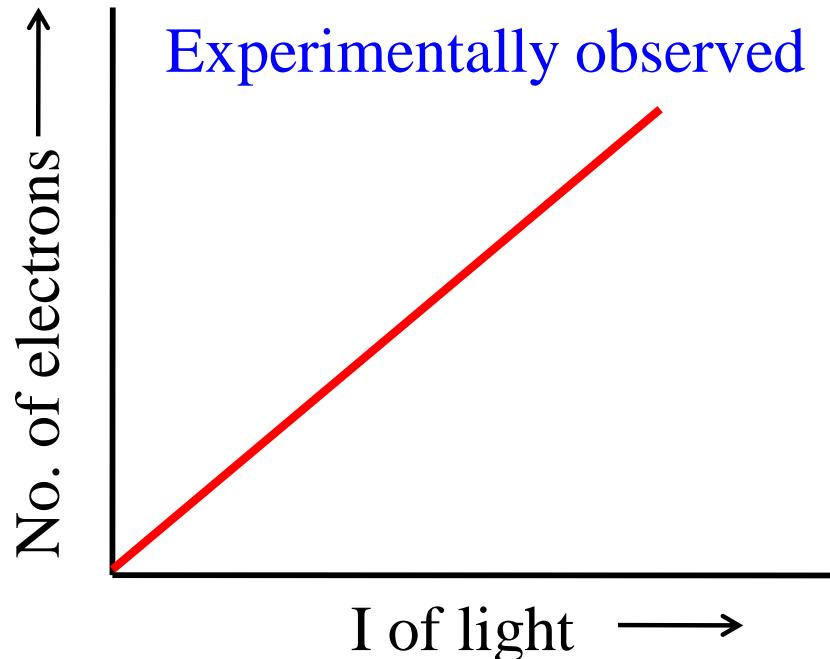
Photoelectric Effect



Emission of electrons from metals when exposed to (ultraviolet) radiation.

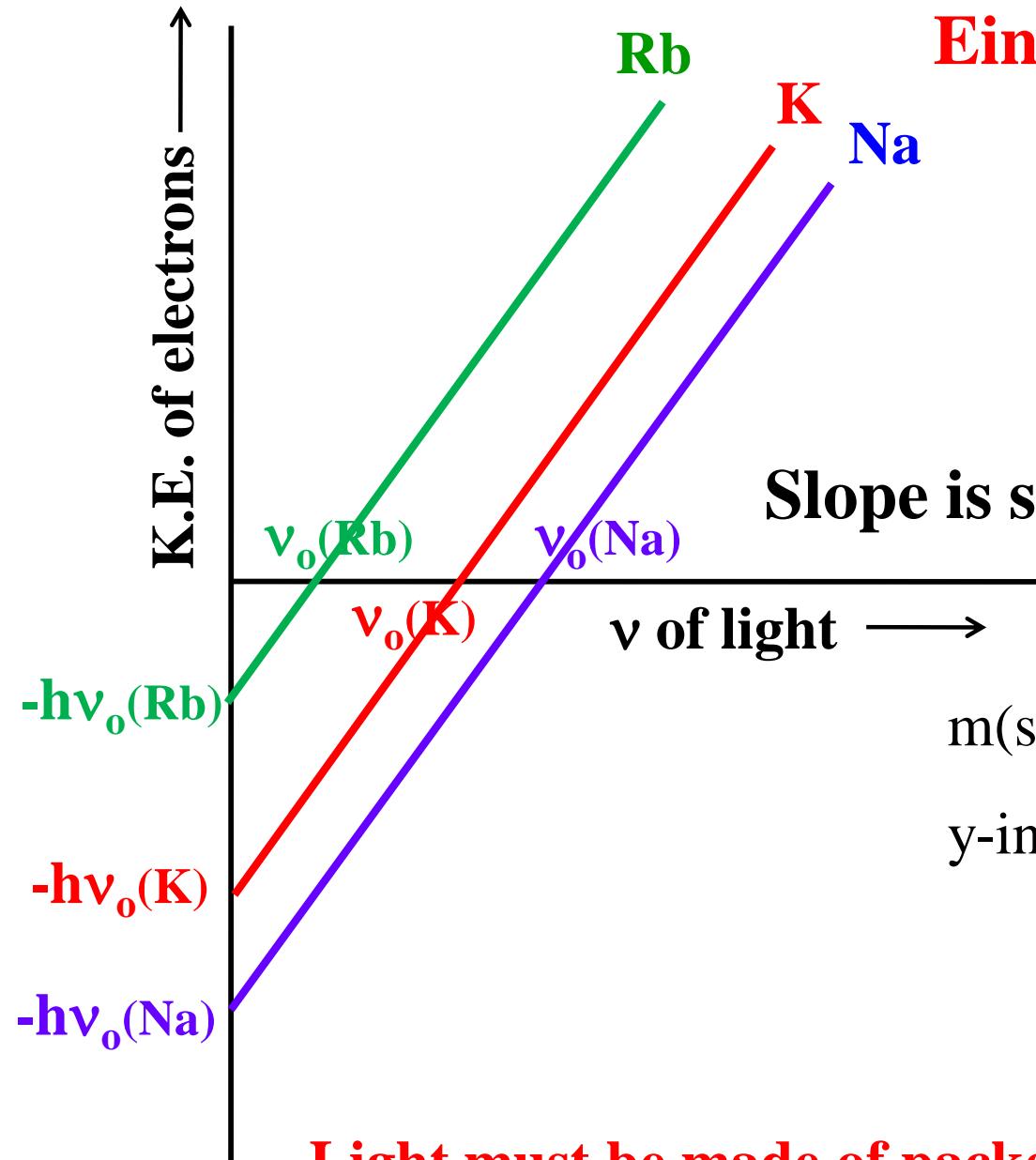
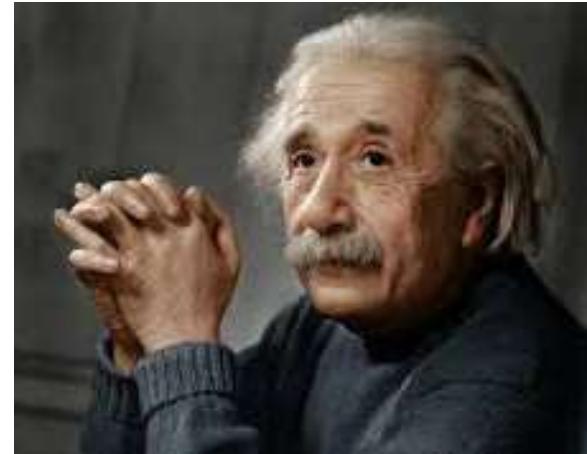






- No emission of electrons if the frequency of radiation is below a threshold value characteristic of the metal, however high the intensity of the light.
- Kinetic energy of emitted electrons varies linearly with the frequency, and is independent of light intensity.
- For frequencies above the threshold value, emission of electrons is instantaneous, no matter how low the intensity of the light.

Wave nature of light (classical theory) fails to explain this



Slope is same irrespective of metal

$$y = mx + c$$

$$m(\text{slope}) = 6.626 \times 10^{-34} \text{ Js}$$

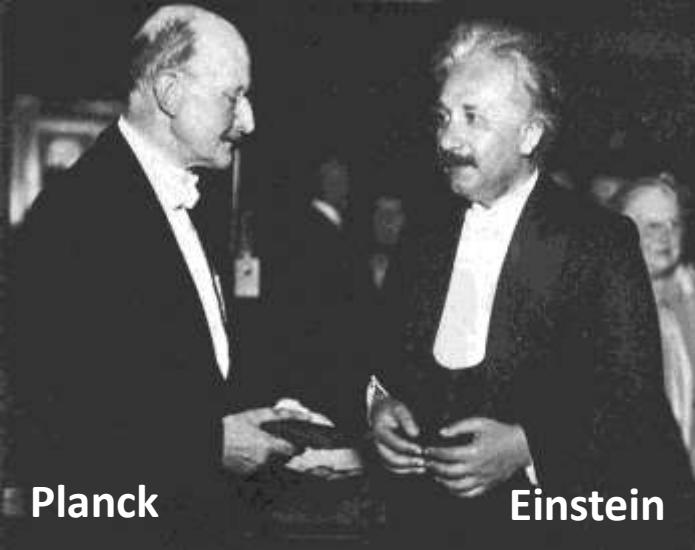
$$\text{y-intercept} = -6.626 \times 10^{-34} \nu_0$$

$$\text{K.E.} = h\nu - h\nu_0$$

$$E = h\nu$$

Light must be made of packets of energy called photon

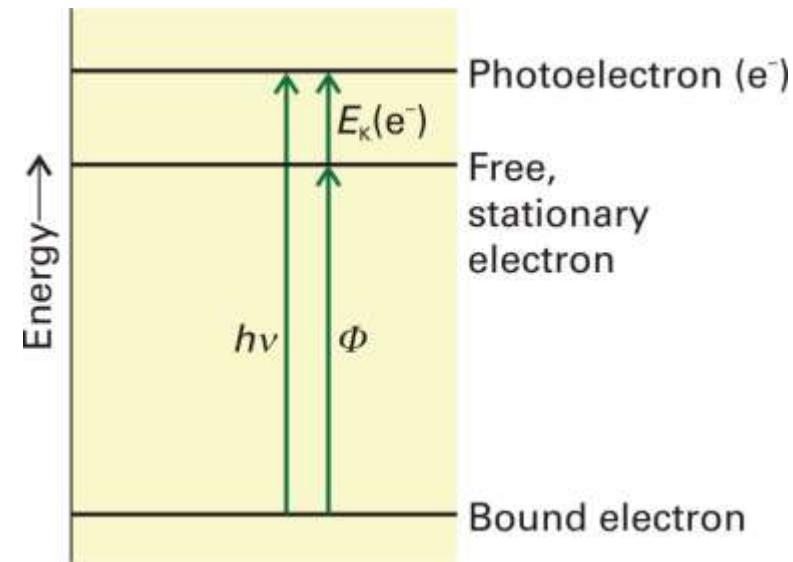
Energy of photon $\propto \nu$



Einstein (1905): Extended Planck's quantum theory.

Dual Nature of Light:

Light has both wave as well as particle character. $E = mc^2 = h\nu$



The kinetic energy of the emitted electron

$$\text{K.E} = h\nu - \Phi$$

ν is the frequency of incident radiation

Φ is the work function (minimum energy required to remove an electron from the metal surface)

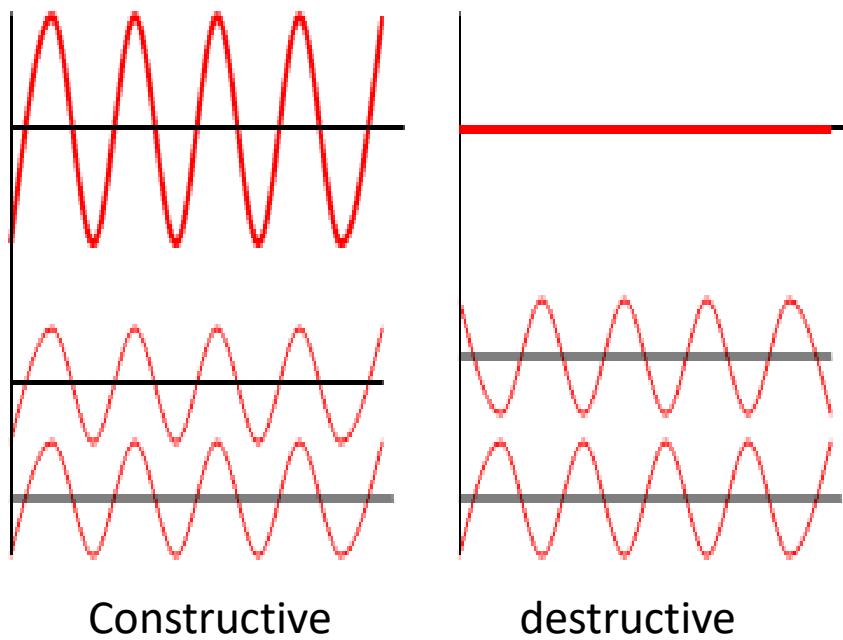
$\Phi = h\nu_0$, ν_0 is the threshold frequency

For radiation with $\nu > \nu_0$, electron is emitted instantaneously irrespective of the intensity

Wave-Particle Duality

Common concept of particle in nature: electrons, Light (photoelectric effect)

Common concept of wave: diffraction, interference; again exhibited by Light!!!!



Interference: Superposition of two or more waves to generate new patterns

Photon Momentum

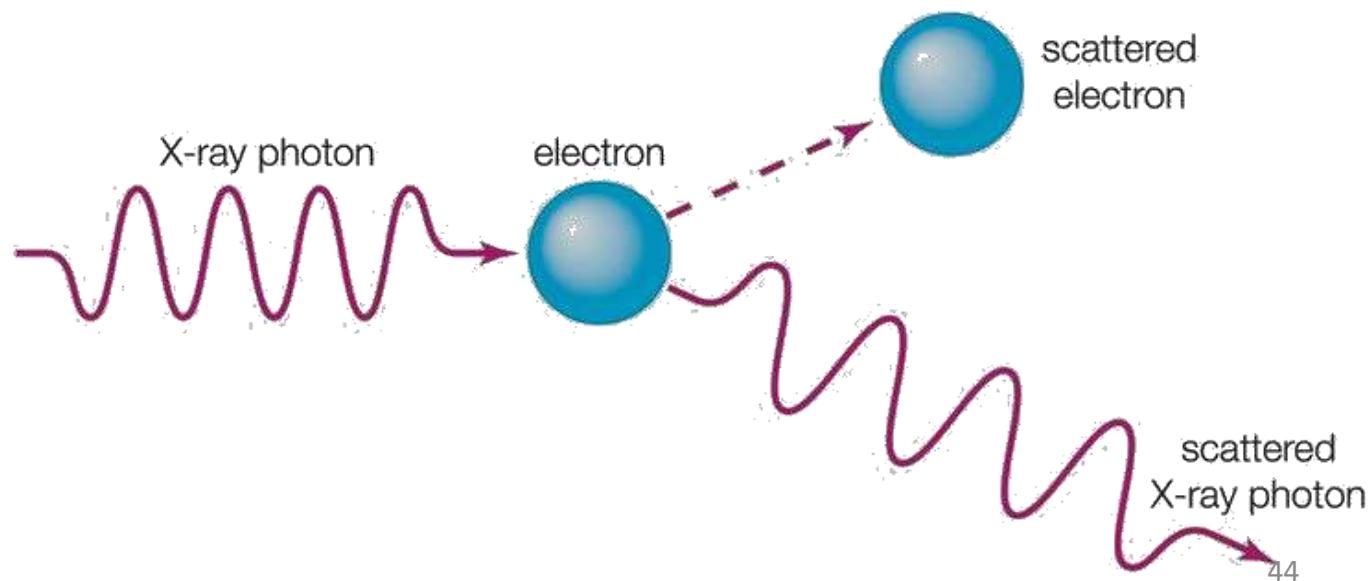
If light is a particle, it should have momentum ‘p’

Photon does not have mass but has momentum!!

$$p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

Experimental proof for momentum of photon (Compton Scattering)

Compton scattering: discovered by **Arthur Holly Compton:** the inelastic scattering of a photon (an X-ray or gamma ray photon) by a charged particle, usually an electron.



de Broglie (1924): Wave-Particle Duality

Nobel Prize : 1929

Just as light exhibits both ‘wave-like’ and ‘particle-like’ characteristics, so should all material objects.



For light (photon) $E = pc = hc/\lambda \Rightarrow \lambda = h/p$

de Broglie suggested that this is more generally true of all material objects.

A particle (mass m) moving with linear momentum p (velocity v), has an associated ‘matter-wave’ of wave length:

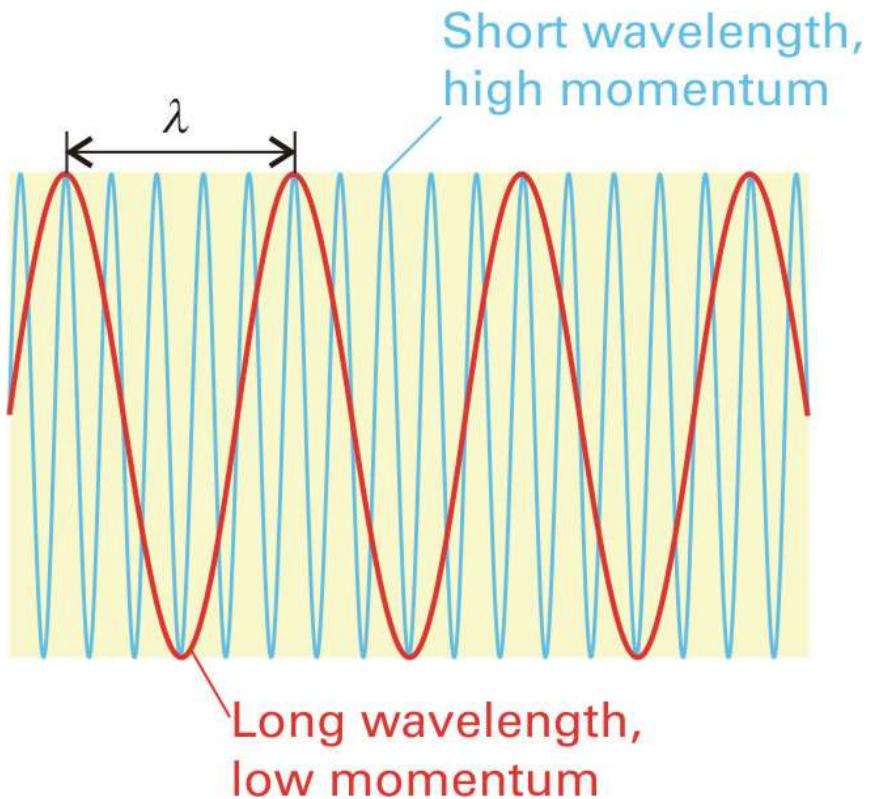
$$\lambda = h/p = h/mv$$

Q2. Calculate the de Broglie wave length of

- (i) *an electron moving with velocity 10^4 m/sec. [mass of e = 9.1×10^{-31} kg]*
- (ii) *A 400 g Frisbee moving at 10 km/h*

Ans. (i) 72 nm

(ii) 5.96×10^{-34} m (immeasurable)



Macroscopic objects are so massive that the de Broglie wave lengths are immeasurably small.

How much large object's wave – manifestation is observable and known?

C₆₀ fullerene's wave manifestation: Large, massive object (diameter is in nm range)

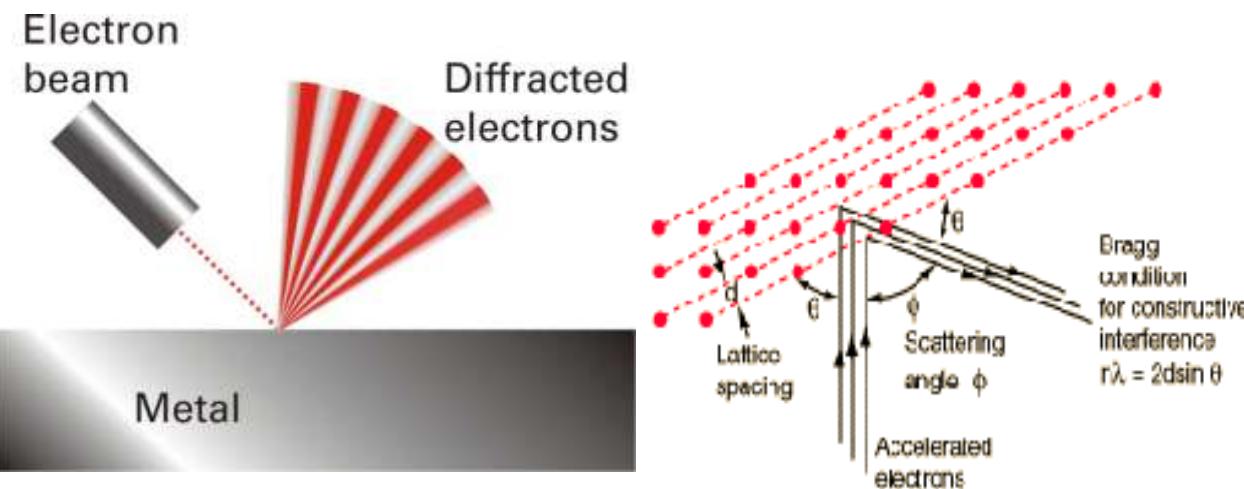
de Broglie wavelength is 2.5 pm i.e. about 400 times smaller than diameter.

Largest object for which quantum-mechanical wave-like properties have been directly observed in diffraction.

•Journal: Nature 401: 680-682, 1999

Experimental proof of de Broglie's hypothesis

Davisson–Germer experiment (1923-1927) confirms the de Broglie's hypothesis (wave-particle duality).



They discovered the **wave nature of electron** by getting a diffraction pattern from a Ni crystal by bombarding a beam of electron.

Electron beam was scattered by the surface atoms at the exact angles predicted for the diffraction of waves, with a typical wavelength

Heisenberg's uncertainty principle (1927)



*"The more precisely the position is known
the less precisely the momentum is known
in this instant, and vice versa"*

-Heisenberg

$$\Delta x \Delta p_x \geq h/4\pi$$

The more precisely we can define the position of an electron the less certainly we are able to define its velocity, and vice versa.

Complementary variables: increase in the precision of one possible only at the cost of a loss of precision in the other.

Momentum: Position

Energy: Time

Hence orbits are replaced by orbitals (*the probability of finding an electron in a given space*).

de Broglie and Heisenberg principles and the electron diffraction experiments established that electrons are not ordinary particles; they are also waves

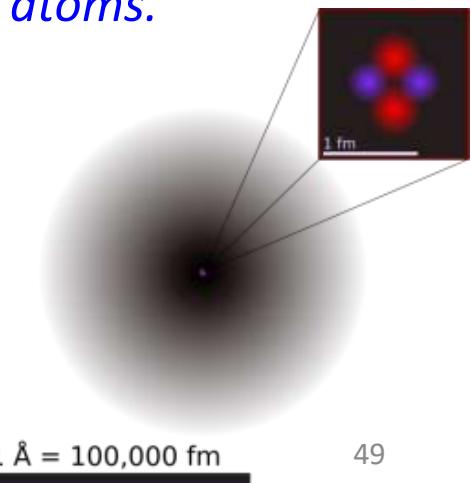
Schrödinger Model (electron cloud model)- 1926

Pictured electron as wave

- An equation is needed to describe matter
- Matter can be described by a corresponding wave
- This equation should also describe the probabilistic nature of matter
- The quantum nature of matter: energy, linear momentum, angular momentum should turn out to be quantized/ discrete from solution of this equation
- Behavior of light and matter for example, can be described by a differential equation in terms of **WAVE FUNCTION**
- Such wave function should give the probability of finding the particle at a point correctly



*Nobel Prize in 1933
for Schrödinger wave equation for H-like atoms.*



$1 \text{ \AA} = 100,000 \text{ fm}$

Schrödinger's equation

Schrodinger proposed that if electrons could behave like waves then the equations of wave motion can be successfully applied for them

Schorinder used the classical time-independent wave equation to describe the particle wave but substituted de Broglie's relation for λ

Why time-independent??

Many problems of interest to chemists can be treated by using only stationary-state (time-independent) wave functions.

The fundamental wave equation describing the behaviour of a small particle in one direction in terms of wave motions is

$$\frac{d^2\psi}{dx^2} = - \frac{4\pi^2\psi}{\lambda^2}$$

ψ : wave function
(= amplitude of the wave in classical wave equation)
 x : displacement in the x-direction
 λ : wavelength

Using de Broglie's equation $\lambda = h/mv$

$$\frac{d^2\psi}{dx^2} = - \frac{4\pi^2 m^2 v^2 \psi}{h^2} \quad \Rightarrow \quad m^2 v^2 = - \frac{h^2}{4\pi^2 \psi} \frac{d^2\psi}{dx^2}$$

Stationary wave associated with particle in terms of coordinate system is

$$\psi = A \sin \frac{2\pi x}{\lambda} - \textcircled{1}$$

A = Max. value of ψ

A = Amplitude
of wave function

x = distance from nucleus / displacement
 x -direction

λ = wavelength.

Diff eqn $\textcircled{1}$ w.r.t x , we get

$$\frac{\partial \psi}{\partial x} = A \cos \frac{2\pi x}{\lambda} \left(\frac{2\pi}{\lambda} \right)$$

$$\frac{\partial \psi}{\partial x} = \frac{2\pi A}{\lambda} \cos \frac{2\pi x}{\lambda} - \textcircled{2}$$

Again diff eq $\textcircled{2}$ w.r.t. x , we get

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{2\pi A}{\lambda} \left(-\sin \frac{2\pi x}{\lambda} \right) \left(\frac{2\pi}{\lambda} \right)$$

$$= -\frac{4\pi^2}{\lambda^2} \underbrace{A \sin \frac{2\pi x}{\lambda}}_{\psi} - \textcircled{3}$$

From eqn $\textcircled{1}$ & $\textcircled{2}$, we get

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

$$\lambda^2 = -\frac{4\pi^2}{\partial^2 \psi / \partial x^2}$$

Acc. to deBroglie equ.

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

$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

$$m^2 v^2 = -\frac{h^2}{4\pi^2 \psi} \frac{d^2 \psi}{dx^2} \Rightarrow KE = -\frac{h^2}{8\pi^2 m \psi} \frac{d^2 \psi}{dx^2} \quad (KE = \frac{1}{2} mv^2)$$

$$\frac{d^2 \psi}{dx^2} = -\frac{8\pi^2 m}{h^2} (E - V) \psi \quad \text{Total energy } E = KE + PE = KE + V$$

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

→ **Schrodinger's equation** in one dimension

For motion in three dimensions

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

← **Schrodinger's equation**

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \text{Laplacian Operator}$$

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \Rightarrow \left[\frac{-h^2}{8\pi^2 m} \nabla^2 + V \right] \psi = E \psi$$

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

Schrodinger's equation

$$\hat{H} = \left[\frac{-h^2}{8\pi^2 m} \nabla^2 + V \right] = \text{Hamiltonian Operator}$$

E = Total energy of electron

Ψ = wave function of electron

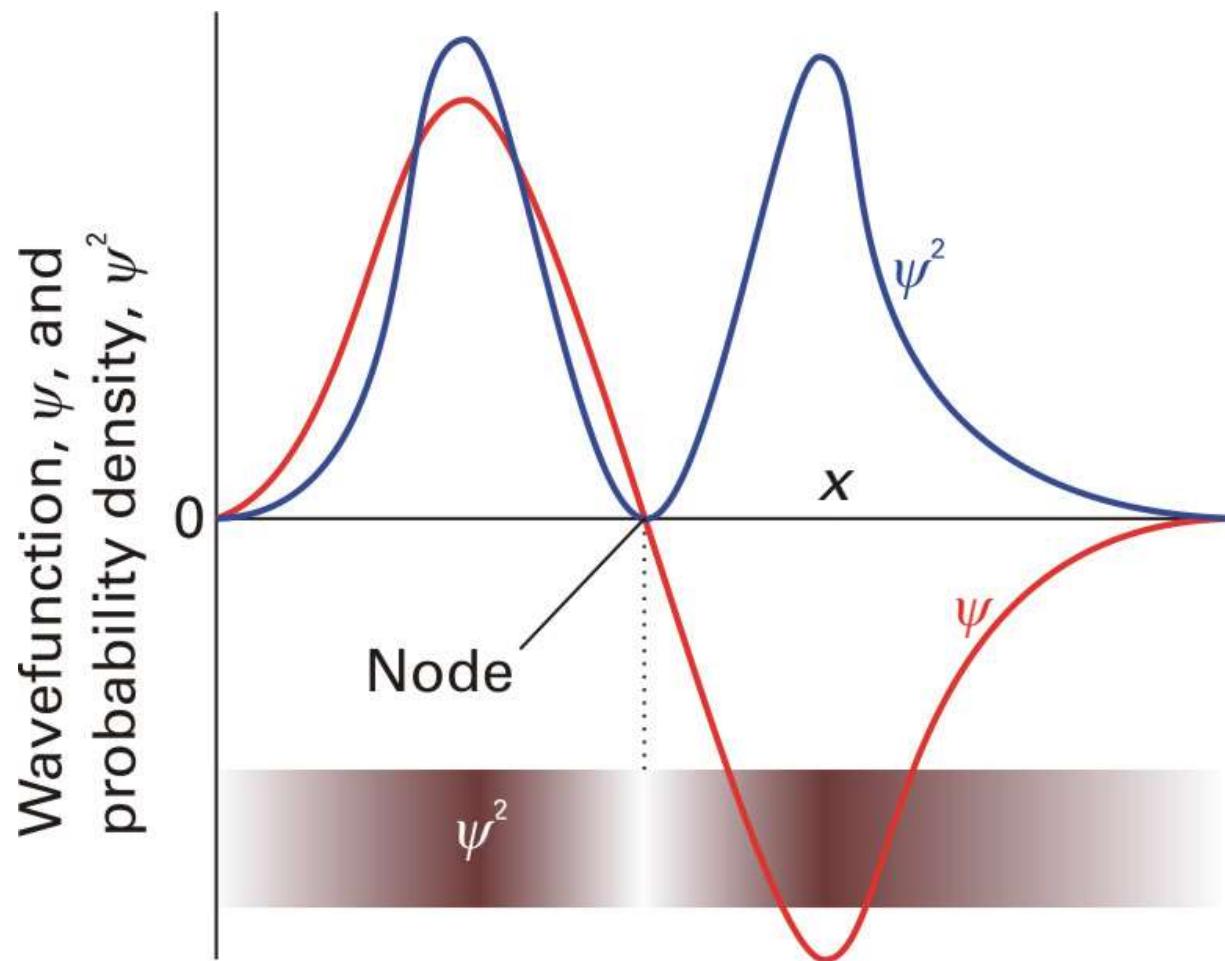
V = potential energy

**When ψ is *operated* upon by \hat{H} ,
returns the ψ multiplied by E**

A category of equation called **eigen (=own) value eqn.**

Wave function (Ψ) (PSI)

1. The wavefunction ψ by itself has no physical significance. It is neither an observable nor measurable.
2. A wavefunction is a mathematical function (like $\sin x$, e^x). Like any mathematical function it can have large value at some place, small in other and zero elsewhere.
3. A wavefunction contains all information about the state of the system.
4. It can be real or complex, ψ^* is the complex conjugate of ψ (can be obtained by replacing $i (= \sqrt{-1})$ by $-i$. $[(a + ib)(a - ib) = a^2 + b^2]$)
5. ψ^2 or $\psi\psi^*$ (where ψ is complex) can be related to experimentally determined quantity and physical interpretation can be given to it.
6. ψ^2 or $\psi\psi^*$ always represents a real quantity and is a measure of probability density for finding an electron at a point (Born Interpretation)
7. If ψ is large at a point in space, the particle has a large probability at that point



ψ^2 is physically significant

Wave function (Ψ) (PSI)

How to determine the observables from wavefunction (Ψ)

By performing a set of well defined mathematical operations on Ψ .

These mathematical operations are called operators

(operator) (function)= (constant factor) (same function)

$$\frac{d}{dx} \left(e^{ax} \right) = a \left(e^{ax} \right)$$


(operator) (eigenfunction)= (eigenvalue) (eigenfunction)

Identifying an eigenfunction

Q1. Show that e^{ax} is an eigenfunction of the operator d/dx , and find the corresponding eigenvalue.

Q2. Show that e^{ax^2} is not an eigenfunction of d/dx .

$$d/dx(e^{ax^2}) = 2ax (e^{ax^2})$$

This is not an eigenvalue even though the same function occurs on the right, because the function is now multiplied by a variable factor ($2ax$), not a constant factor.

Conditions for Acceptable Wave Function

- **The function ψ must always remain finite:**

Infinite value of $\psi \Rightarrow$ infinite probability of finding particle at that point (absurd)

- **ψ must be single valued at a particular point** \Rightarrow probability at any given point must be an unambiguous quantity

- **ψ and functions $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ and $\frac{\partial\psi}{\partial z}$ must be continuous:** their values must not change abruptly at any point

Any function that is finite, single-valued and continuous is considered as a well-behaved wave function

Normalization:

How to extract the information about the location of electron from the wave function Ψ

How to get the TOTAL probability: integrate over whole space: **TOTAL probability must be 1** (*particle should be somewhere and should not vanish*)

$$\int \psi \psi^* dx = 1$$

For three dimensional space

$$\int \psi \psi^* dx dy dz = 1 \quad \text{or} \quad \int \psi \psi^* d\tau = 1$$

Where $d\tau = dx dy dz$ = small element of the configuration space of the system

A wave function that satisfies the above condition is called normalized wave function.

If a wave function does not satisfy the condition of normalization then it must be multiplied by a constant factor called “**normalization factor**” so that normalization condition will be fulfilled

$$\int \psi \psi^* dx = N$$

$$\frac{1}{N} \int \psi \psi^* dx = 1 \rightarrow \int \left(\frac{1}{\sqrt{N}} \psi \right) \left(\frac{1}{\sqrt{N}} \psi^* \right) dx = 1$$

$(1/\sqrt{N})$: Normalization factor : a constant independent of x

$$\int \psi_i \psi_j^* dx = 0 \rightarrow \Psi_i \text{ and } \Psi_j \text{ are called Orthogonal wave functions}$$

$$\int \psi_i \psi_j^* dx = 0 \text{ if } i \neq j \rightarrow \Psi_i \text{ and } \Psi_j \text{ are called Orthonormal}$$

$$\int \psi_i \psi_j^* dx = 1 \text{ if } i = j \text{ wave functions}$$

Understanding the Schrödinger Equation

(Hamiltonian operator) (Eigenfunction) = (Eigenvalue) (Eigenfunction)

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

- Eigenfunction is the wave function of an electron corresponding to the energy E.
Click to add text
- Eigenfunction is **different** for each eigenvalue.
- By solving Schrödinger equation one can find the **wave functions** (eigenfunctions) and the corresponding **allowed energies** (eigenvalues).

(operator corresponding to an observable) (Ψ) = (value of observable) (Ψ)

Hamiltonian operator is used to find out the total energy

Solutions of Schrödinger equation

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

There are many solutions to the above equation. However, the acceptable solutions must satisfy following conditions.

1. Ψ must be single valued.
2. Ψ must be continuous.
3. Ψ must be finite.

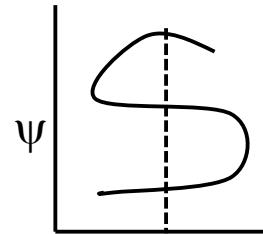
- For an atom several wave functions (Ψ_1, Ψ_2, Ψ_3) will satisfy these conditions and each of these has a corresponding energy (E_1, E_2, E_3)
- These wave functions are called as orbitals analogy to orbits in Bohr's theory.
- Each orbital is described uniquely by a set of three **quantum numbers**, n, l, m_l .

Solutions of Schrödinger equation

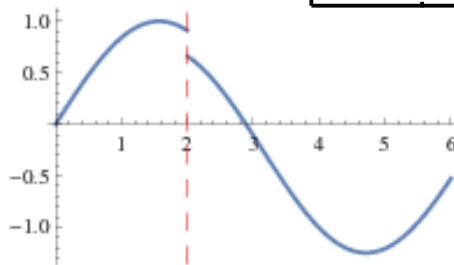
$$[-\hbar^2/8\pi^2m \nabla^2 + V] \Psi = E \Psi$$

There are many solutions to the above equation. However, the acceptable solutions must satisfy following conditions.

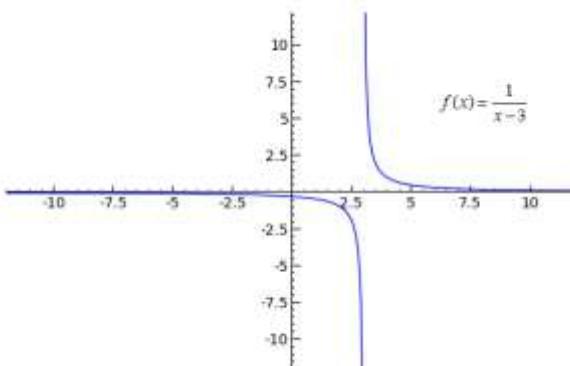
1. Ψ must be single valued.



2. Ψ must be continuous.



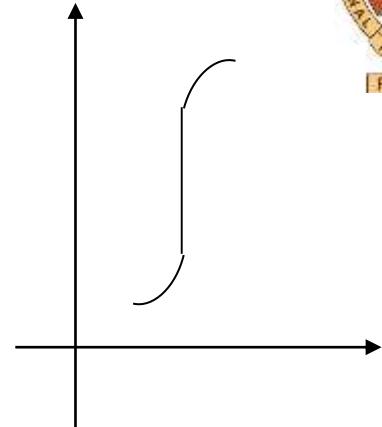
3. Ψ must be finite.





Solutions of Schrödinger equation

4. First derivative of Ψ w.r.t. its variables must be continuous.



5. Probability of finding particle over the whole space must be unity ([Normalization Condition](#))

$$\int_{-\infty}^{+\infty} \psi^2 d\tau = 1 \quad (d\tau \text{ gives the volume element given by } dx, dy \text{ and } dz)$$

If ψ is a complex function, $\int_{-\infty}^{+\infty} \psi \psi^* d\tau = 1$

6. Condition of Orthogonality

If ψ_1 and ψ_2 are two acceptable wave functions, they are orthogonal.

$$\int_{-\infty}^{+\infty} \psi_1 \psi_2 d\tau = 0$$



- For an atom several wave functions (Ψ_1 , Ψ_2 , Ψ_3) will satisfy these conditions and each of these has a corresponding energy (E_1 , E_2 , E_3)
- The wave function of the electron in the hydrogenic atom is called an atomic orbital. An orbital is a one-electron wave function.
- Each orbital is described uniquely by a set of three quantum numbers, n , l , m_l .

Hydrogen (Hydrogen like) atom

Hydrogen has special significance

- No approximation is required in solution of Schrödinger equation
- Can get expression for energy levels

$$\hat{H} \psi = E \psi \quad \left[\frac{-\hbar^2}{8\pi^2 m} \nabla^2 + V \right] \psi = E \psi$$

Interact according to the Coulomb potential

$$V = -Ze^2/4\pi\epsilon_0 r \quad (\text{Note only } r \text{ dependence})$$

$$\left[\frac{-\hbar^2}{8\pi^2 m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi = E \psi$$

Schrodinger equation for hydrogen like atom
For hydrogen $Z = 1$

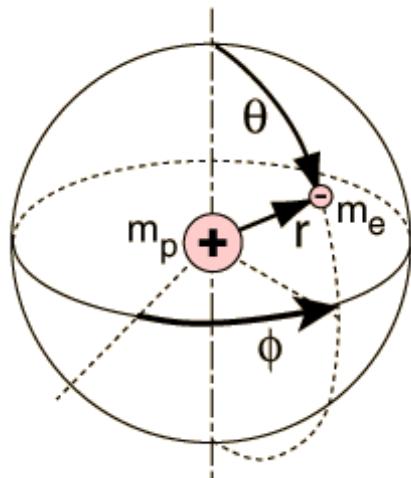
- The wavefunction of the electron in the hydrogenic atom is called an atomic orbital.
- An orbital is a one-electron wavefunction.
- Electron described by a particular wavefunction is said to occupy that orbital.
- In order that the wavefunction is finite and well-behaved certain quantum restrictions are introduced. These restrictions appear in the form of quantum numbers.
- Atomic orbitals (wavefunctions) are specified by three quantum numbers n , l , and m_l .

It is convenient to describe the solutions to the Schrodinger equation in spherical polar coordinates (r, θ, ϕ) rather than cartesian (x, y, z)

r = represents the distance from the nucleus.

θ = is the angle from z-axis, it varies from $0-\pi$: zenith angle

ϕ = is the angle from x-axis, it varies from $0-2\pi$: azimuthal or longitudinal angle

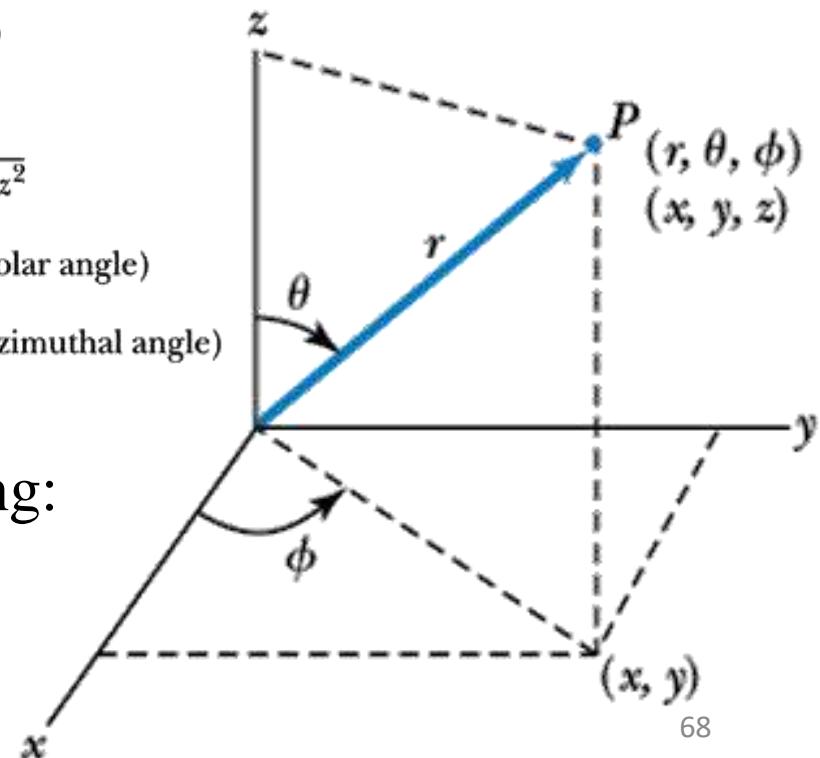


$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta\end{aligned}$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \cos^{-1} \frac{z}{r} \text{ (Polar angle)}$$

$$\phi = \tan^{-1} \frac{y}{x} \text{ (Azimuthal angle)}$$



$\Psi(x, y, z)$ can be converted to $\Psi(r, \theta, \phi)$ using:

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

Using this relation Schrodinger equation for hydrogen like atom can be expressed as

$$\left[-\frac{\hbar^2}{8\pi\mu r^2} \left\{ \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi = E\psi$$

On slight rearrangement

$$\left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{8\pi^2 \mu r^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = 0$$

Ψ may be separated into radial component and two angular components

$$\Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$

Combining the two angular components

$$\Psi(r, \theta, \phi) = \textcolor{red}{R(r)} \textcolor{blue}{Y(\theta, \phi)}$$

↑
radial
function

↖
angular
function

Equation involving only r

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 \mu r^2}{h^2} \left(E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) = l(l+1)$$

Equation involving only θ

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m_l^2$$

Equation involving only φ

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m_l^2$$

Atomic orbitals (wavefunctions) are specified by three quantum numbers n , l , and m_l .

Radial part	Angular part	Angular part
$\Psi(\mathbf{r},\theta,\phi) = \mathbf{R}(\mathbf{r})$	$\Theta(\theta)$	$\Phi(\phi)$
<i>q.no. = n,l</i>	<i>q.no. = l,m_l</i>	<i>q.no. = m_l</i>

$$\Psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r) \Theta_{l,m_l}(\theta) \Phi_{m_l}(\phi)$$

With quantum number dependence indicated:

$$\Psi_{n,l,m_l}(\mathbf{r},\theta,\phi) = \mathbf{R}_{n,l}(\mathbf{r}) \mathbf{Y}_{l,m_l}(\theta,\phi)$$

The radial function, R(r) :

- The radial function R depends only on r
- It is determined by the quantum numbers n and l .
- The radial probability density is derived from the radial part of the wave function.
 - Describes the probability of finding the electron at a given distance (an infinitesimal volume) from the nucleus.

$$R(r) = - \left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} \rho^l L_{n+l}^{2l+1} e^{-\rho/2}$$

$$\rho = \frac{2Zr}{na_0} \quad L_{n+l}^{2l+1} = \text{Laguerre polynomial}$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = \text{Bohr's radius}$$

How the *radial function* looks!

$R_{n,l}$

$$2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\rho/2}$$

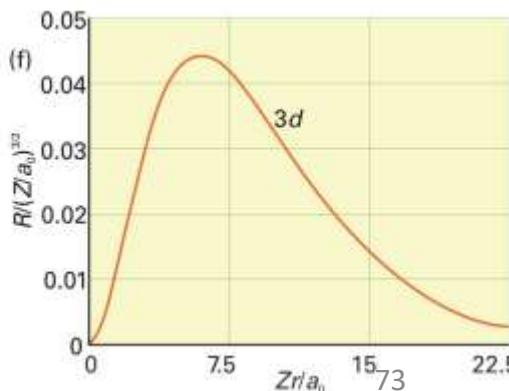
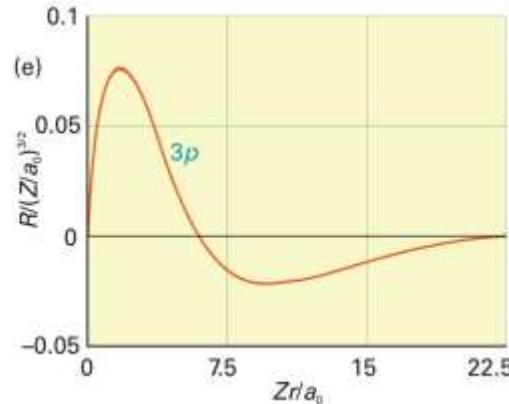
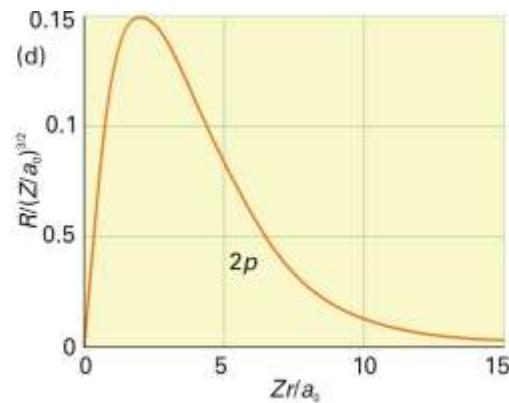
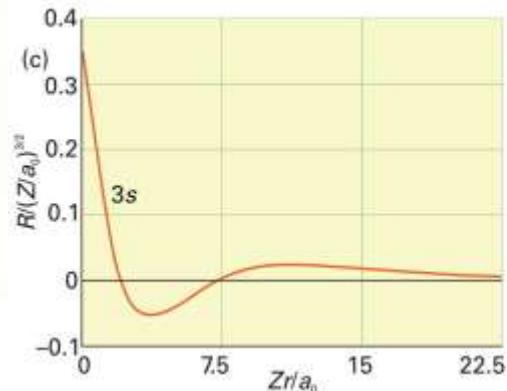
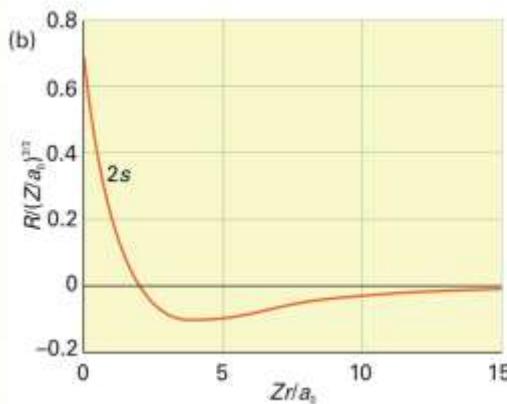
$$\frac{1}{2(2)^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \frac{1}{2}\rho) e^{-\rho/4}$$

$$\frac{1}{4(6)^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} \rho e^{-\rho/4}$$

$$\frac{1}{9(3)^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} (6 - 2\rho + \frac{1}{9}\rho^2) e^{-\rho/6}$$

$$\frac{1}{27(6)^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} (4 - \frac{1}{3}\rho) \rho e^{-\rho/6}$$

$$\frac{1}{81(30)^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} \rho^2 e^{-\rho/6}$$



The angular functions $\Theta(\theta)\Phi(\phi)$: ($\mathbf{Y}_{l,m_l}(\theta,\phi)$)

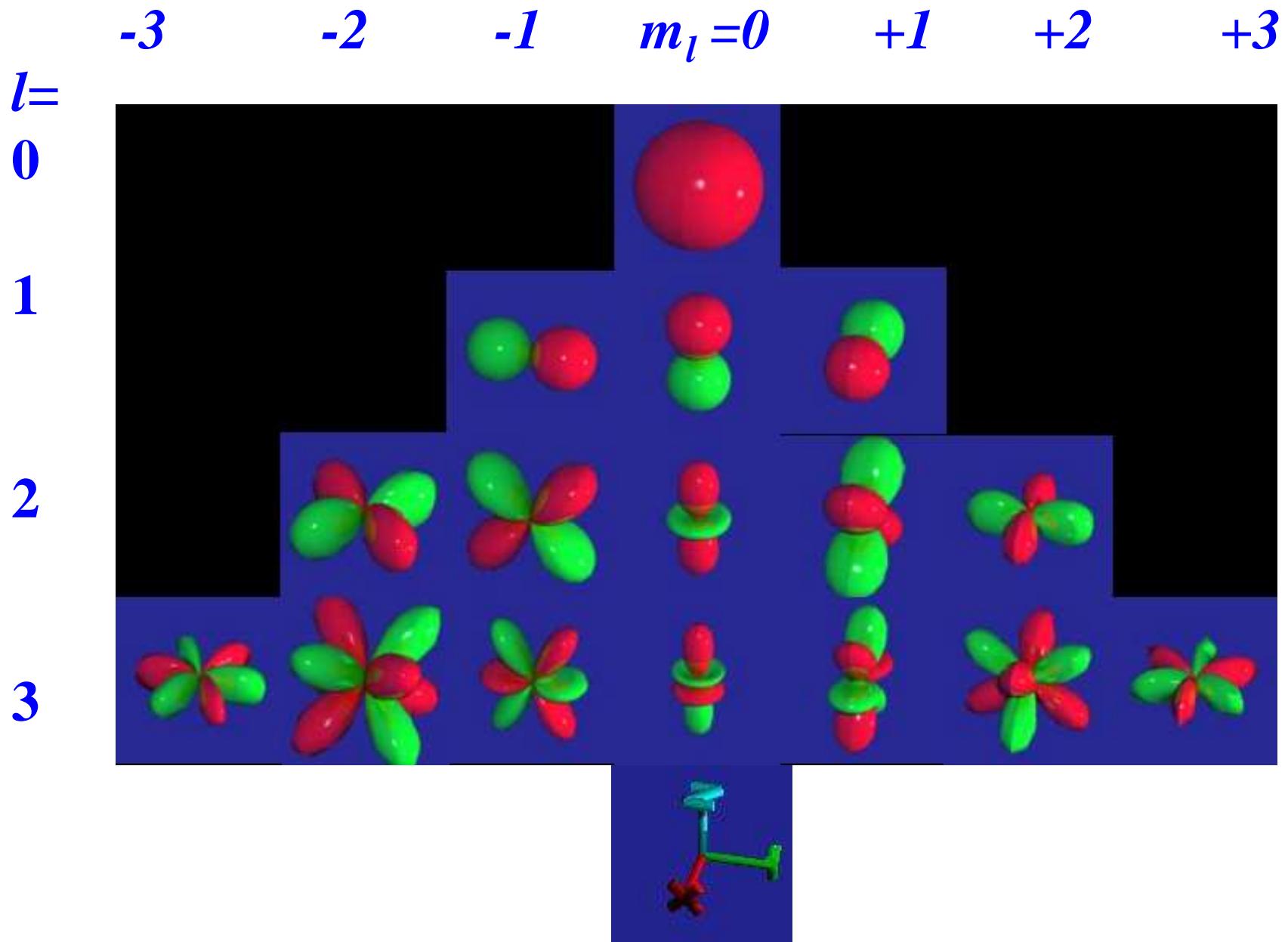
- The angular function is determined by the quantum numbers l and m_l .
- The two functions $\Theta(\theta)\Phi(\phi)$ taken together give the angular distribution of electrons
- The angular functions, $\Theta(\theta)\Phi(\phi)$, describes shape of the orbitals and their orientation in space.

$$\Theta(\theta) = (-1)^{m_l} \sqrt{\frac{(2l+1)(l-m_l)!}{2\pi(l+m_l)!}} P_l^m(\cos \theta)$$

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im_l \phi)$$

P_l^m = Associated Legendre Polynomial s

How the *angular function* looks!



Quantum Numbers

There are four quantum numbers.

Orbital is defined by three quantum numbers (n, l, m_l).

An electron is defined by four quantum numbers (n, l, m_l, m_s).

- In the solution to the Schrodinger eqn for the hydrogen atom, three quantum numbers arise
- Fourth one arises from electron spin
- Quantum numbers set limits on the number of electrons which can occupy a given state
 - No two electrons can have an identical set of quantum numbers : *Pauli exclusion principle*

Principal Quantum number 'n'

What information it gives/ is related?

Appeared in Radial (r dependent) part of solution

Labels the energy levels

Determines the total energy of an electron

$$E = -\frac{Z^2 e^4 \mu}{8\epsilon_0^2 n^2 h^2}$$

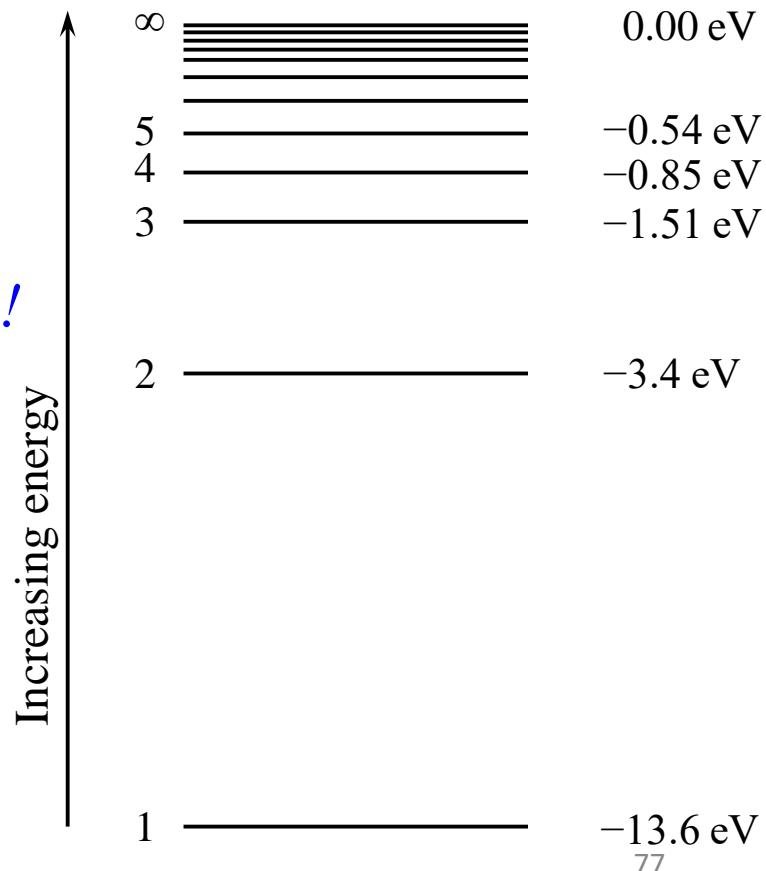
Have you come across this equation before!!

Bohr's model

$\mu = m_N/(m+m_N) \approx m$ and $Z=1$ for hydrogen atom

$$E = \frac{-13.6}{n^2} \text{ eV}$$

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



Orbital Angular Momentum Quantum number 'l'

What information it gives/ is related?

Appeared in Angular (θ dependent) part of solution

- Describes angular dependency of the wave function
- Provides information about the shape of orbital
- Estimation of orbital angular momentum and rotational kinetic energy

$$\text{Angular momentum} = \sqrt{l(l+1)} \hbar$$

$$l = 0, 1, 2, 3, \dots, n-1$$

$$s, p, d, f$$

Why $l < n$!!

l Magnitude of
 Angular
 momentum

0	0
1	$\sqrt{2} \hbar$
2	$\sqrt{6} \hbar$

What property is quantized!!

Recall Bohr's Assumption

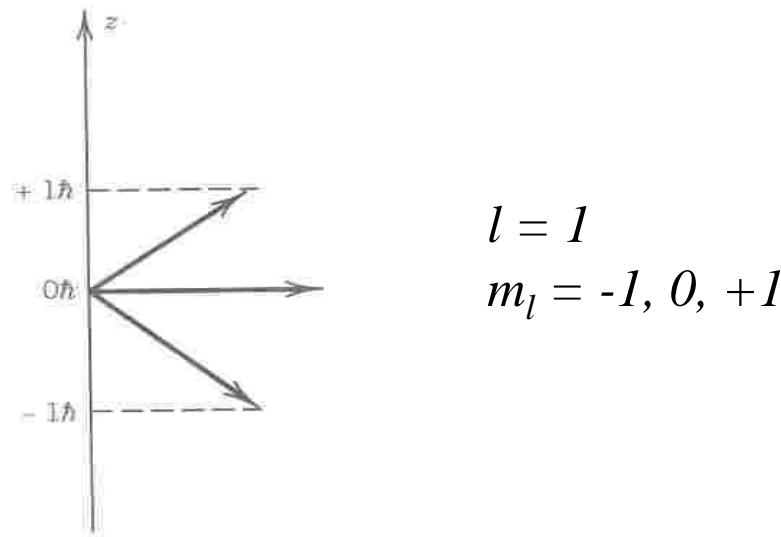
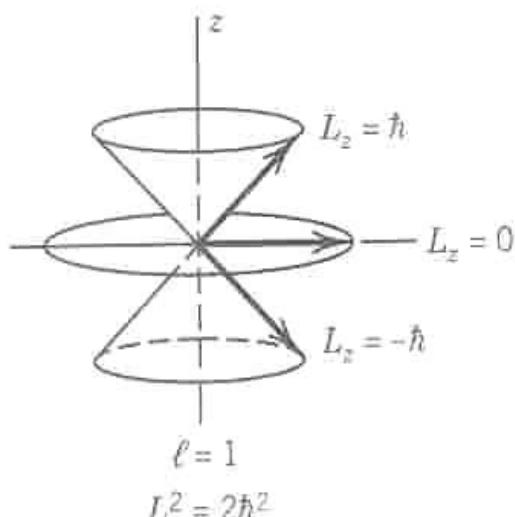
Magnetic Quantum number ' m_l '

What information it gives/ is related?

Appeared in Angular (θ and ϕ dependent) part of solution

- Describes orientation of orbital in space.
- Refers, to the direction of the angular momentum vector
- It is the z-component of angular momentum = $L_z = m_l \hbar$
(so it never be larger than the ' l ' value)
- It may have +ve z-component or -ve z-component

$$m_l = -l, \dots, 0, \dots, +l$$



Spin magnetic quantum number (m_s):

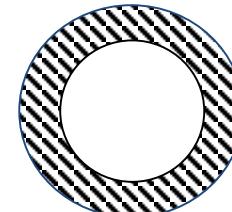
- Spin: an intrinsic property of electron (have an intrinsic angular momentum *other* than orbital angular momentum) like its other intrinsic properties such as mass or charge
- Describes orientation of electron spin in a magnetic field.
- The value of m_s either $+1/2$ (in the direction of the field)
or $-1/2$ (opposed to it)
- Arises due to spinning of electron
- Spin quantum number parameterizes the intrinsic angular momentum (or spin angular momentum) of a given particle

Representation of orbitals – their visualization

- An electron is much more likely to be found in certain regions of the atom than in others.
- Given this, a boundary surface can be drawn so that the electron has following features:
 - ✓ High probability to be found anywhere within the surface,
 - ✓ All regions outside the surface have low values
- Although the precise placement (*Uncertainty Principle*) of the surface is arbitrary, but any reasonably compact determination must follow a spatial pattern specified by the behavior of ψ^2
- This boundary surface is what is meant when the "shape" of an orbital is mentioned
- n determines the energy (exclusively) and size (roughly)
- Roughly, l determines the shape and m_l determines orientation

Radial distribution functions (RDF)

- Relating the probability of an electron at a point in space to the probability of an electron in a spherical shell of thickness dr at a radius r (an orbit-like picture)
- Radial Distribution Function (RDF) = Probability density \times volume of the spherical shell
- Volume of a spherical shell of thickness $dr = 4\pi r^2 dr$



$$4\pi r^2 dr$$

$$\text{RDF}(r) = 4\pi r^2 [R(r)]^2 dr$$

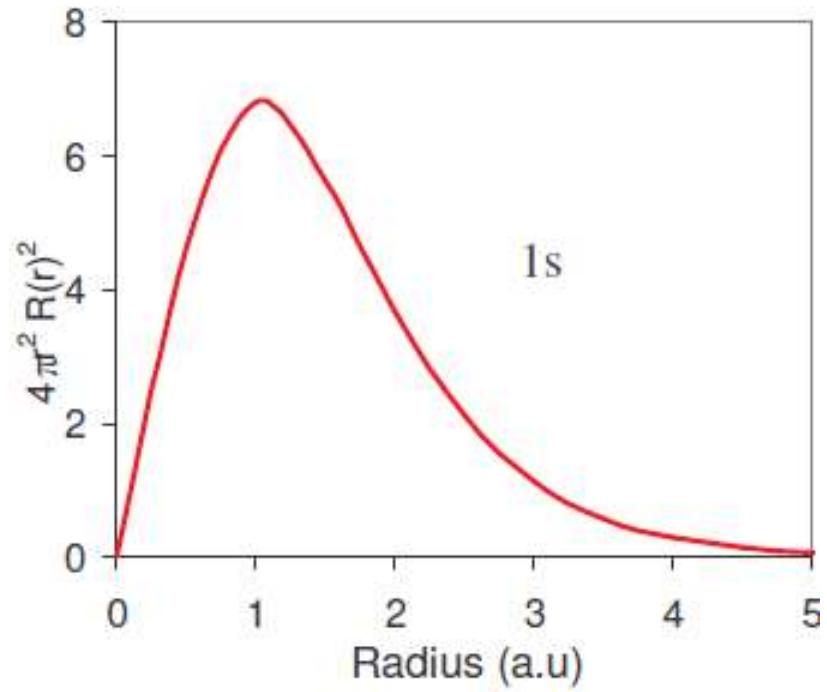
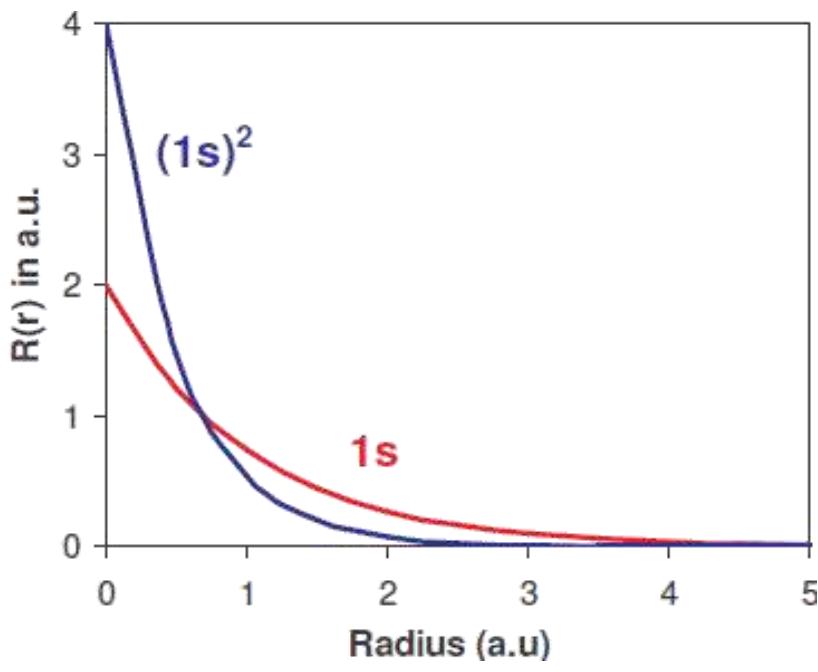
By plotting $4\pi r^2 [R(r)]^2$ against r one can get the radial distribution plot

In order to visualize an orbital generally three types of plots are useful

1. Radial Plot

2. Radial Probability Plot

3. Radial Distribution Plot



1s atomic orbital ($n = 1, l = 0, m_l = 0$)

$$\Psi_{1s} = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\rho/2} \left(\frac{1}{4\pi} \right)^{1/2}$$

Radial part

Angular part

Z = effective nuclear charge

a_o = Bohr radius

$\rho = 2Z r/n a_o$

r = distance from the nucleus

n = principal quantum number

$$R_{n,l} = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\rho/2}$$

$$Y_{l,m_l}(\theta, \phi) = \left(\frac{1}{4\pi} \right)^{1/2}$$

$$R_{n,l} = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\rho/2}$$

$$Y_{l,m_l}(\theta, \phi) = \left(\frac{1}{4\pi} \right)^{1/2}$$

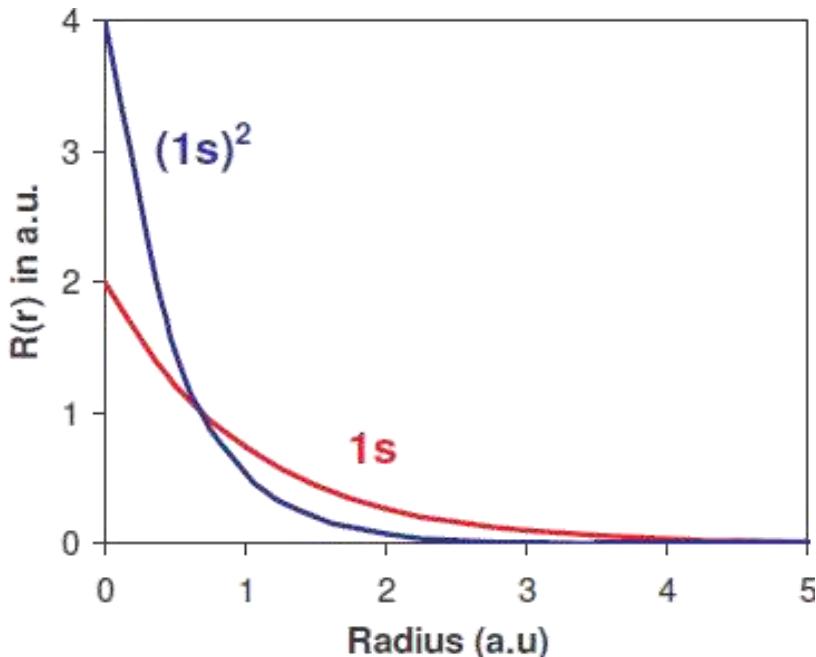
For hydrogen : $Z = 1$ and $a_0 = 1$ (in atomic units) and $\rho = 2r$

$$R(r) = 2e^{-r}$$

It decays exponentially with r

It has a maximum at $r = 0$

- $R(r)$ has no physical meaning.
- $R(r)^2$: represents the probability density of the electron at a point in space
- $R(r)^2$ is a maximum at $r = 0$



Probability of finding the electron in the 1s (ns) orbital is maximum near to the nucleus

- Y is a constant (true for all n) → Does not depend on θ and ϕ
- **s-orbitals are spherically symmetrical**

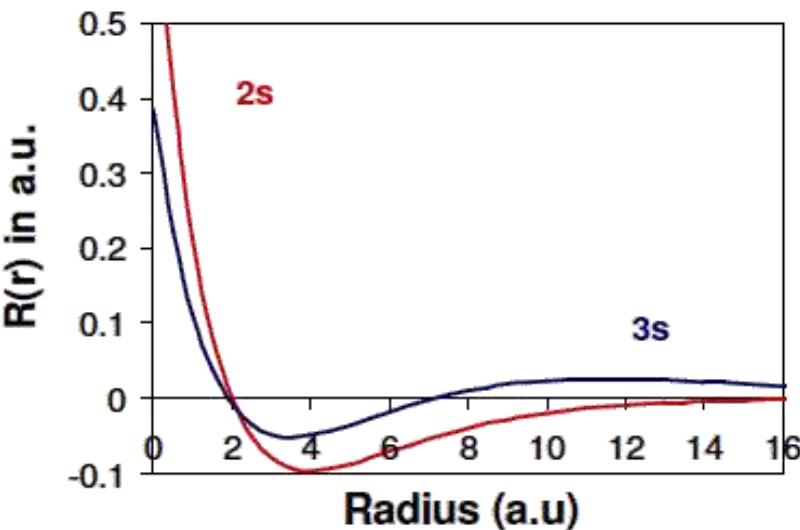
Wave functions of ns orbitals ($n, l = 0, m_l = 0$)

$2s(r)$

$$R_{2s} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \rho) e^{-\rho/2}$$

so for H $2s$, $Z=1$, $n=2$, $a_0=1$, $\rho = (2Zr/na_0) = r$

$$R_{2s} = \frac{1}{2\sqrt{2}} (2 - r) e^{-r/2}$$



$r < 2 \rightarrow \psi_{2s}$ is positive

$r = 2 \rightarrow \psi_{2s}$ is zero ($R(r) = 0 \Rightarrow$ RADIAL NODE)

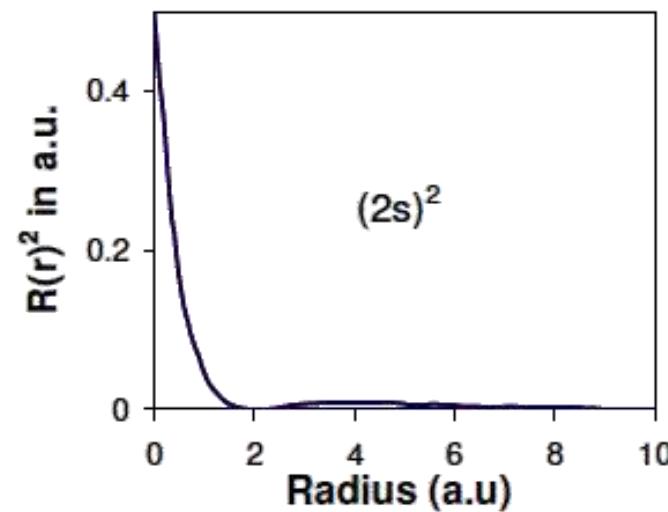
$r > 2 \rightarrow \psi_{2s}$ is negative

$3s(r)$

$$R_{3s} = \frac{1}{9\sqrt{3}} \left(\frac{Z}{a_0} \right)^{3/2} (6 - 6\rho + \rho^2) e^{-\rho/2}$$

so for H $3s$, $Z=1$, $n=3$, $a_0=1$, $\rho = (2/3)r$

$$R_{3s} = \frac{1}{9\sqrt{3}} \left[6 - 4r + \left(\frac{2}{3}r \right)^2 \right] e^{-r/3}$$



Radial Nodes

The point at which $R(r) = 0$ (not including the origin) is called a radial node

$$\text{Number of radial node} = n - l - 1$$

$$1s = 1 - 1 - 0 = 0$$

$$2s = 2 - 1 - 0 = 1$$

$$3s = 3 - 1 - 0 = 2$$

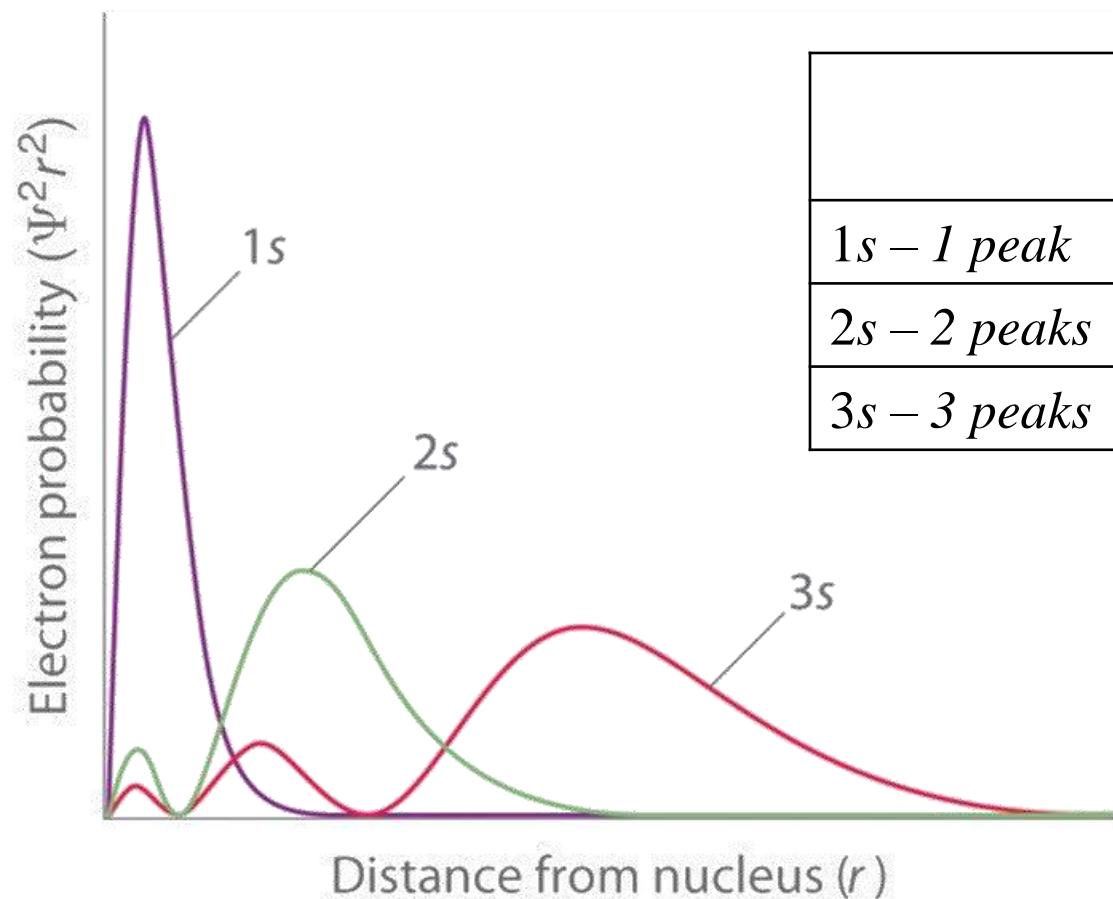
$$2p = 2 - 1 - 1 = 0$$

$$3p = 3 - 1 - 1 = 1$$

$$3d = 3 - 1 - 2 = 0$$

RDFs of *ns* orbitals

These maximum correspond to the distance from the nucleus at which the electron has the highest probability of being found i.e. the optimum size of a sphere of very small thickness in which to find an electron in a 1s, 2s or 3s orbital.



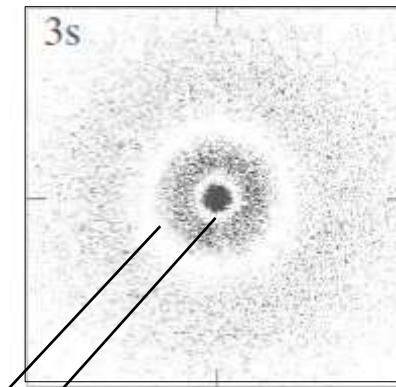
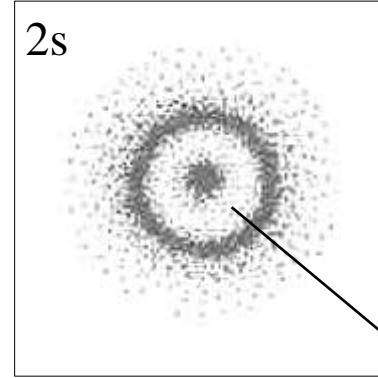
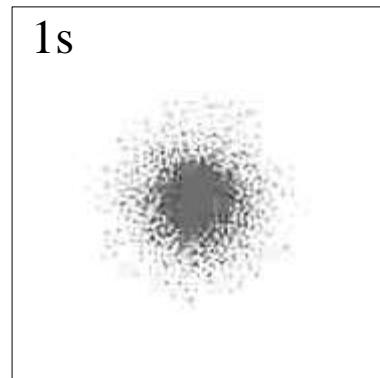
	Wave mechanics maximum	Bohr's Model Radius
1s – 1 peak	$r = a_0$	a_0
2s – 2 peaks	$r \approx 5a_0$	$4a_0$
3s – 3 peaks	$r \approx 13a_0$	$9a_0$

Three dimensional plots of probability (ψ^2) against distance (r) are shown by

- (i) Dot -population picture
- (ii) Equal-probability contour or the boundary surface plots

Dot Population Diagrams

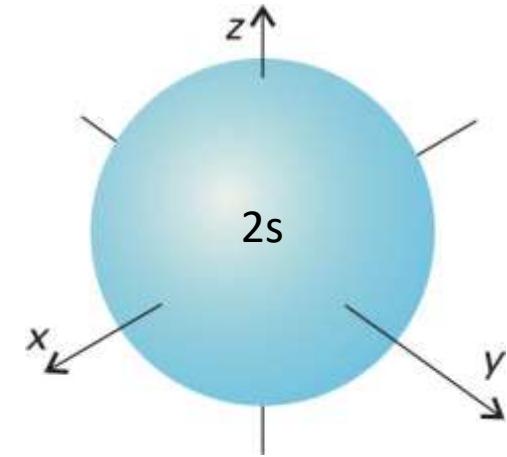
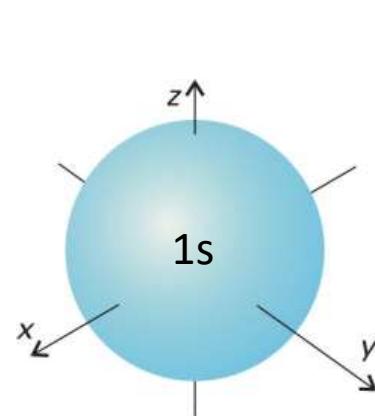
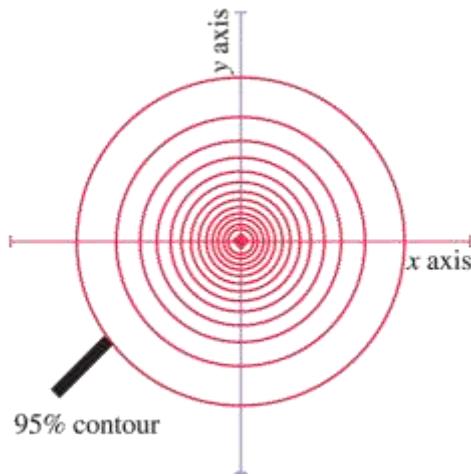
- Exhibit the relative probability at a given location by the density of dots near that location
- Provides the most realistic description of the electron's time average distribution



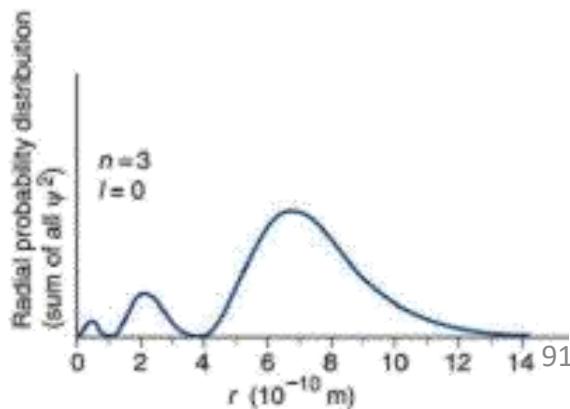
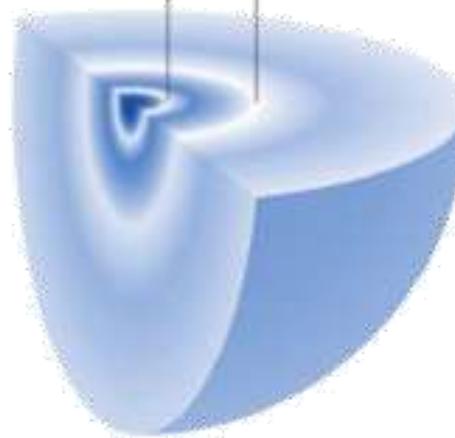
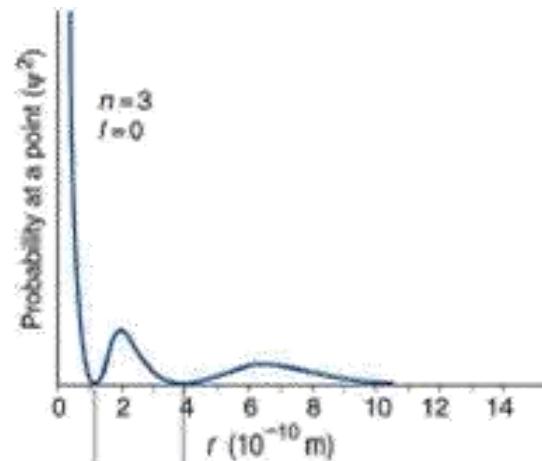
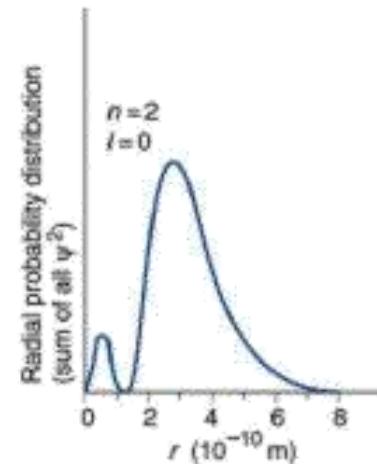
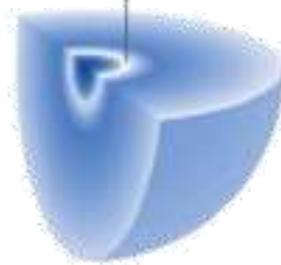
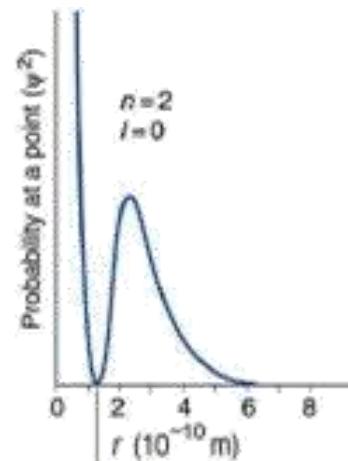
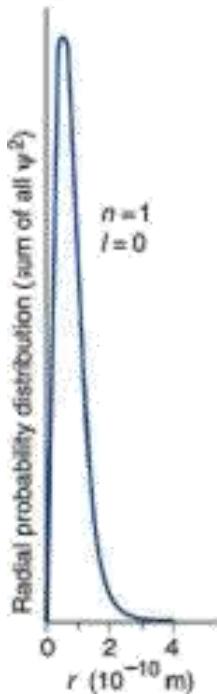
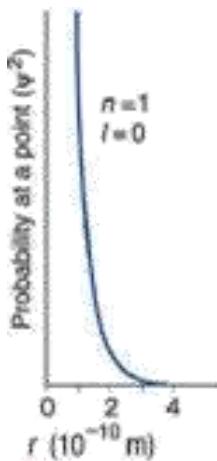
Radial Nodes

Equal-probability contour or the boundary surface plots

- The contours are drawn by joining the points of identical probability
- Defines the surface such that it encloses a space in which the electron spends most of its time
- The surface now depicts outer shape and size of the orbital
- The inner structure of the wave function is hidden beneath the surface
- For s-orbitals these contours are spherical in nature



Putting All the Representations Together



2p atomic orbitals ($n = 2$, $l = 1$, $m_l = +1, 0, -1$)

- There are three p orbitals for each value of n (p_x, p_y, p_z)
- The radial function is the same for all np orbitals
- The angular terms are different → different orientations

Wave function for $2p$ (radial)

$$R_{2p} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \rho e^{-\rho/2}$$

$$R_{2p} = \frac{1}{2\sqrt{6}} r e^{-r/2} \quad (n = 2 \rightarrow \rho = r)$$

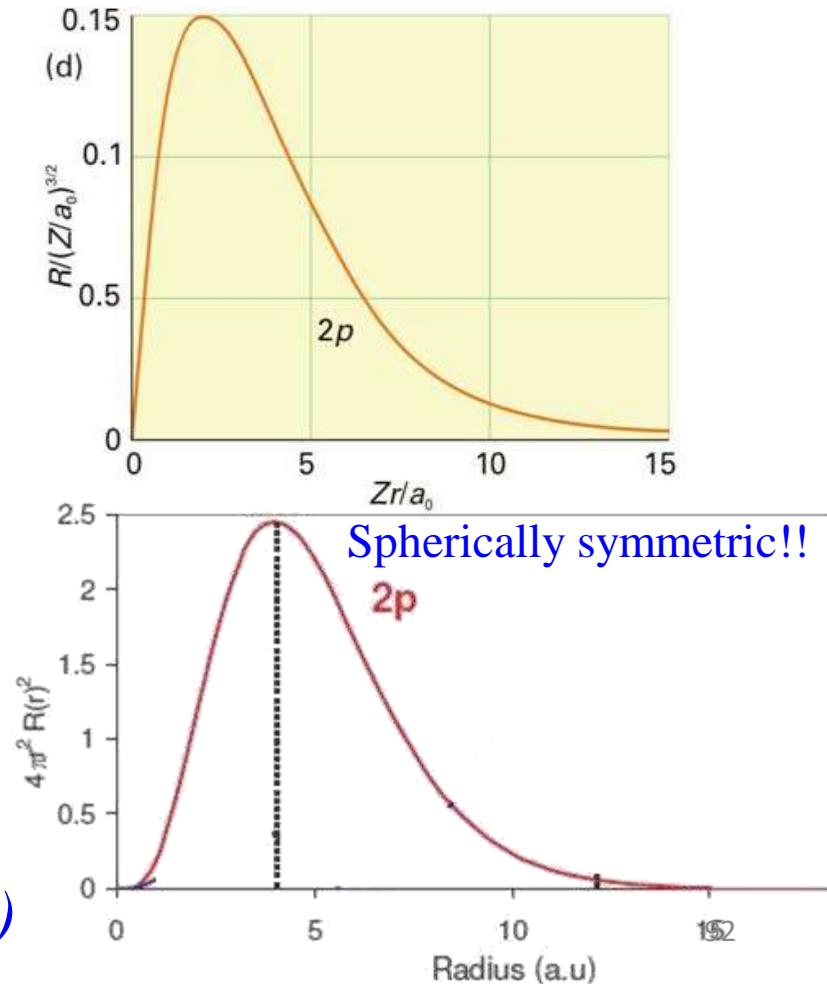
No. of radial nodes = $n - l - 1 = 0$

All p orbitals are multiplied by r

$$\rightarrow R(r) = 0 \text{ at } r = 0$$

All p orbitals have the same shape

2p function – no nodes, maximum at $r = 4a_0$ (same as $n = 2$ for Bohr's model)



p orbitals – angular functions boundary surfaces

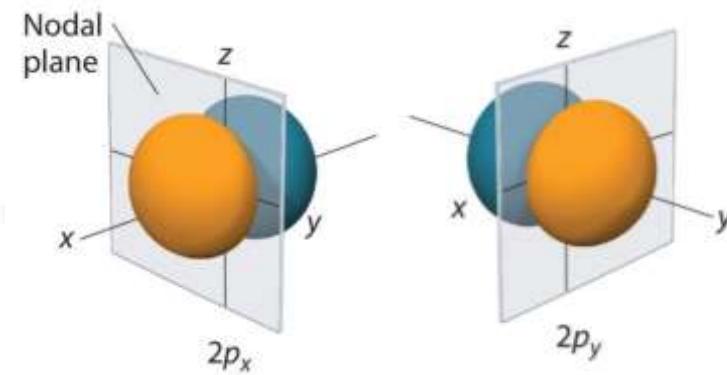
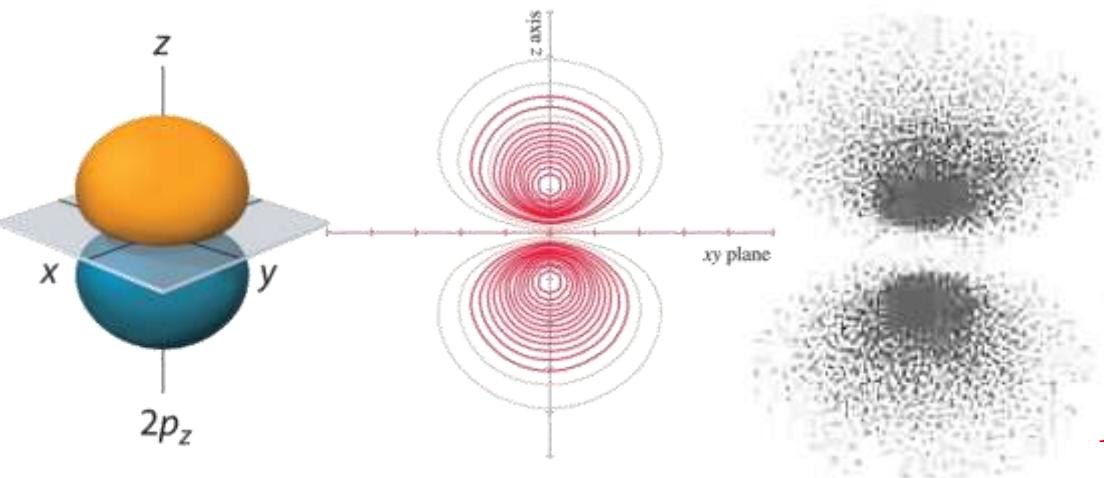
Angular function give rise to direction: $m_l = 0(p_z)$, $m_l = \pm l(p_x, p_y)$

$$Y(p_z) = \left(\frac{3}{4\pi} \right)^{1/2} \cos(\theta) \quad (\text{Since, } z/r = \cos\theta)$$

$$Y(p_x) = \left(\frac{3}{4\pi} \right)^{1/2} \sin(\theta) \cos(\phi) \quad (\text{Since, } x/r = \sin\theta \cos\phi)$$

$$Y(p_y) = \left(\frac{3}{4\pi} \right)^{1/2} \sin(\theta) \sin(\phi) \quad (\text{Since, } y/r = \sin\theta \sin\phi)$$

- The radial coordinate will have **maximum positive and negative values** along the z-axis when $\theta = 0$ and $\theta = \pi \rightarrow$ two spheroidal lobes about the z-axis
- On the **xy-plane** $\theta = \pi/2 \rightarrow \cos(\theta) = 0 \rightarrow$ **nodal point (nodal plane)** \rightarrow angular node



1 nodal plane: p_x (yz plane), p_y (xz plane)

Nodes in Atomic Orbitals

- Nodal surface is a surface with zero electron density.
- Nodes appear naturally as a result of the wave nature of the electron.
- At the nodal surface the wave function changes its sign.

At nodal surface, $\Psi = 0 \rightarrow R(r) = 0$ or $Y(\theta, \phi) = 0$

- If $R(r) = 0$, radial nodes or spherical nodes result.

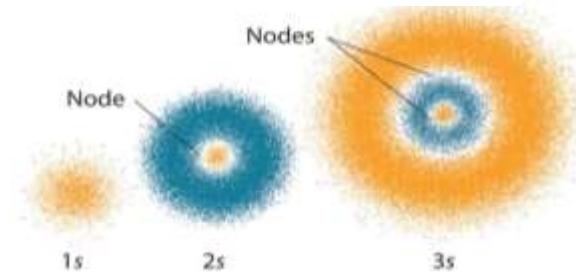
• Number of radial nodes = $n-l-1$

- If $Y(\theta, \phi) = 0$, angular nodes result.

- Angular nodes are planar or conical.

• Number of angular nodes = l

Radial node



Total number nodes = $n - 1$

Planar Angular node

Orbital No. of angular nodes

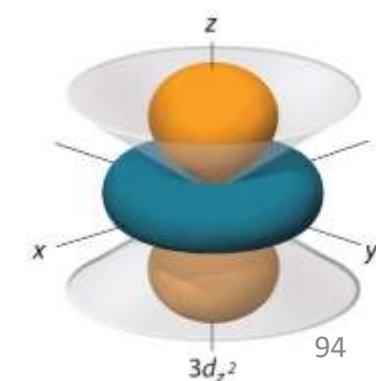
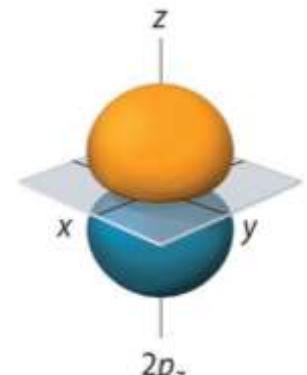
s-orbital 0

p-orbital 1

d-orbital 2

f-orbital 3

Conical Angular node



d orbitals – wave functions

Five d orbitals for each value of n , $l = 2$, $m_l = -2, -1, 0, 1, 2$

Radial wave functions same for all $3d$ orbital

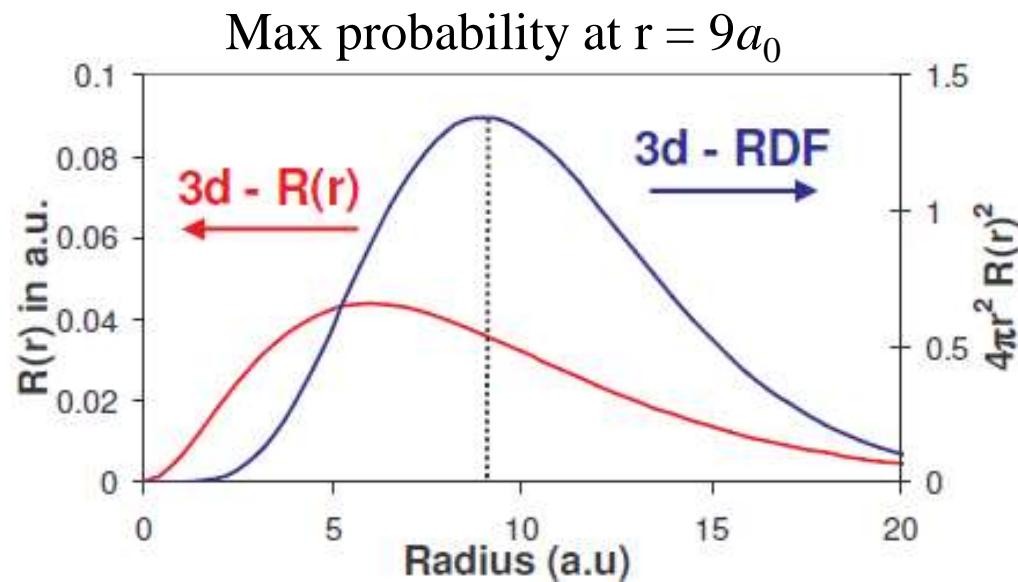
$$R(3d) = \frac{1}{9\sqrt{30}} \left(\frac{Z}{a_0} \right)^{3/2} \rho^2 e^{(-\rho/2)}$$

For $3d$ orbitals

Total no. of nodes: $2 (n-l)$

No. of radial node: $n-l-1 = 3-1-2 = 0$

No. of angular nodes: $l = 2$



3d atomic orbitals ($n = 3, l = 2, m_l = +2, +1, 0, -1, -2$)

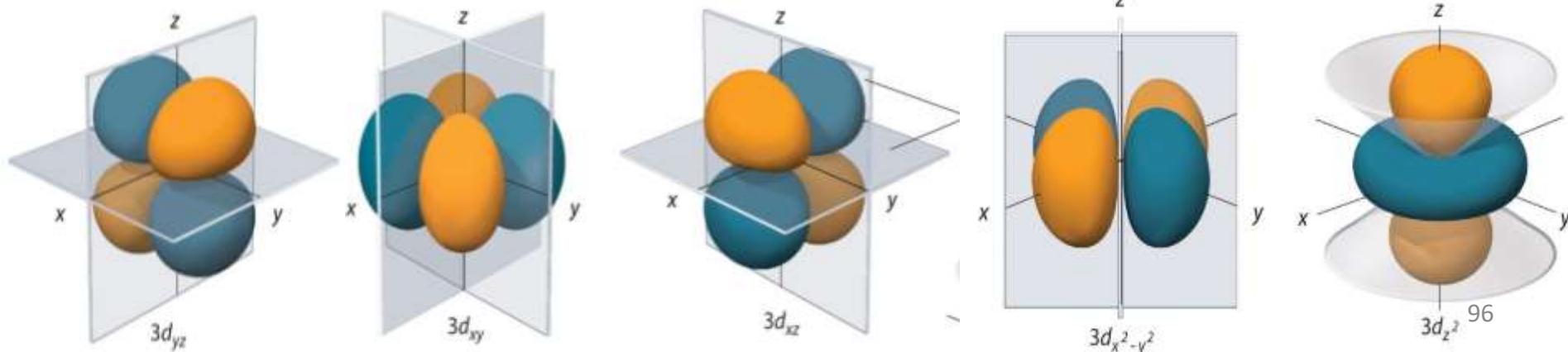
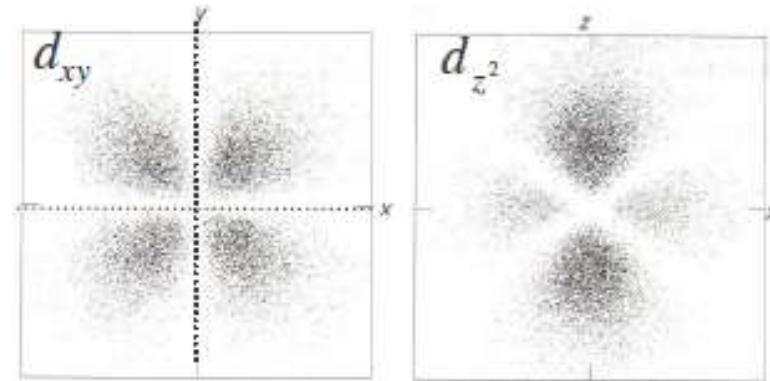
$$\Psi(3d_{xy}) = R_{n,l} \underbrace{\frac{1}{4} \left(\frac{15}{\pi}\right)^{1/2}}_{Y(\theta, \phi)} \frac{xy}{r^2}$$

Similarly the d_{xz}, d_{yz}

$$\Psi(3d_{x^2-y^2}) = R_{n,l} \frac{1}{4} \left(\frac{15}{\pi}\right)^{1/2} \frac{x^2 - y^2}{r^2}$$

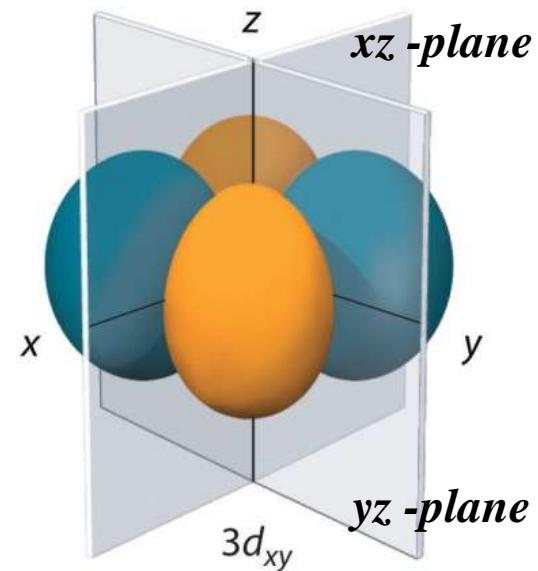
$$\Psi(3d_{z^2}) = R_{n,l} \frac{1}{4} \left(\frac{15}{\pi}\right)^{1/2} \frac{2z^2 - x^2 - y^2}{r^2}$$

Since the angular part contains two or more variables, so these orbitals have shapes in two axial directions or more.



Q. Describe the nodal surfaces for a $3d_{xy}$ orbital, whose angular wave function is

$$Y = \frac{1}{4} \left(\frac{15}{\pi} \right)^{1/2} \frac{xy}{r}$$



Ans. In nodal surfaces, $Y = 0$

$Y = 0$, when either $x = 0$ or $y = 0$

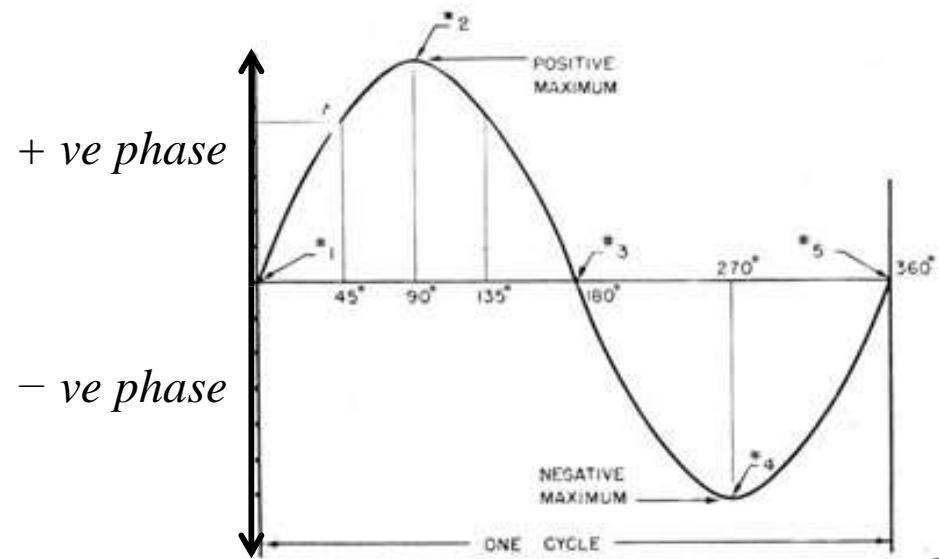
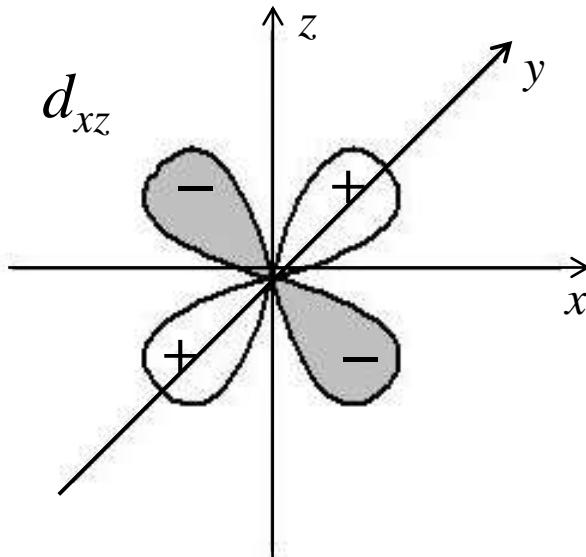
So the nodal surfaces are $x = 0$ (yz plane) and $y = 0$ (xz plane)

Sign of atomic orbital

Sign of lobes **does not mean** electronic charge.

It represents the phase/direction of wave function.

Atomic orbital along **positive axial** direction has a **positive sign** and **negative axial** direction has a **negative sign**.



Sign of atomic orbital

The angular part of s-orbitals contain constant value, no variables. So there is no change in sign.

The angular part of p-orbital contains either x or y or z. Since the x, y, or z direction may be positive or negative, so the wave function along **positive axis has a positive sign and along negative axis has negative sign.**

The angular part of d_{xy} , d_{xz} , d_{yz} contain product of two component. **So the product of signs gives the sign of the lobe.**

For $d_{x^2-y^2}$, the angular part contains x^2-y^2 . so the wave function is **positive along x-direction (positive and negative) and negative along y direction.**

For d_{z^2} , the angular function contains $2z^2-x^2-y^2$, so the wave function is **positive along z direction (both positive and negative) and negative in xy-plane.**

CY1101 (General Chemistry)



Dr. Vaidyanathan Sivakumar

Associate Professor

Department of chemistry

NIT Rourkela

vsiva@nitrkl.ac.in

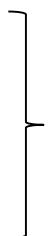
Welcome to CY1101 (general chemistry)



Scope and Objective

The course provides a comprehensive survey of the concepts involved in the study of the

- Electronic structure of atoms
- Chemical bonding
- Coordination chemistry



Inorganic Prof. V. Sivakumar

- Spectroscopy
- Thermodynamics
- Electrochemistry
- Chemical kinetics



Physical Prof (Mrs). Usharani Subuddhi

- Organic Chemistry (Stereochemistry).

Organic Prof (Mrs). Sabita Patel



Books:

1. *Inorganic Chemistry* by Gary L. Miessler and Donald A. Tarr
2. *Atkins' Physical Chemistry* by Peter Atkins and Julio de Paula
3. *Fundamentals of molecular spectroscopy*, C. N. Banwell, E. N. McCash, 1994.
4. *Organic Chemistry*, Clayden, Greeves, Warren and Wothers, Oxford, 2001.
5. *Principles of physical Chemistry*, B. R. Puri, L. R. Sharma, M. S. Pathania, 2001.

Chemical Bonding

Chemical Bonding



Chemical Bond: Force that holds groups of two or more atoms together and makes them function as a unit.

Why a chemical bond forms?

To minimize the energy of the system.

Who participate in the formation of a chemical bond?

Electrons

What information one will get from chemical bond?

Bond length (Equilibrium distance between atoms in a molecule)

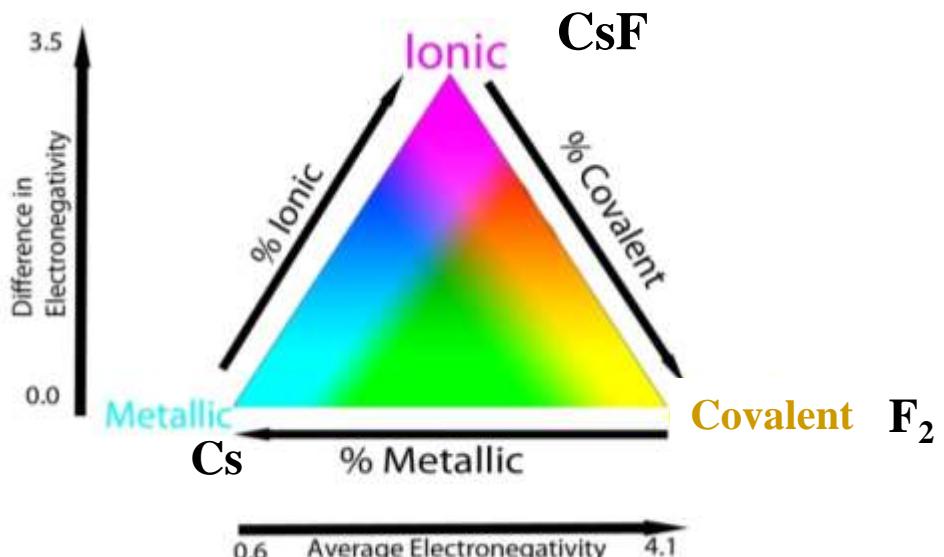
Bond energy (Energy required to break a bond)



Types of Chemical Bond

There are three (important) types of bonding exist among atoms.

- Metallic bonding
- Ionic bonding
- Covalent bonding



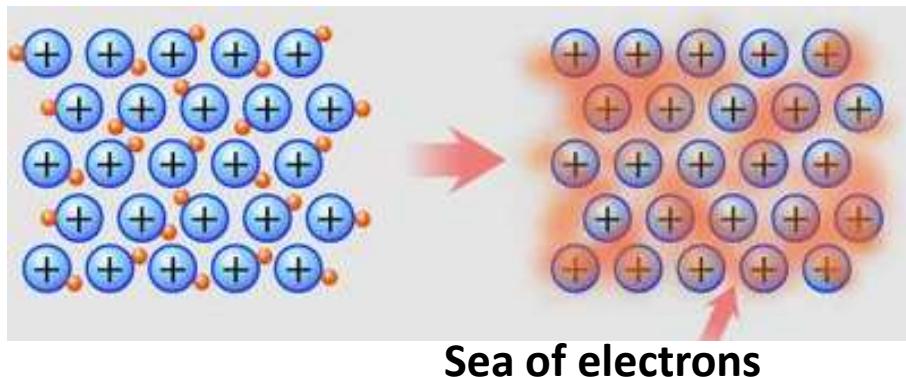
Most of compounds have more than one type of bonding interaction.

van Arkel-Ketelaar triangle of bonding

Metallic bonding

Bonding that results from the electrostatic attractive force between positively charged metal ions and the surrounding sea of electrons.

Occurs among electropositive elements (mostly in metals)



The outer electrons are so weakly bound to metal atoms that they are free to roam across the entire metal. Having lost their outer electrons, individual metal atoms are most like positive ions in a sea of electrons.

Valence electrons do not belong to any one atom. Valence electrons are shared among all the positively charged ions .

Ionic bonding



Definition: Type of chemical bond that involves the electrostatic attraction between oppositely charged ions.

Occurs between a electropositive and electronegative elements.

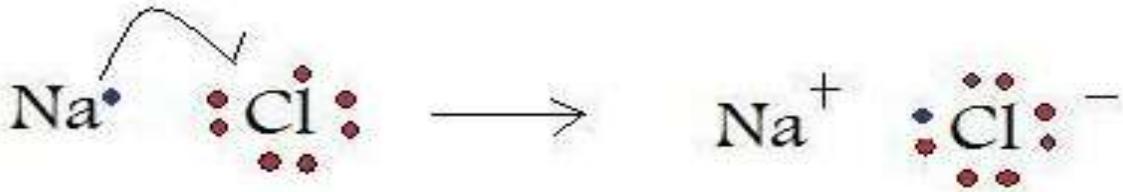
Primarily between metals (Groups 1A, 2A and transition metals) and nonmetals (oxygen and halogens)

Complete electron transfer from an element of low E.N. (metal) to an element of high E.N. (nonmetal)

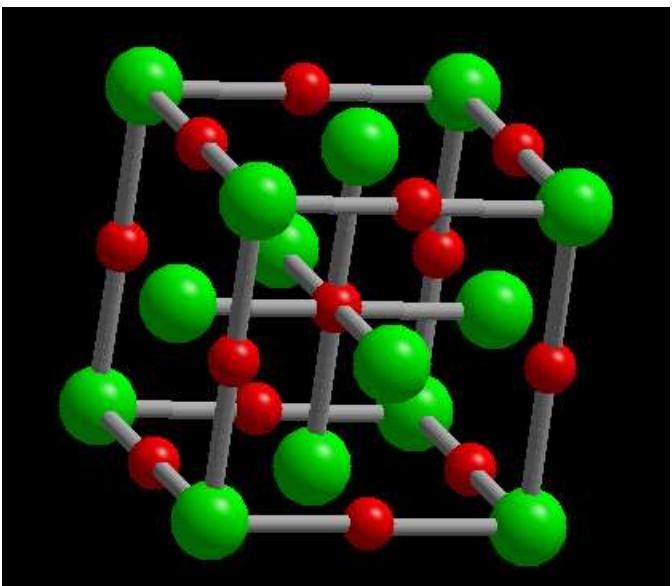
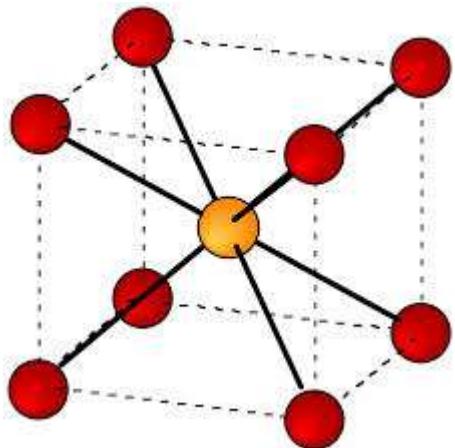


- ***NON-DIRECTIONAL bonding via Coulomb (charge) interaction***

Ionic bonding



How it looks like?



Each sodium ion is surrounded by six chlorides

Each Cs atom is surrounded by eight chloride ion.

Coordination number depends on the relative size of cation and anion (radius ratio).



Covalent bonding

In CY1101, we will concentrate on covalent bonding only!

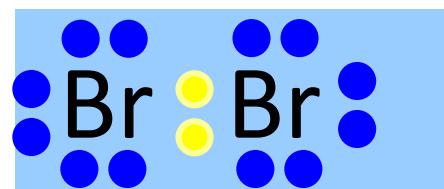
Covalent bond is formed by sharing of the VALENCE ELECTRONS of each atom in a bond.

Occurs between two or more electronegative atoms.

Covalent bonds are directional in nature.

Electrons are divided between **core** and **valence** electrons.

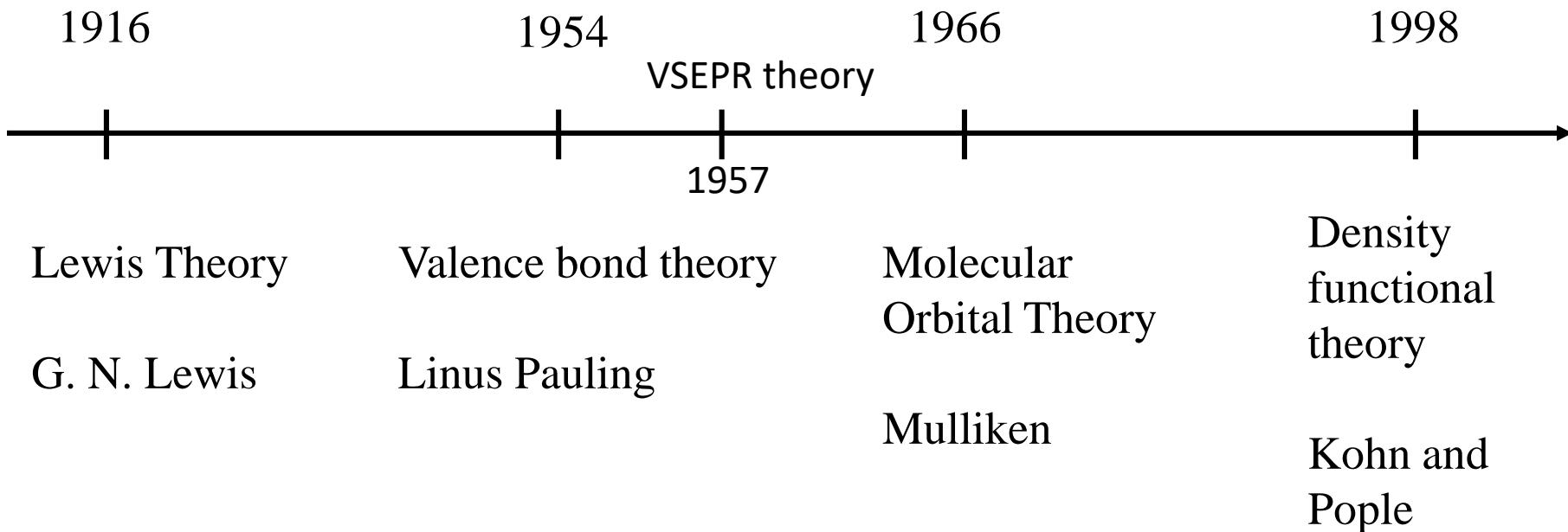
ATOM	core	valence
Br	[Ar] 3d ¹⁰ 4s ² 4p ⁵	[Ar] 3d ¹⁰ 4s ² 4p ⁵



Development of theories to understand covalent bonding

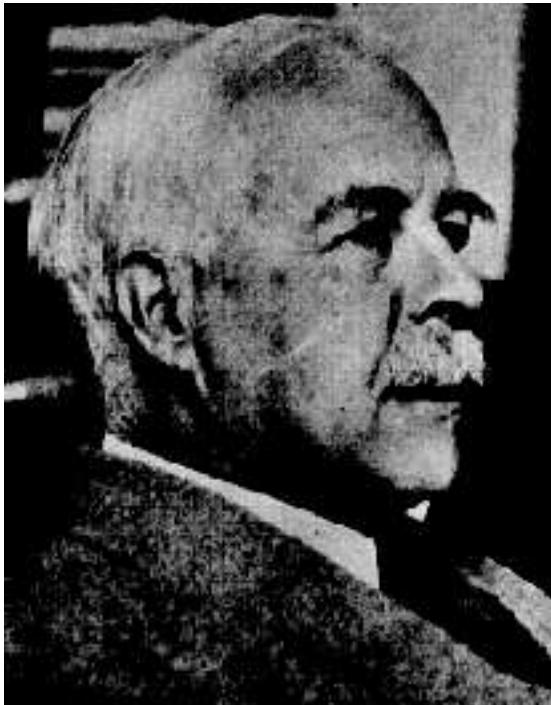


Several theories were developed to explain shape and electronic structure of covalent molecules.





Lewis Theory



G. N. Lewis
1875 - 1946

This is a LEWIS ELECTRON DOT structure.

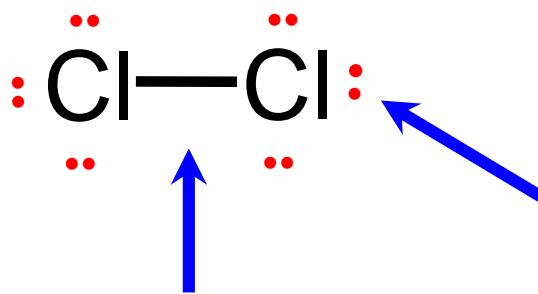
If two electrons are shared between two atoms, it makes a bond and bind the atoms together.

Valence electrons are distributed as shared or **BOND PAIRS** and unshared or **LONE PAIRS**.

Except for H, total no. of valence electrons:

$$\# \text{Bond Pairs} + \# \text{Lone Pairs} = 4 \text{ pairs or } 8 \text{ electrons}$$

Atoms in a molecule tends to have eight valence electrons to form stable arrangement as in noble gases. This is called as OCTET RULE.



shared or bond pair

Unshared or lone pair (LP)

Electron dot structure of Sulfite ion, SO_3^{2-}



Step 1. Central atom = S

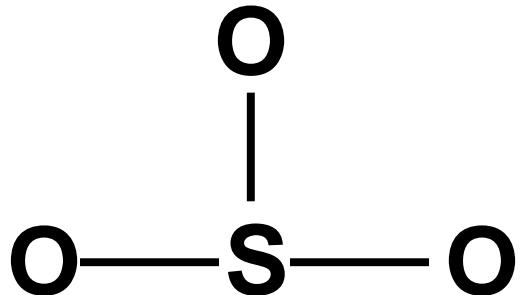
Step 2. Count valence electrons

$$\text{S} = 6$$

$$3 \times \text{O} = 3 \times 6 = 18$$

$$\text{Negative charge} = 2$$

$$\text{TOTAL} = 6 + 18 + 2 = 26 \text{ e- or } 13 \text{ pairs}$$

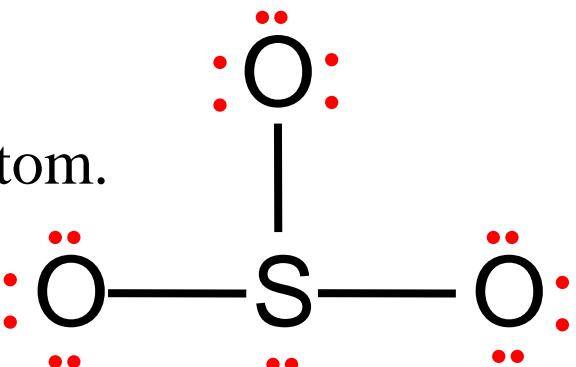


Step 3. Form three covalent bonds with three oxygen atoms

10 pairs of electrons are left.

Step 4: Remaining pairs become lone pairs,
first on outside atoms then on central atom.

Each atom is surrounded by an octet of electrons.



Electron Dot Structure of NH₃



Ammonia, NH₃ (Central atom = N; surrounding atoms = H)

Count valence electrons

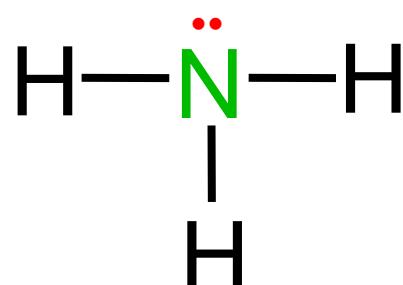
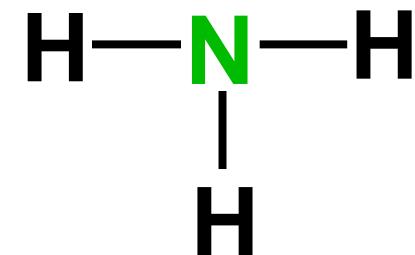
$$\text{H} = 1 \text{ and } \text{N} = 5$$

$$\begin{aligned}\text{Total} &= (3 \times 1) + 5 \\ &= 8 \text{ electrons or 4 pairs}\end{aligned}$$

Form a sigma bond between the central atom and surrounding atoms.

Remaining electrons form LONE PAIRS to complete octet as needed.

3 BOND PAIRS and 1 LONE PAIR





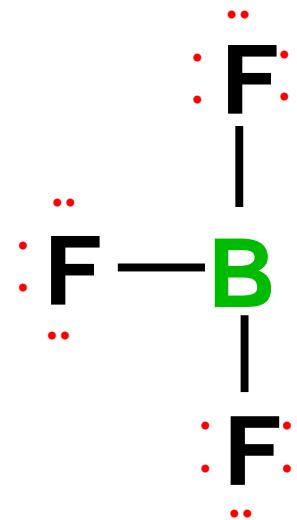
Limitations of the Octet Rule



Central atom = B

Valence electrons = $3 + 3*7 = 24$ (12 electron pairs)

The B atom has a share in only 6 electrons
(or 3 pairs). B atom is electron deficient.



In order to satisfy octet rule, we should have multiple bonds.
Multiple bond results unusual formal charges.



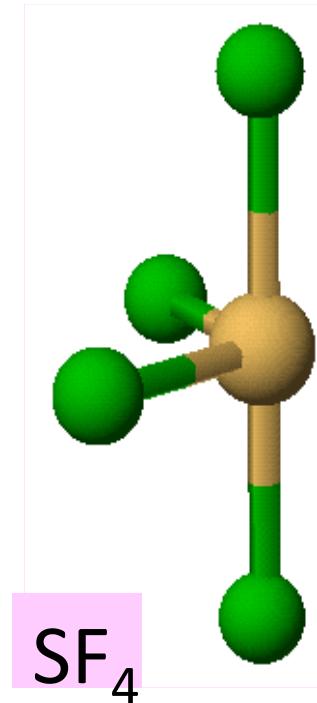
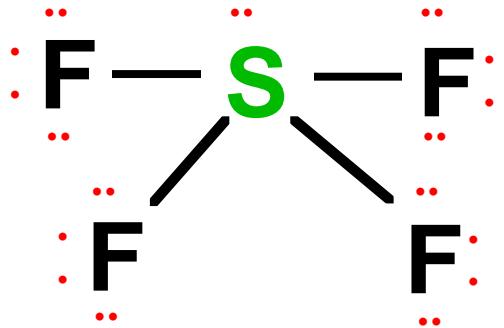
Limitations of the Octet Rule



Central atom = S

Valence electrons = $6 + 4*7 = 34$ e- or 17 pairs.

Form sigma bonds and distribute electron pairs.

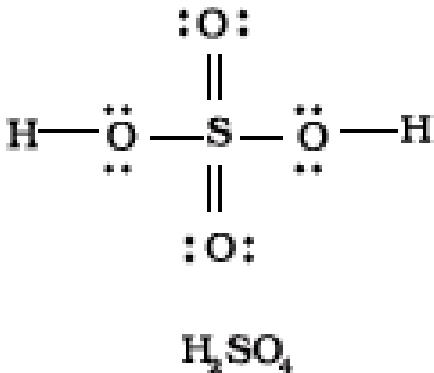
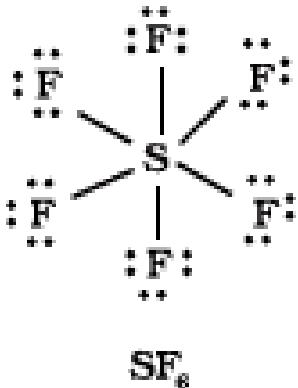
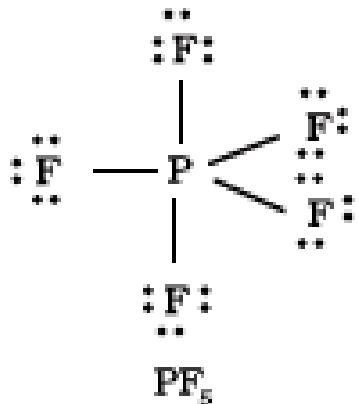


5 pairs around the S atom. Violates octet rule



Limitations of the Octet Rule

- Expanded octet

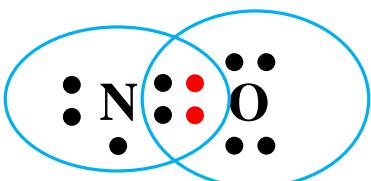


10 electrons around
the P atom

12 electrons around
the S atom

12 electrons around
the S atom

- Odd-electron molecules





Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , XeOF_2 etc.,
- It does not explain the relative stability of the molecules, being totally silent about the energy of a molecule.
Click to add text
- This theory does not account for the shape of molecules.



Valence bond theory

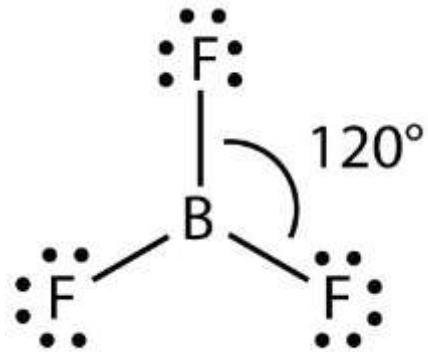
Developed by Linus Pauling for which he was awarded nobel prize in 1954.

Valence bond theory is a localized quantum mechanical approach to describe the bonding in molecule.

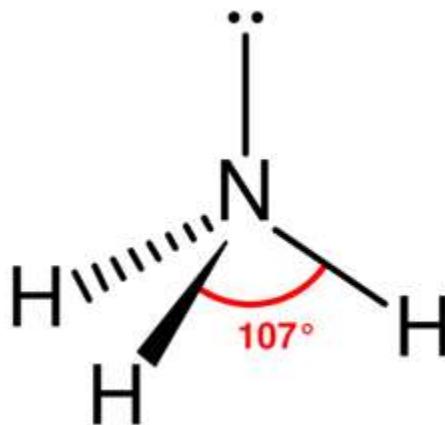
Valence Shell Electron Pair Repulsion (VSEPR) Theory



- The theory was suggested by **Sidgwick** and **Powell** in 1940 and was developed by **Gillespie** and **Nyholm** in 1957.
- A Method for predicting the shapes of individual molecules based on electron pair repulsion.



Trigonal planar



Pyramidal



VSEPR theory may be summarized as:

The bonds around the central atom and hence the shape of molecule depends on number of electron pairs surrounds it.

For a given number of electron pairs in the valence shell of the central atom, the preferred arrangement is that which minimizes their repulsion.

A lone pair of electrons takes up more space around the central atom than a bond pair.

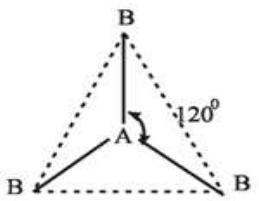
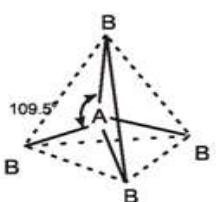
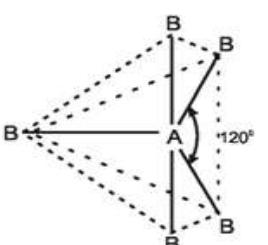
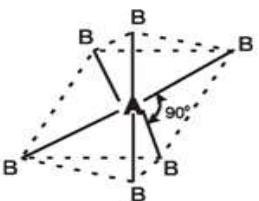
*lp belongs to central atom
bp belongs to both atoms*

And hence, **lp-lp repulsion > lp-bp repulsion > bp-bp repulsion**

The space occupied by a bond pair electron around the central atom decreases with increase in electronegativity of ligand.

Double bond occupy more space around the central atom than single bond, and triple bond occupy more space around central atom than double bond

Shape of molecules with general formula AB_n

No. of shared electron pairs around central atom.	Geometry of the molecules	Shape of the molecule	Examples
2.		Linear	$\text{BeF}_2, \text{BeCl}_2, \text{MgF}_2, \text{MgCl}_2$
3.		Trigonal planar	$\text{BF}_3, \text{BCl}_3, \text{AlF}_3, \text{AlCl}_3$
4.		Tetrahedral	$\text{CH}_4, \text{CCl}_4, \text{SH}_4, \text{SCI}_4$
5.		Trigonal Biyuramidal	$\text{PF}_5, \text{PCl}_5, \text{SbF}_5$
6.		Octahedral	$\text{SF}_6, \text{TeF}_6$

Effect of lone pair



A. Molecules with four electron pairs (steric numbers)

CH ₄	4 bp	0 lp	Tetrahedral	109.5 degree
NH ₃	3 bp	1 lp	Trigonal pyramid	106.7
H ₂ O	2 bp	2 lp	Bent or angular	104.5

In NH₃, due to the lp-bp repulsion, the bond angle decreases to 107.8 degree

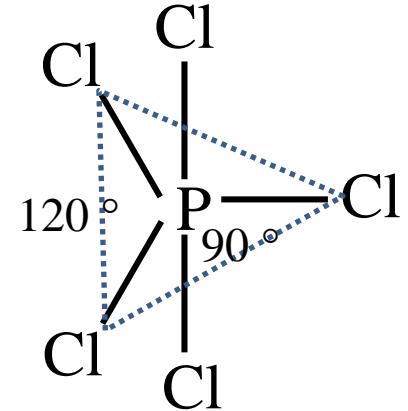
In H₂O, (2bp and 2lp) we have lp-lp repulsion which makes H-O-H bond angle even smaller (104.5) than H-N-H

Effect of lone pair



B. Molecules with five electron pairs (steric numbers)

I. PCl_5 (5 bp + 0 lp) trigonal bipyramidal geometry (all bonds are identical)



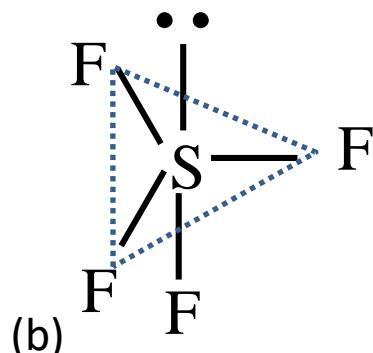
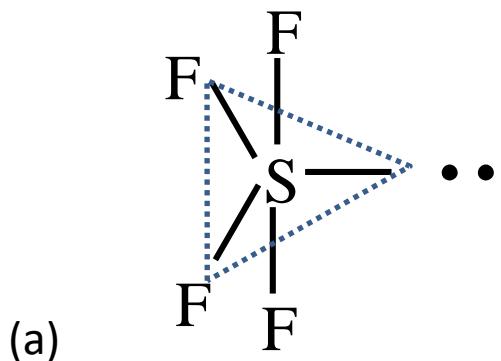
II. SF_4

Valence electron of S = 6

Contribution from each 4F = 4×1

Total = 10 VE (4 bp + 1 lp)

There are two possible structure (a) lone pair at equatorial position or (b) lone pair at axial position.





Effect of lone pair

II. SF₄

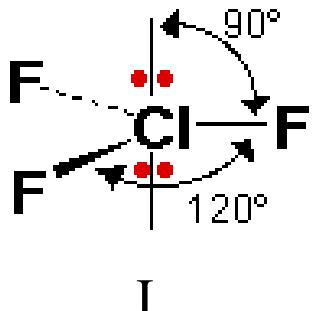
	(a)	(b)
lp-lp	----	---
Lp-bp	2@120, 2@90	1@180, 3@90

If the angle is $>120^\circ$, the repulsions have same effect on the structure. So 120 and 180 repulsions have same effect on the structure.

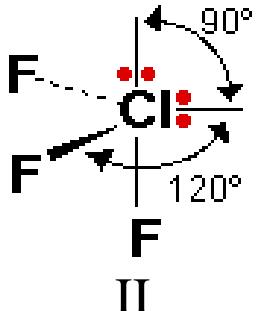
Since in structure (a), there are only 2@90 lp-bp repulsions, so it is the preferred structure for SF4.

III. ClF₃ (Home work)

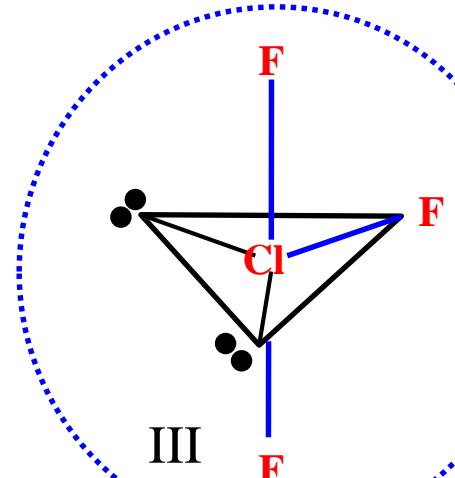
ClF_3



(Both LPs at axial position)

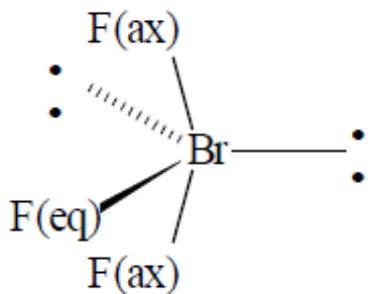


(one axial and another equatorial position)



(Both LPs at equatorial position)

Shape : T shape



Lone pairs occupy equatorial positions of trigonal bipyramidal

C. Molecules with six electron pairs (steric numbers)

SF_6 (6BP)

BrF_5 (5BP+1LP)

XeF_4 (4BP + 2LP)

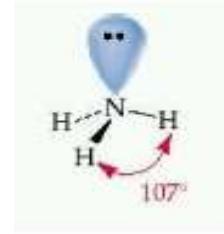
Effect of Electronegativity



With same central atom, if the ligand has larger electronegativity, the smaller is the bond angle.



- The high electronegativity of F pulls the bonding electrons away from N in NF_3 than in NH_3
- Thus repulsion between bp-bp is less in NF_3 than in NH_3



With same ligands, if the central atom has larger electronegativity, the larger is the bond angle.



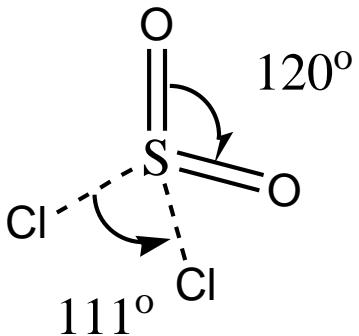
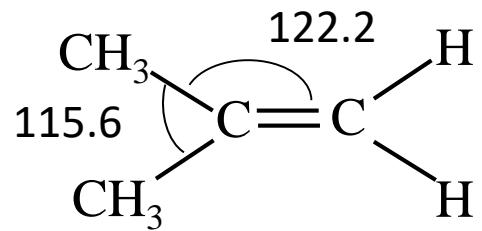
Q1. Among NH_3 and PH_3 , which one has larger bond angle?

Q2. Among PBr_3 and AsBr_3 , which one has larger bond angle?

Effect of Double bond



Double bond has very similar effect as that of the lone pair.



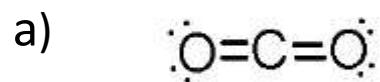
Q. Draw all possible structures of the following molecules and explain which one is the preferred structure based on VSEPR theory.

- (a) SO_2Cl_2 , (b) ClOF_3

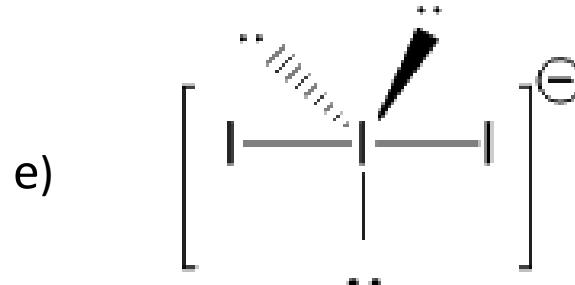
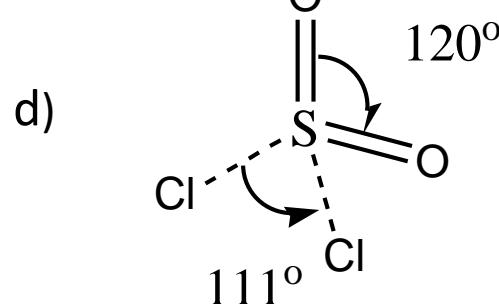
1. Using VSEPR theory, predict the geometries of the following compounds (derive each step and draw the final structure):



ANSWER



c) see-saw (distorted tetrahedron)





Valence bond theory

Valence bond theory is a localized quantum mechanical approach to describe the bonding in molecule.

Proposed by [Heitler and London in 1927](#)

This theory was further developed by [Linus Pauling \(Nobel Prize 1954\)](#)

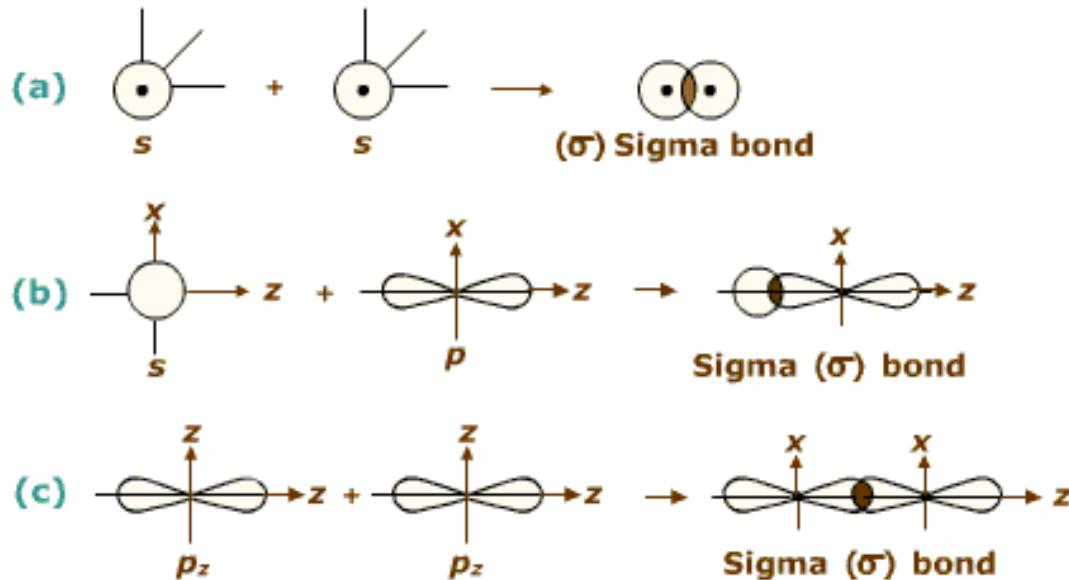
Sigma (σ) bond



sigma bonds (σ bonds) are formed by head-on overlapping between atomic orbitals.

Sigma bonds are cylindrically symmetric about the inter nuclear axis.

More overlap and hence the sigma bonds are strongest type of covalent chemical bond.



Formation of a sigma bond due to (a) The $s - s$ overlap

(b) The $s - p$ overlap (c) The $p_z - p_z$ overlap

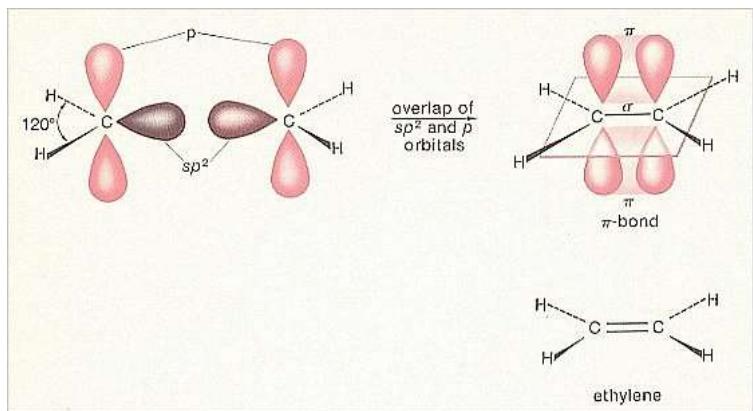
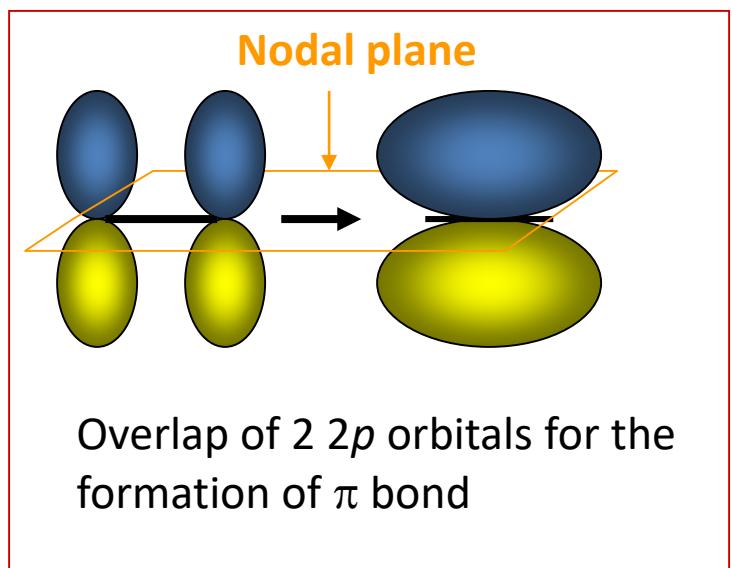
Pi (π) bond

Pi bonds (π bonds) are formed by sideways overlap of orbitals.

Pi bonds have electron density in two lobes, one each side of the bond axis.

Pi bond has one nodal plane containing the inter-nuclear axis and the sign of the lobe changes across the axis.

Pi bond is not as strong as sigma - less overlap.



Multiple bond



Single bond: must be one sigma bond

Double bond: one sigma + one pi bond

Triple bond: one sigma + two pi bonds

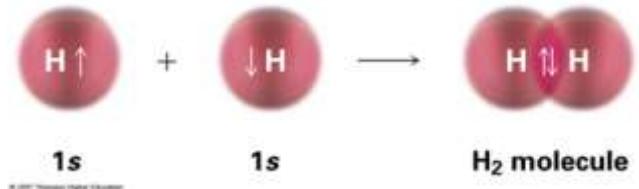
Sigma bonds and the lone pairs are responsible for shape/geometry of molecule. Pi bond only shorten the bond distance.



VBT to understand binary compounds

<i>s-s</i>	<i>s-p</i>	<i>s-d</i>	<i>p-p</i>
H–H	H–C	H–Pd	C–C
Li–H	H–N		F–F
	H–F		

H_2 molecule: 1s-1s sigma bond



F_2 molecule: 2p–2p sigma bond between two fluorine atoms

O_2 molecule: 2p_z–2p_z sigma bond; 2p_y/2p_x pi bonding.

Hybridization



The bonding in simple diatomic molecule can be explained by overlap of PURE atomic orbitals on each atom.

However, for polyatomic molecule, this is not the case. The valence orbitals (of central atom) undergo hybridization before making chemical bond.

sp 2 sp hybrid orbitals from mixing of a s and a p orbital

sp^2 3 sp^2 hybrid orbitals from mixing of a s and 2 p orbital

sp^3 4 sp^4 hybrid orbitals from mixing of a s and 3 p orbital

sp^3d 5 sp^3d hybrid orbitals from mixing of a s and 3 p and a d orbital



Hybridization

Consider n atomic orbitals with wave functions $\psi_1 \dots \psi_n$ undergo Hybridization to form n hybrid orbitals $\Psi_1 \dots \Psi_n$ are formed

$$\Psi_1 = C_{1,1} \psi_1 + C_{1,2} \psi_2 \dots \dots \dots + C_{1,n} \psi_n$$

.....

.....

$$\Psi_n = C_{n,1} \psi_1 + C_{n,2} \psi_2 \dots \dots \dots + C_{n,n} \psi_n$$

How the coefficients are determined?

Each atomic orbital must be completely distributed over all the hybrid orbitals.
(Unit atomic orbital contribution)

$$C_{1,1}^2 + C_{2,1}^2 + \dots \dots \dots + C_{n,1}^2 = 1$$

Hybrid orbitals must satisfy normalization condition.

$$C_{1,1}^2 + C_{1,2}^2 + \dots \dots \dots + C_{1,n}^2 = 1$$

Hybrid orbitals constructed based on symmetry of A.O.



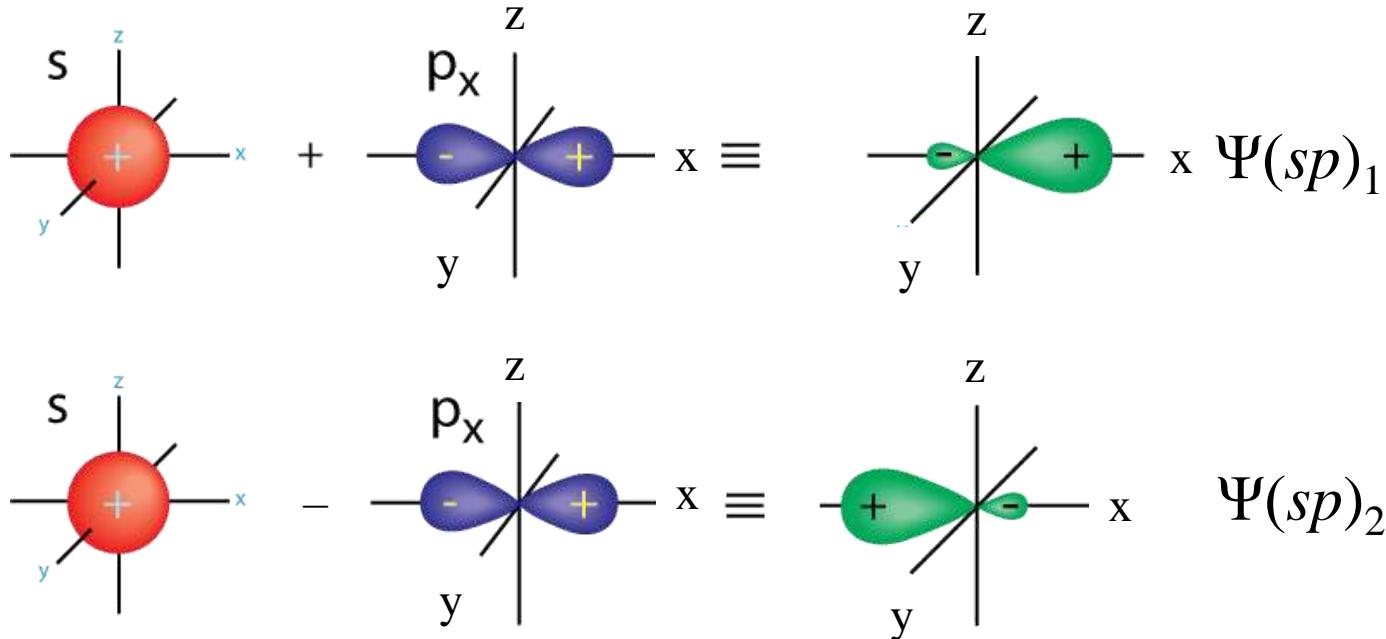
The *sp* Hybridization

hybridization of s and p orbitals = 2 *sp* hybrid orbitals (linear geometry)

$$\Psi_{sp1} = C1\psi_s + C2 \psi_{p_x}$$

Shape and orientation of hybrid orbitals??

$$\Psi_{sp2} = C3\psi_s + C4\psi_{p_x}$$



The *sp* Hybridization

hybridization of s and p orbitals = 2 *sp* hybrid orbitals (linear geometry)

$$\Psi_{sp1} = 1/\sqrt{2}\psi_s + 1/\sqrt{2} \psi_{p_x}$$

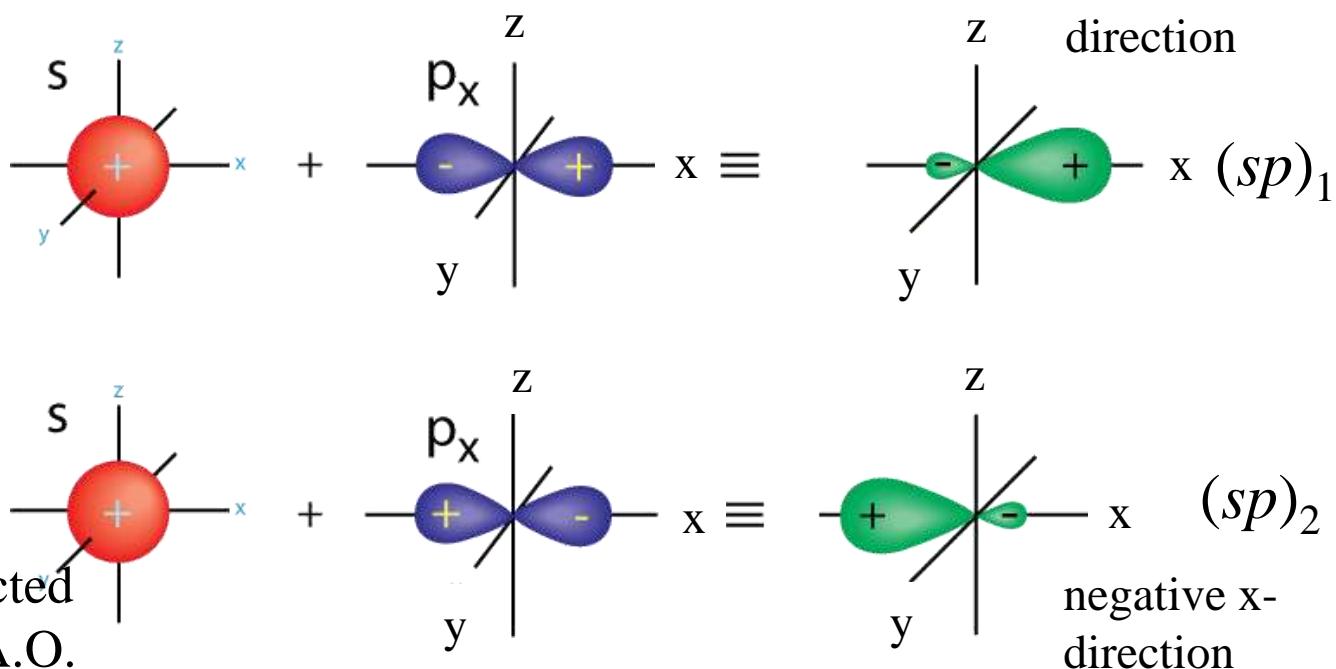
$$\Psi_{sp2} = 1/\sqrt{2}\psi_s - 1/\sqrt{2} \psi_{p_x}$$

Each atomic orbital must completely distributed over all hybrid orbitals.

Hybrid orbitals must satisfy normalization condition.

Hybrid orbitals constructed based on symmetry of A.O.

Square of the coefficient indicates the contribution of individual atomic orbital to the hybrid orbital.



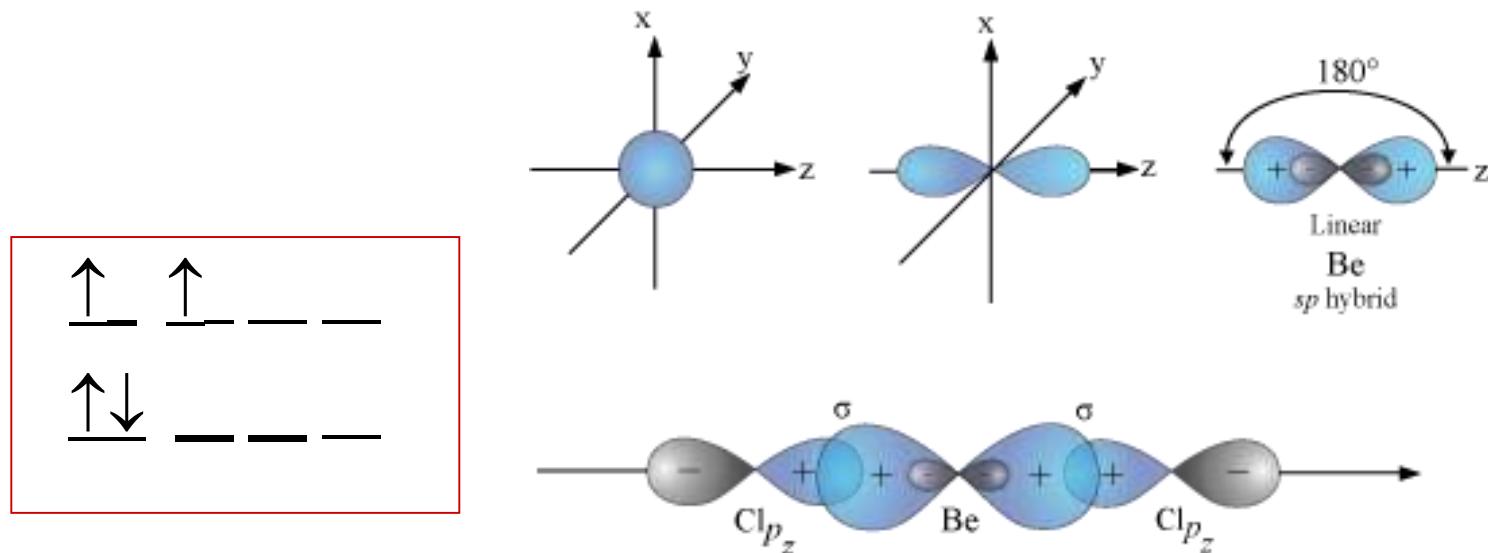
Examples of *sp* Hybridization



Beryllium bonded to two chlorine atoms. So, Be undergo *sp* hybridization.

Since there are two hybrid orbitals , so they aligned linearly with bond angle 180.

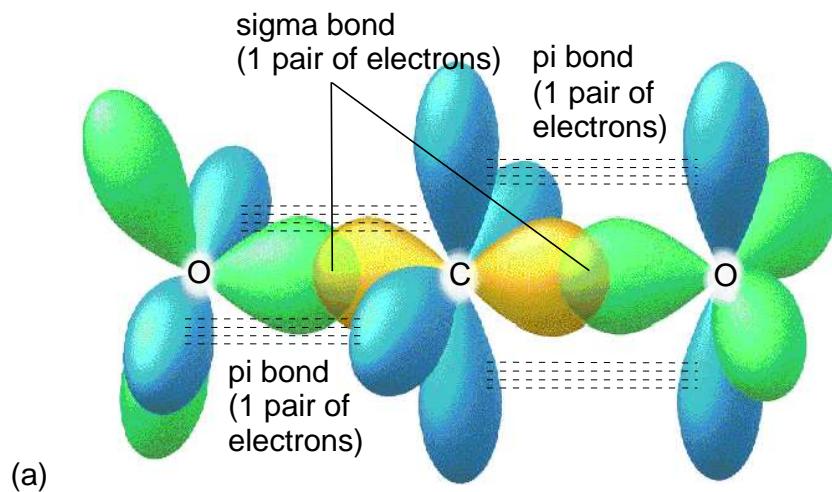
Each *sp* hybrid orbitals of beryllium atom overlap with the p-orbital of chlorine atom resulting sigma bond.



Examples of *sp* Hybridization



The hybridization of the central atom(s) is important.





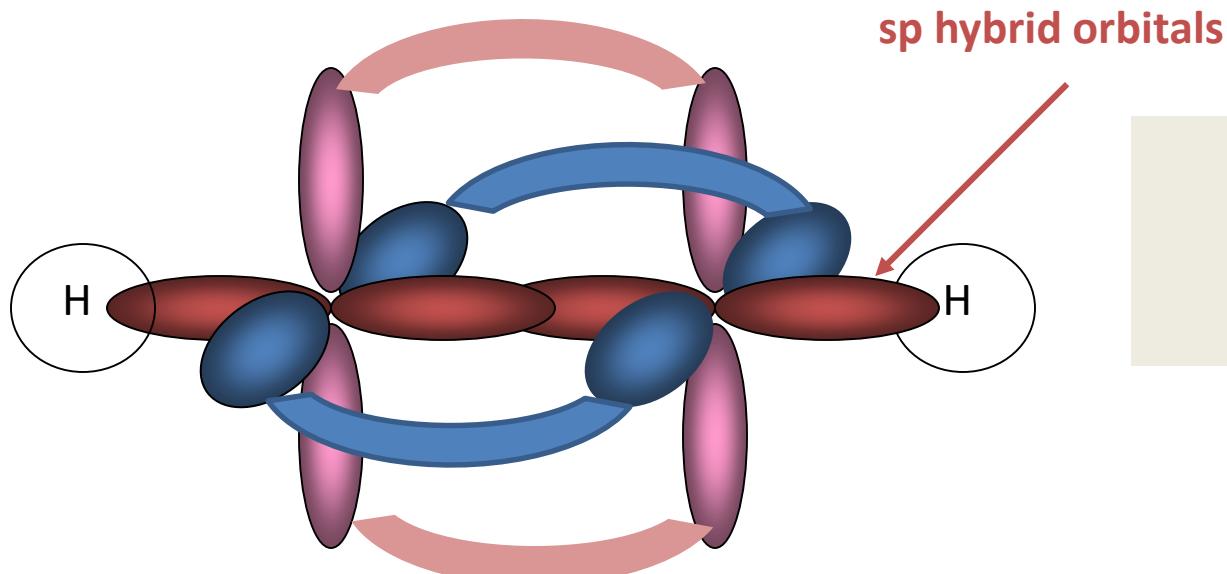
Examples of *sp* Hybridization



H-C-C-H: three σ bonds due to overlapping of $1s_{\text{H}} - sp_{\text{C}}$; $sp_{\text{C}} - sp_{\text{C}}$; and $sp_{\text{C}} - 1s_{\text{H}}$.

Two π bonds in $\text{HC}\equiv\text{CH}$ are due to overlapping of *p* orbitals results.

in π bond



Two **nodal planes** of *p* bonds are perpendicular to each other.

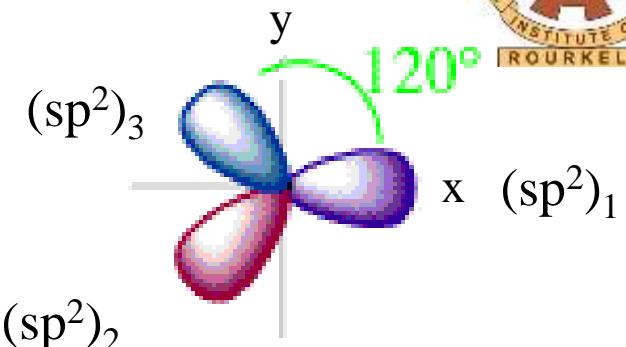
examples of sp^2 hybridization



Experimentally observed that BH_3 has trigonal planar structure.

All the B-H bonds are in XY-plane, so p_z orbital do not participate in hybridization.

s , p_x and p_y orbitals hybridized to give three sp^2 hybrid orbitals.



$$(SP^2)_1 = C_1 S + C_2 P_x + C_3 P_y$$

$$(SP^2)_2 = C_4 S + C_5 P_x + C_6 P_y$$

$$(SP^2)_3 = C_7 S + C_8 P_x + C_9 P_y$$

The coefficients can be deduced based on three principles.

1. symmetry
2. Unit orbital contribution ($C_1^2 + C_4^2 + C_7^2 = 1$)
3. Normalization $\psi^2 = 1$ ($C_1^2 + C_2^2 + C_3^2 = 1$)



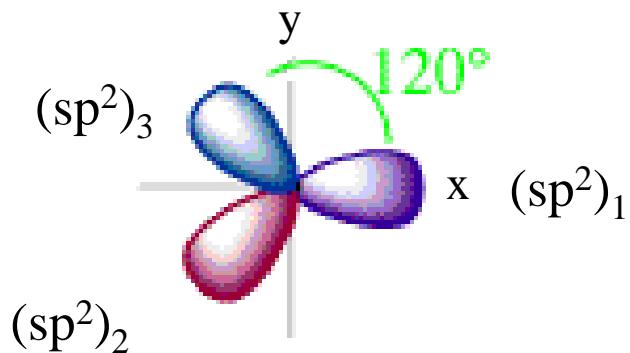
The sp^2 Hybridization

hybridization of s and p_x and p_y orbitals = 3 sp^2 hybrid orbitals
(trigonal planar geometry)

$$(sp^2)_1 = 1/\sqrt{3} \text{ s} + 2/\sqrt{6} \text{ p}_x$$

$$(sp^2)_2 = 1/\sqrt{3} \text{ s} - 1/\sqrt{6} \text{ p}_x - 1/\sqrt{2} \text{ p}_y$$

$$(sp^2)_3 = 1/\sqrt{3} \text{ s} - 1/\sqrt{6} \text{ p}_x + 1/\sqrt{2} \text{ p}_y$$



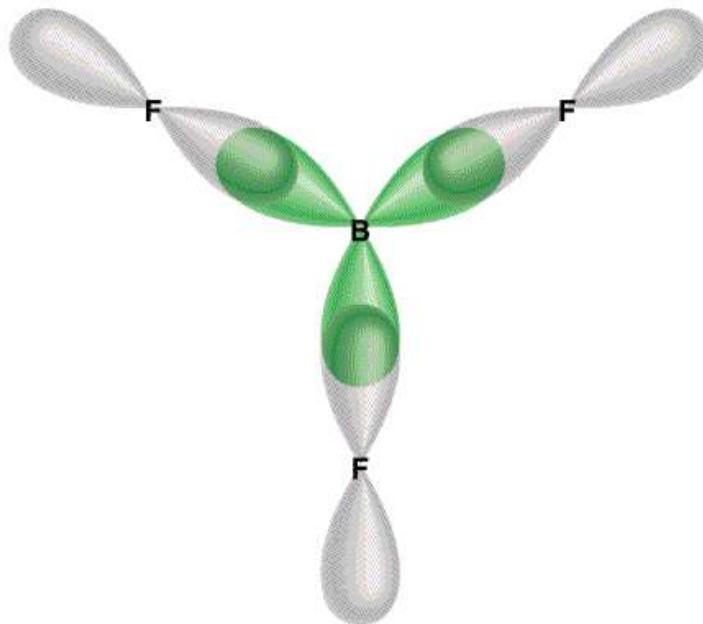


examples of sp^2 hybridization

Compounds involving sp^2 hybrid orbitals: BF_3 , CO_3^{2-} , H_2CO , $\text{H}_2\text{C}=\text{CH}_2$, SO_2 , NO_3^- , etc

Total number of hybrid orbitals = total number of sigma bonds (of central atom) + lone pairs on central atom

Boron Trifluoride





The sp^3 Hybridization

hybridization of s and p_x , p_y and p_z orbitals = 4 sp^3 hybrid orbitals
(tetrahedral geometry)

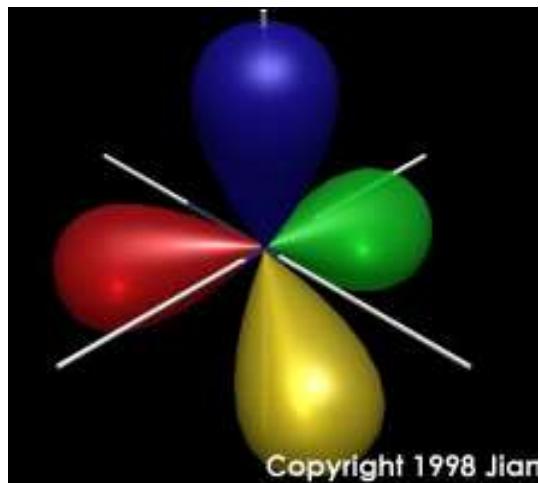
In tetrahedral geometry none of the hybrid orbitals is directed along axial direction and each hybrid orbital has equal contributions from all four atomic orbitals.

$$(sp^3)_1 = 1/\sqrt{4} s + 1/\sqrt{4} p_x + 1/\sqrt{4} p_y + 1/\sqrt{4} p_z$$

$$(sp^3)_2 = 1/\sqrt{4} s + 1/\sqrt{4} p_x - 1/\sqrt{4} p_y - 1/\sqrt{4} p_z$$

$$(sp^3)_3 = 1/\sqrt{4} s - 1/\sqrt{4} p_x - 1/\sqrt{4} p_y + 1/\sqrt{4} p_z$$

$$(sp^3)_4 = 1/\sqrt{4} s - 1/\sqrt{4} p_x + 1/\sqrt{4} p_y - 1/\sqrt{4} p_z$$

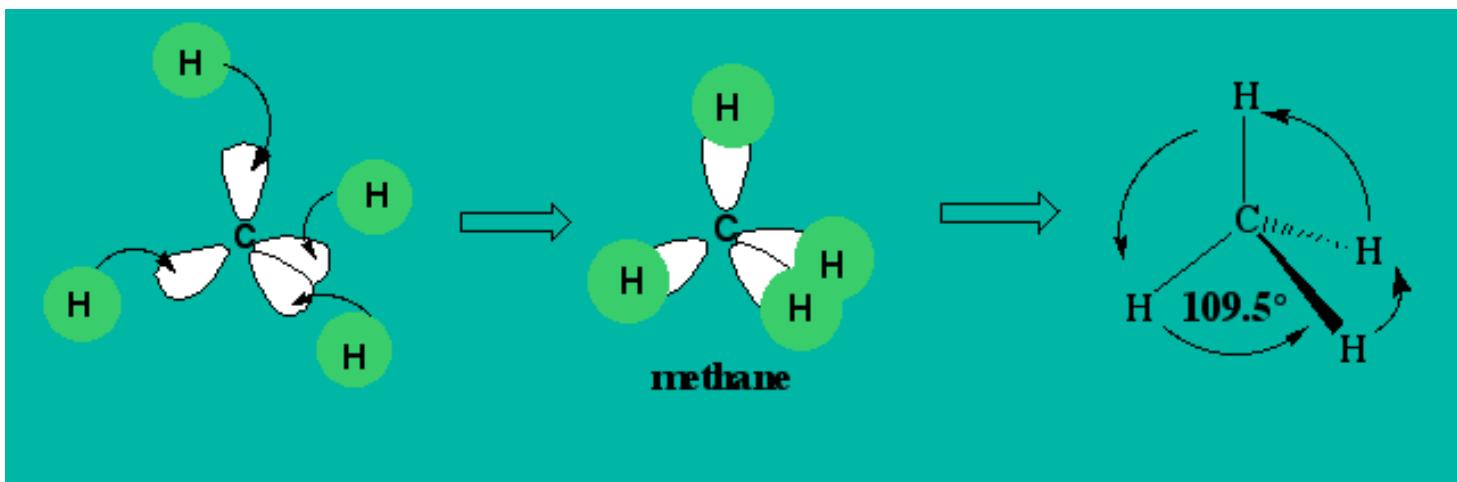


examples of sp^3 hybridization

Compounds involving sp^3 hybrid orbital: CF_4 , CH_4 , :NH_3 , $\text{H}_2\text{O}::$, SiO_4^{4-} , SO_4^{2-} , ClO_4^- , etc

Each sp^3 hybrid orbital has one electron and can form a strong covalent bond with another atom, eg methane formation with four hydrogens:

Electron pairs repel so the best arrangement is a tetrahedral geometry for the four bonds eg methane:



The sp^2 Hybridization

hybridization of s and p_x and p_y orbitals = 3 sp^2 hybrid orbitals
(trigonal planar geometry)

$$(sp^2)_1 = 1/\sqrt{3} s + 2/\sqrt{6} p_x$$

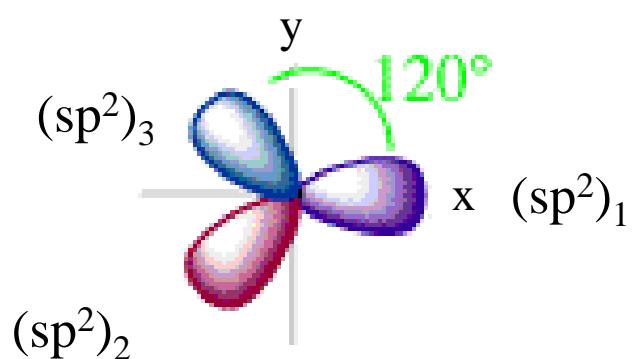
Coefficients of each hybrid orbitals can be derived

$$(sp^2)_2 = 1/\sqrt{3} s - 1/\sqrt{6} p_x - 1/\sqrt{2} p_y$$

Each atomic orbital must be completely distributed over all the hybrid orbitals.

$$(sp^2)_3 = 1/\sqrt{3} s - 1/\sqrt{6} p_x + 1/\sqrt{2} p_y$$

Hybrid orbitals must satisfy normalization condition.



Symmetry of atomic orbital



The sp^3d Hybridization

hybridization of s and p_x , p_y , p_z and d_{z^2} orbitals = 5 sp^3d hybrid orbitals
(trigonal bipyramidal)

sp^3d (TBP geometry) has two sets of hybrid orbitals

Three sp^3d hybrid orbitals in XY-plane.

$$(sp^3d_{z^2})_1 = 1/\sqrt{3} s + 2/\sqrt{6} p_x$$

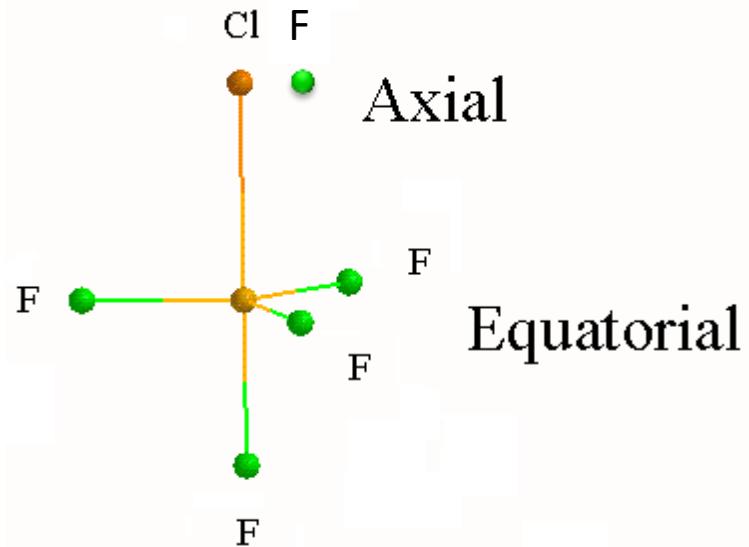
$$(sp^3d_{z^2})_2 = 1/\sqrt{3} s - 1/\sqrt{6} p_x - 1/\sqrt{6} p_y$$

$$(sp^3d_{z^2})_3 = 1/\sqrt{3} s - 1/\sqrt{6} p_x + 1/\sqrt{6} p_y$$

Two sp^3d hybrid orbitals along Z-axis.

$$(sp^3d_{z^2})_4 = 1/\sqrt{2} p_z + 1/\sqrt{2} d_{z^2}$$

$$(sp^3d_{z^2})_5 = -1/\sqrt{2} p_z + 1/\sqrt{2} d_{z^2}$$

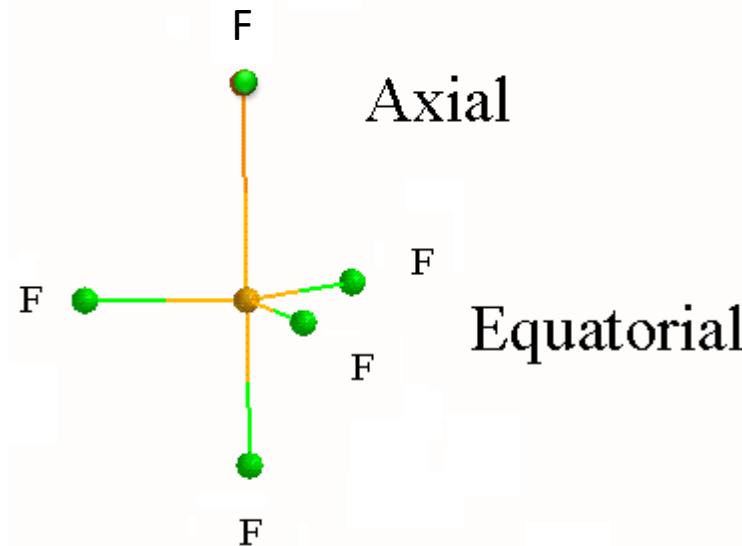
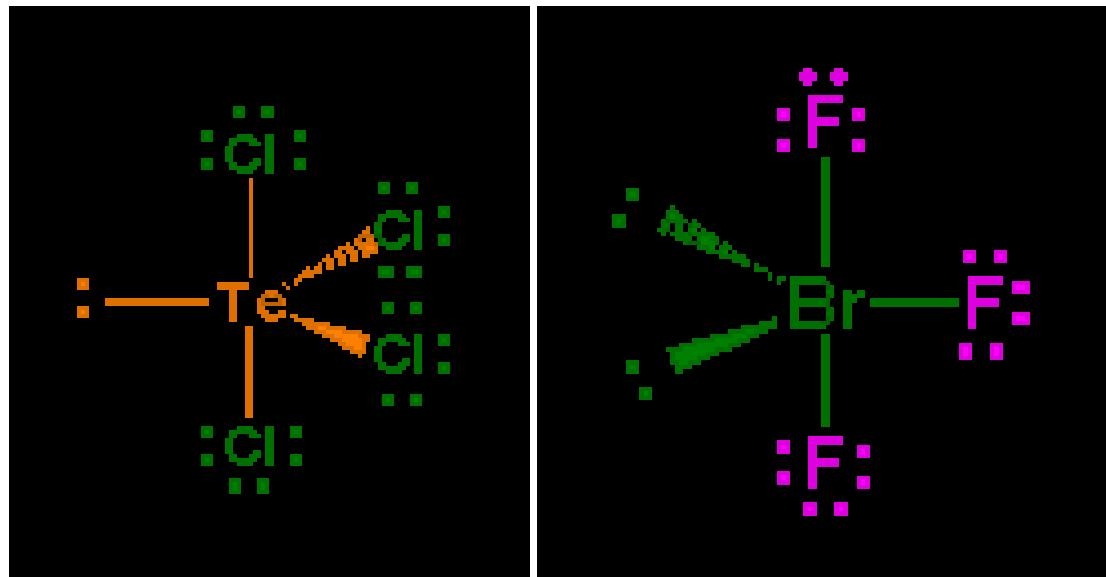




examples of sp^3d hybridization

Some structures due to these type of orbitals are

PF_5 , $PClF_4$, $TeCl_4$, and BrF_3 .





Draw backs of VBT

1. Does not tell anything about the excited states of molecule.
2. Not able to explain paramagnetic nature of O₂ molecule.

Paramagnetic compound: compounds/elements having unpaired electrons.

Diamagnetic compound: All electrons are paired up, no unpaired electron.

3. Can't explain the delocalized pi-electrons in certain molecules.
Ex- benzene.

Because of orbital overlap, the bonding electrons localize in the region between the bonding nuclei



Bent's Rule

sp^3d hybrid orbitals are combination of two sets of hybrid orbitals. sp_xp_y hybrids and p_zd_{z2} hybrid orbitals.

sp^2 hybrid orbitals are form stronger bond and are shorter than weak axial p_zd_{z2} hybrid orbitals.

PCl₅ has sp³d hybridization. When the electronegativities of the substituents on the phosphorous atom differ (PCl_{5-x}F_x), it has been experimentally observed that the more electronegative substituent occupies axial position.

Bent's rule

More electronegative substituents prefer hybrid orbitals having less s-character (small bond angle) and vice versa.

Empirical rule proposed by **H. A. Bent**, in the chlorofluorides of phosphorous, 1960.

It has been used to supplement VSEPR interpretation of structure of molecules



Bent's Rule

Ex. CH_2Cl_2 , H-C-H bond angle is more than 109.5 degree, indicating more than 25% s-character.
Cl-C-Cl bond angle is less than 109.5 degree, indicating less than 25% s-character.

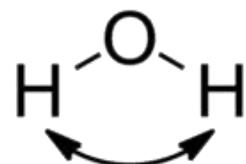
Presence of lone pairs also affect the percent of s and p character in hybrid orbitals.

The relation between bond angle and the %s character (S) or %p character (P) is given by

$$\cos \theta = S/(S-1) = (P-1)/P$$

Where S and P are % of S- and P-character

Q. Calculate the % of s-character of the hybrid orbital of oxygen involved in the O-H bond of H_2O .



104.5°



Molecular Orbital Theory

MOT is developed by Robert S. Mulliken (Got nobel prize in 1966).

Based on delocalized quantum mechanical approach.

Uses symmetry to describe the bonding in molecule.

Basic Principles of MOT

Describes the electrons in a molecule using wave functions called molecular orbitals.

Electrons in these molecular orbitals belong to the molecule as a whole.

The atomic orbitals of different atoms combine to create molecular orbitals. The symmetry and relative energy of atomic orbitals determine how they interact to form molecular orbital.

These molecular orbitals are then filled with available electrons according to the increasing order of energy.



MOT and VBT

VBT

Electrons occupy atomic orbitals, localized to overlap region. (localized electron pair concept)

Hybridization of A. O.s of same atom to explain the geometry of molecule.

Does not tell anything about the excited states of molecule.

MOT

Electrons in molecular orbitals belong to the molecule as a whole. (Delocalized concept)

No concept of hybridization. It does not tell anything about geometry of molecule.

Better describe the excited states of molecule.

MO theory more “accurately predict the bonding” than VB theory and also the properties of molecules.



Molecular Orbital Theory

Procedure for forming molecular orbitals

1. Identify set of symmetry related atomic orbitals with similar energy.
2. MOs form by linear combinations of the atomic orbitals (LCAO).
3. For poly atomic molecule, the LCs of ligands combine with the atomic orbitals of central atom to form MOs.

Application of MOT

(a) Homonuclear diatomic molecule

(b) Heteronuclear diatomic molecule

(c) Polyatomic molecule??



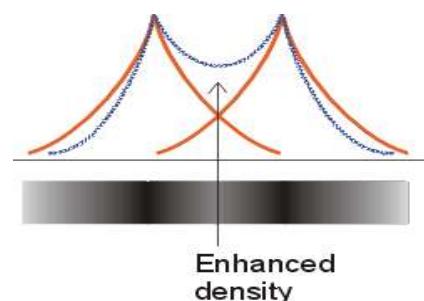
Types of Molecular Orbitals

Combination of atomic orbitals, gives following molecular orbitals:

- Bonding molecular orbital
- Antibonding molecular orbital
- Nonbonding molecular orbital

□ Bonding molecular orbital

- When two orbitals with same sign overlaps, then there is increase in electron density in the overlap region and a bonding MO is formed.
- This is called as constructive interference of atomic orbitals.
- lower energy than atomic orbital

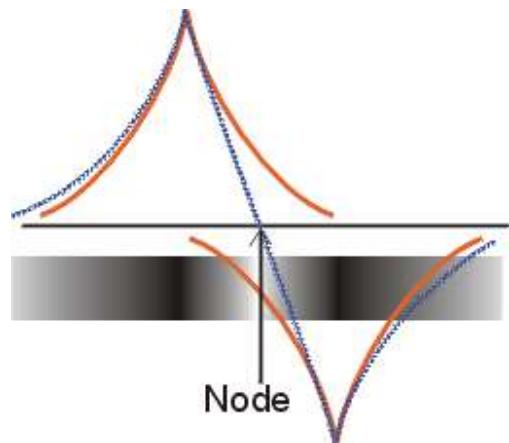




Types of Molecular Orbitals

□ Antibonding molecular orbital

- Destructive interference leads exclusion of electrons for the region between the nuclei
 - Highest electron density is located on opposite sides of the nuclei
- higher energy than atomic orbital





Types of Molecular Orbitals

□ Nonbonding molecular orbital

Nonbonding molecular orbitals have essentially same as that of the atomic orbitals. These may form in following situations:

1. Combination of atomic orbitals whose symmetry do not match and remain unchanged in the molecule.

Ex: interaction of s with p_x or p_y or d_{xy} or d_{yz} etc

2. When there are three atomic orbitals of the same symmetry and similar energy, three MOs are formed: bonding MO (lower energy), antibonding MO (higher energy), and nonbonding MO (same energy as atomic orbital).



Homonuclear diatomic molecule

MOs may be either sigma (σ) or pi (π) orbitals.

σ MO: MO which are symmetric to rotation about the inter-nuclear axis.

π MO: MO which have a nodal plane containing the inter-nuclear axis (not symmetric to rotation about the inter-nuclear axis.)

Molecular orbitals from 1s atomic orbitals:

$$\psi_A (1s) = 1s \text{ orbital wave function of A}$$

$$\psi_B (1s) = 1s \text{ orbital wave function of B}$$

Molecular orbitals are:

$$\psi_{AB} (1) = 1/\sqrt{2}[\psi_A (1s) + \psi_B (1s)] \quad (\text{Bonding MO})$$

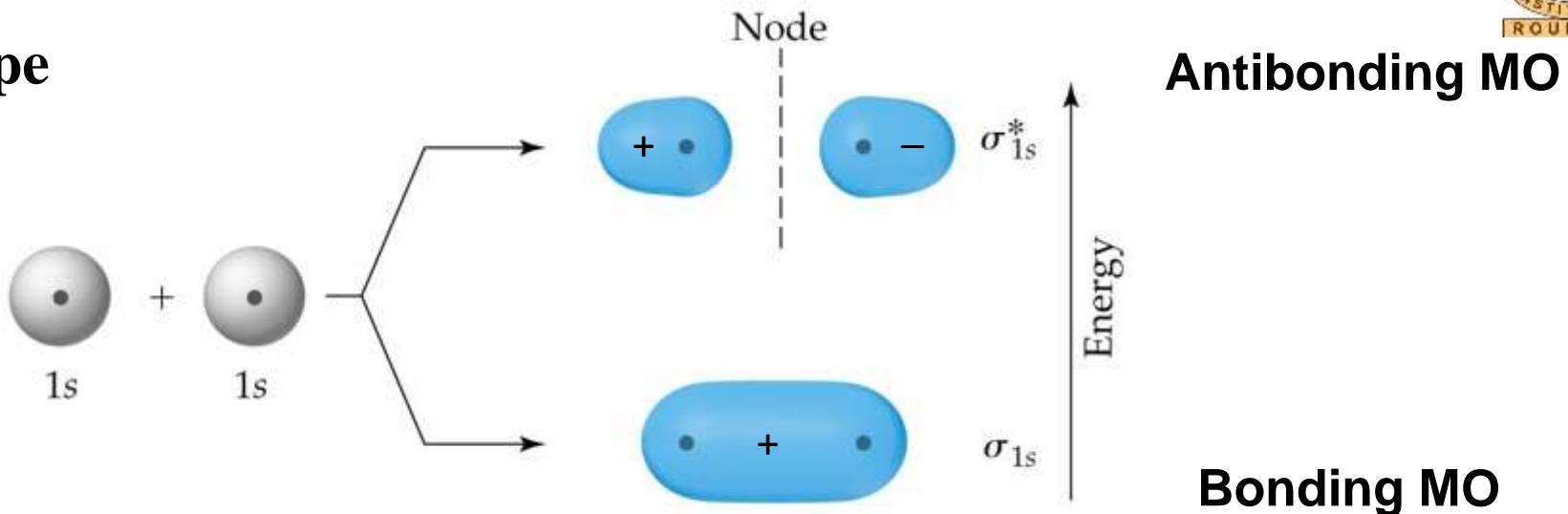
$$\psi_{AB} (2) = 1/\sqrt{2}[\psi_A (1s) - \psi_B (1s)] \quad (\text{Antibonding MO})$$

Note: In homonuclear diatomic molecule, the contribution from each atom to the MO is equal.

Homonuclear diatomic molecule



Shape



Symmetry

σ_{1s} orbital has center of inversion, and hence it has gerade symmetry ($1\sigma_g$).

σ^*_{1s} orbital does not have center of inversion, and hence it has ungerade symmetry ($1\sigma_u$).

Homonuclear diatomic molecule



Molecular orbitals from 2p atomic orbitals

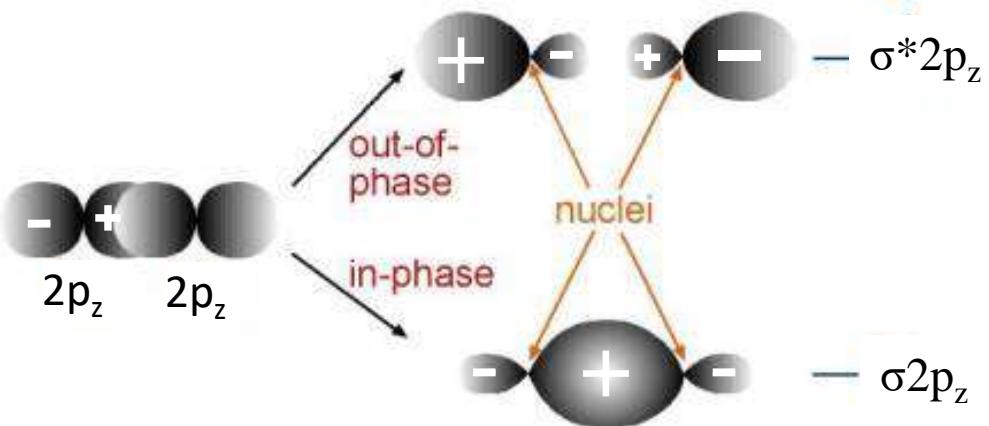
Combination of 2p orbitals gives two sets of molecular orbitals based on symmetry.

If the inter nuclear axis is the z -axis, then the combination of $2p_z$ atomic orbitals [$2p_z(A) \pm 2p_z(B)$] gives MOs that are symmetric about inter nuclear axis.

$$\sigma 2p_z = 2p_z(A) - 2p_z(B)$$

$$\sigma^* 2p_z = 2p_z(A) + 2p_z(B)$$

Shape



Symmetry

$\sigma 2p_z$ bonding MO = gerade symmetry

$\sigma 2p_z$ antibonding MO = ungerade symmetry

Molecular orbitals from 2p atomic orbitals

Combination of $2p_x$ atomic orbitals [$2p_x(A) \pm 2p_x(B)$] gives molecular orbitals having nodal plane containing internuclear axis. MOs are:

$$\pi 2p_x = 2p_x(A) + 2p_x(B)$$

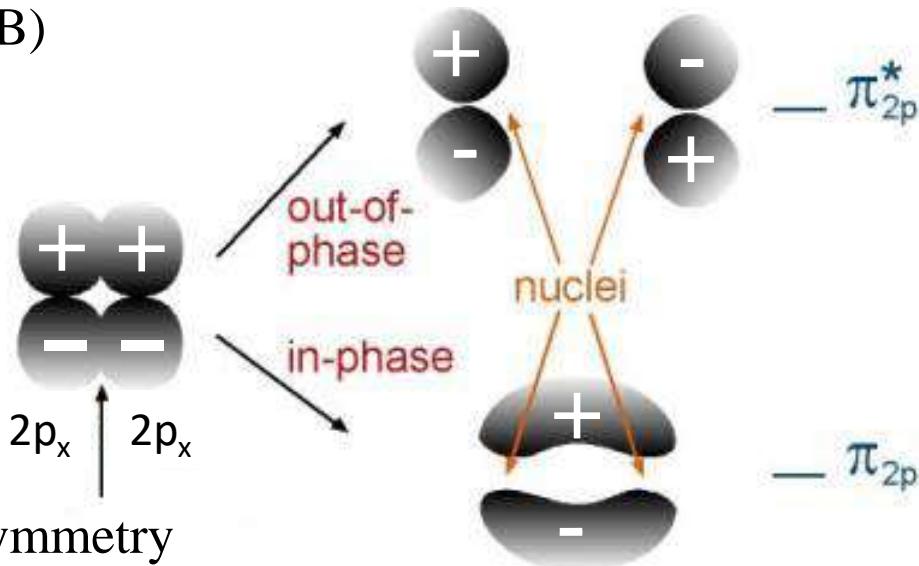
$$\pi^* 2p_x = 2p_x(A) - 2p_x(B)$$

Shape

Symmetry

$\pi 2p_x$ bonding MO = ungerade symmetry

$\pi^* 2p_x$ antibonding MO = gerade symmetry



Similarly, $2p_y$ atomic orbitals combine to give $\pi 2p_y$ and $\pi^* 2p_y$ MOs.

Since the $2p_x$ and $2p_y$ orbitals have identical energy, so the resulting MOs also have same energy. These MOs differ only in spatial orientation.



Energy order of M.O.s

The energy order of molecular orbitals in homonuclear diatomic molecule is-

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

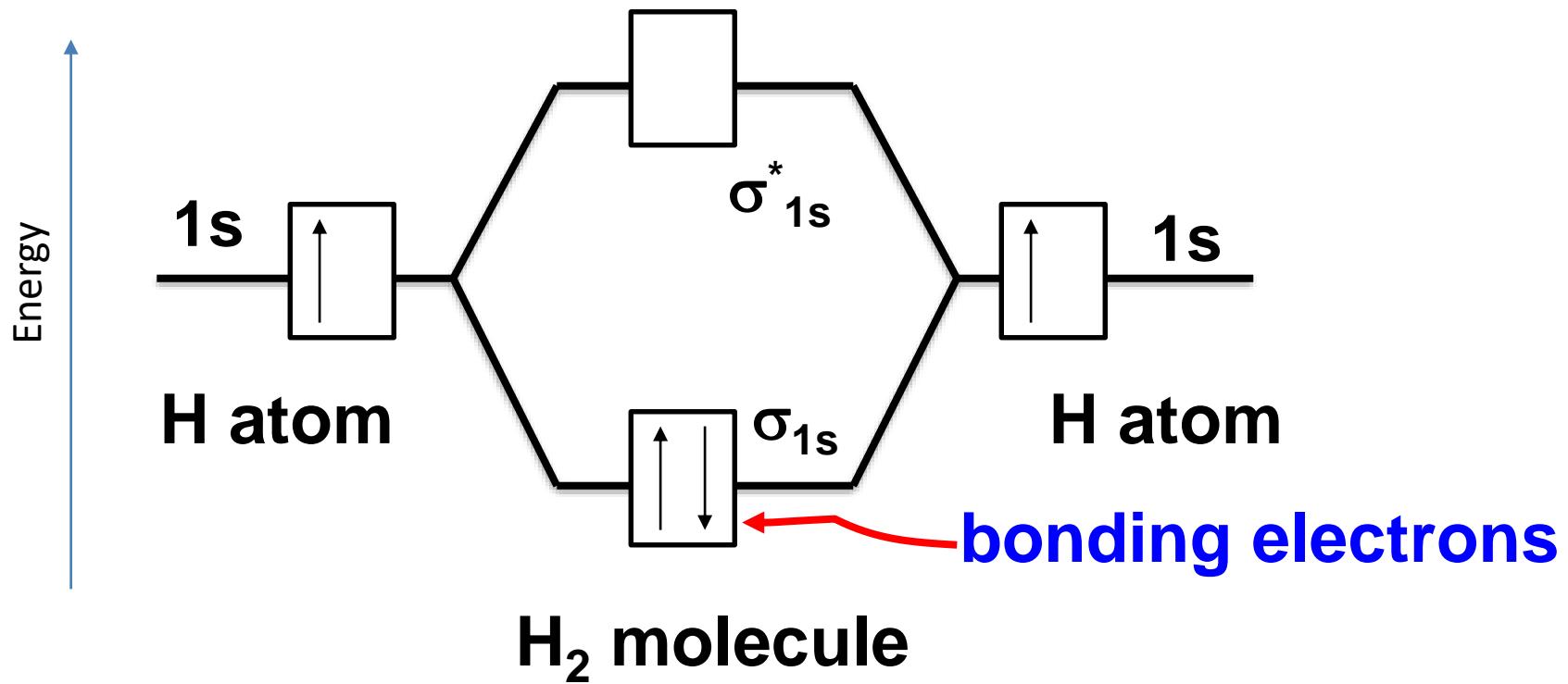
Molecular orbital diagram

An energy level diagram that shows the energy level of molecular orbitals relative to the atomic orbitals from which they're derived

- Draw the skeleton MOs
- Use only the valence electrons of the atoms
- Follow the aufbau principle
- Each MO can hold a maximum of 2 electrons
- Follow Hund's rule.
- Keep electrons unpaired until all MO's having the same energy have one e⁻.

MO diagram for H₂ molecule

Molecular orbital diagram



Electronic configuration

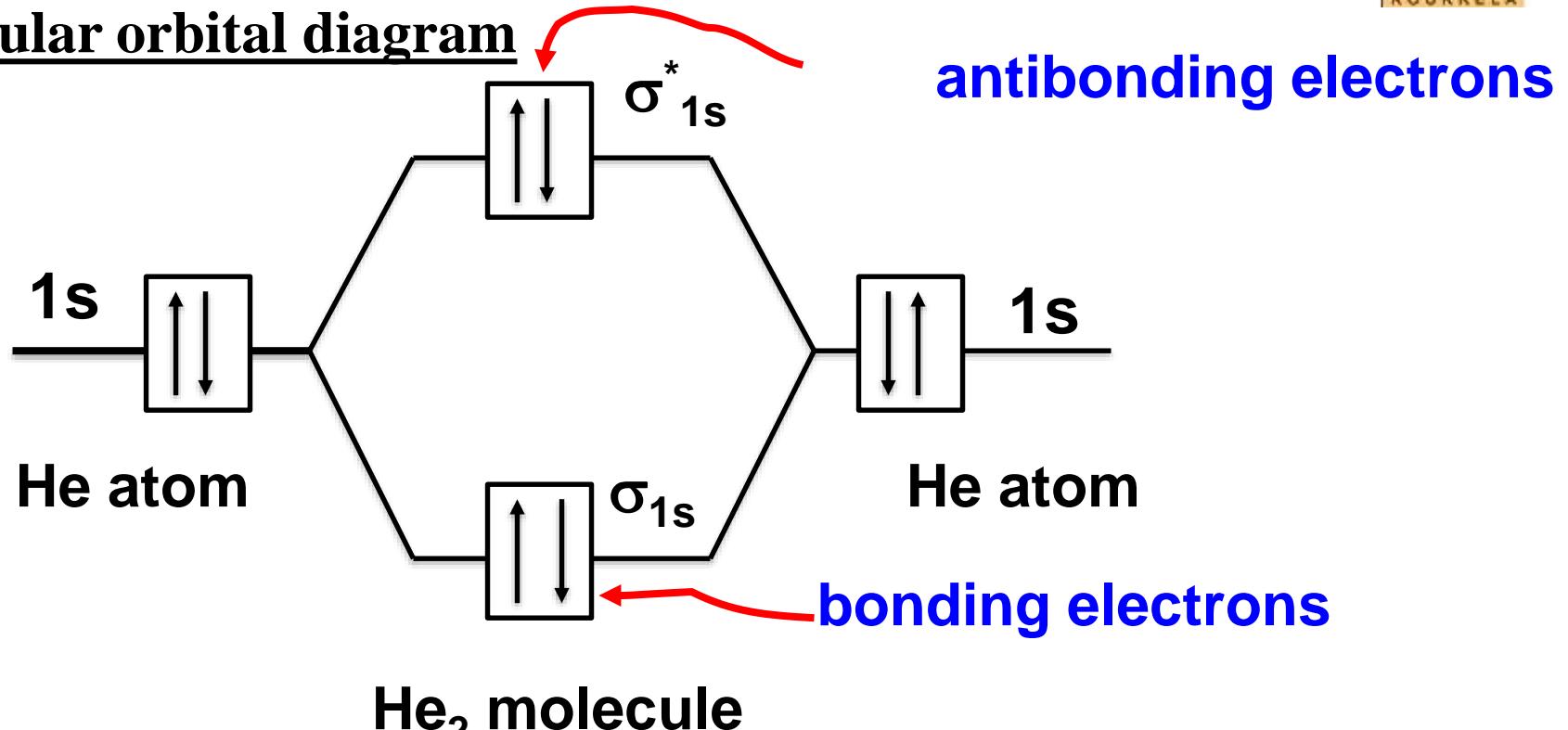
$$(\sigma 1s)^2$$

Since both the electrons occupy the bonding MO, which has lower energy than AOs. So there is net decrease in energy of H₂ molecule.

MO diagram for He_2 molecule



Molecular orbital diagram



Electronic configuration

$$(\sigma 1s)^2, (\sigma^* 1s)^2$$

MO diagram for He₂ molecule



He₂ molecule has 2 bonding electrons and 2 antibonding electrons.

The energy decrease from the 2 electrons in the bonding MO is offset by the energy increase from the 2 electrons in the antibonding MO.

He₂ is not a stable molecule!



Bond order (strength of bond)

In MO Theory, the strength of a covalent bond can be related to its bond order

$$\text{Bond order} = \frac{(\text{no. of bonding } e^- - \text{no. of antibonding } e^-)}{2}$$

bond order = 1 -- Single bond

bond order = 2 -- Double bond

bond order = 3 -- Triple bond

Fractional bond orders also exist!



Bond order (strength of bond)

- The bond order for H₂ molecule

$$\text{Bond Order} = \frac{(2 - 0)}{2} = 1$$

- The hydrogen atoms in an H₂ molecule are held together by a single bond.

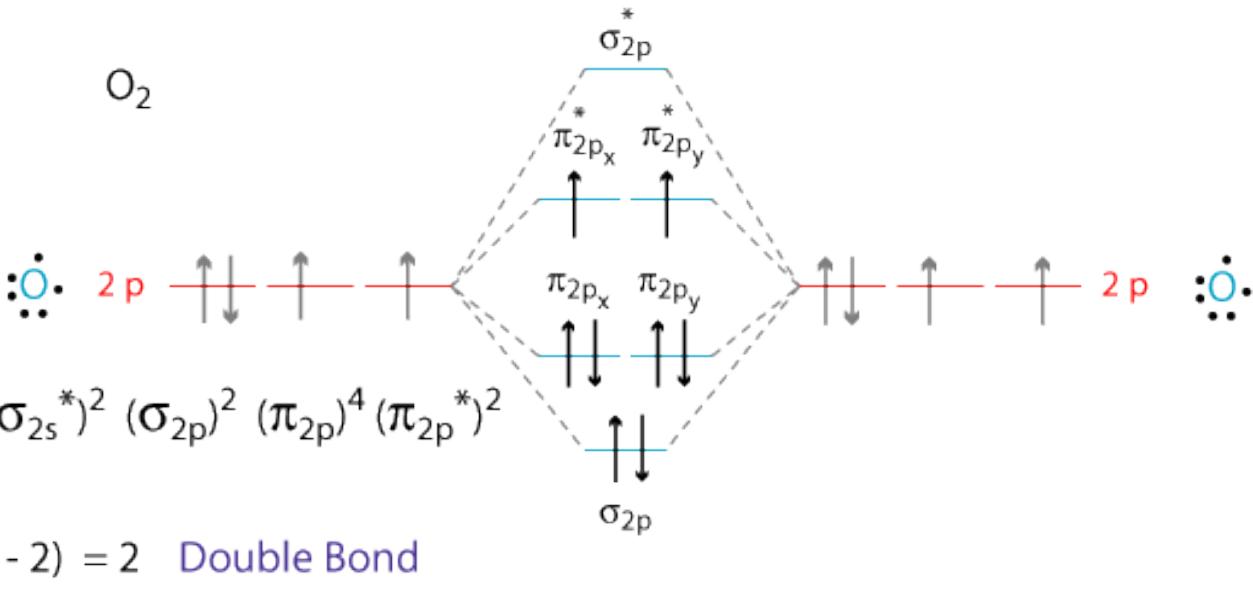
- The bond order for an He₂ molecule:

$$\text{Bond order} = \frac{(2 - 2)}{2} = 0$$

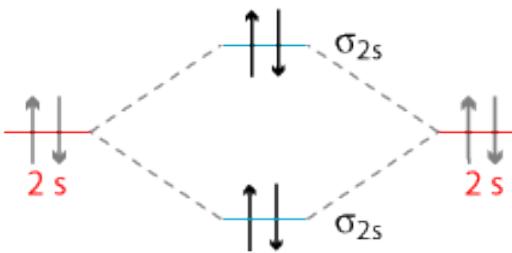
- No bond exists between two He atoms.



Q. Draw the molecular orbital diagram of O₂ molecule. Fill the valence electrons and write down the energy order of MOs. Find out the bond order and show that it is paramagnetic in nature.



Since there are two unpaired electrons present in π_{2px}^* and π_{2py}^* , so oxygen molecule is paramagnetic in nature.





Molecular Orbital Diagram (*s-p* mixing)

Molecular orbitals of the same symmetry and similar energy interact to lower the energy of lower MO and raise the energy of higher MO. This phenomenon is called as **orbital mixing**.

Example: s-p mixing is observed for homonuclear diatomic molecules, Li₂ to N₂.

σ_{2s} & σ_{2p} MOs have same symmetry (gerade) and similarly, σ_{2s}^* & σ_{2p}^* MOs have same symmetry (ungerade) and have small energy difference <13 eV for diatomic molecules Li₂ to N₂.

So these orbitals interact to lower the energy of σ_{2s} and raise the energy of σ_{2p} . Similarly, σ_{2s}^* & σ_{2p}^* interact to lower the energy of σ_{2s}^* and raise the energy of σ_{2p}^* .

So the energy of $\sigma 2p$ for molecules Li₂ to N₂ is higher than $\pi 2p_x = \pi 2p_y$ orbitals.

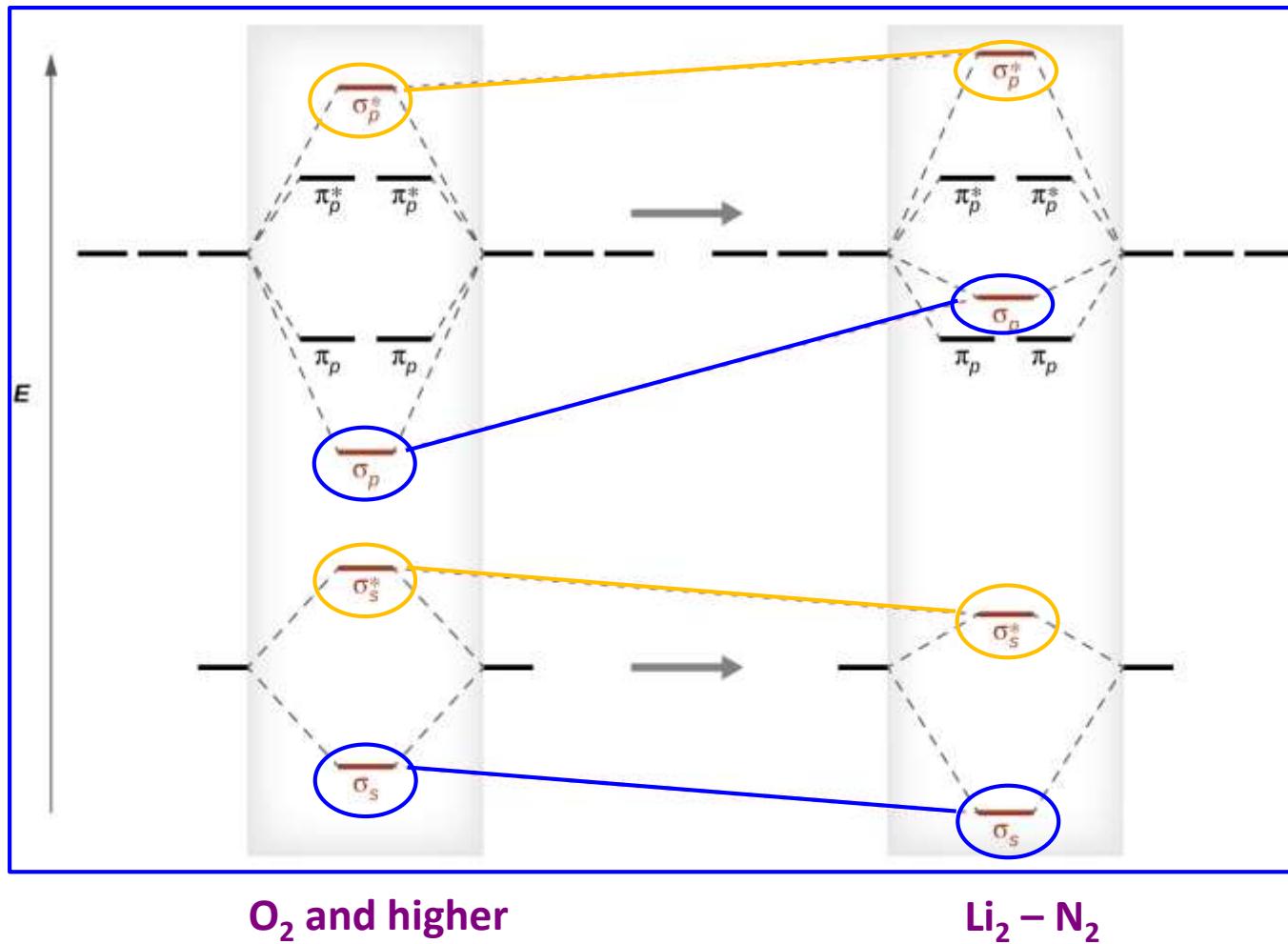
In practical orbitals with energy difference < 13eV generally interact.

atom	orbital	$-\epsilon_i^{\text{TS}}$	$-H$ (eV)
H	1s	12.565	13.6
Li	2s	5.439	5.4
	2p	3.610	3.5
Be	2s	9.663	10.0
	2p	6.072	6.0
B	2s	14.440	15.2
	2p	8.438	8.5
C	2s	19.654	21.4
	2p	11.129	11.4
N	2s	25.366	26.0
	2p	13.900	13.4
O	2s	31.600	32.3
	2p	16.776	14.8
F	2s	38.373	40.0
	2p	19.769	18.1
Na	3s	5.331	5.1
	3p	3.178	3.0

Molecular Orbital Diagram

Homonuclear diatomic molecules

s-p mixing



Homonuclear Diatomics

- $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2pz} < \pi_{2px} = \pi_{2py} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$. (O_2 and higher)
- $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2px} = \pi_{2py} < \sigma_{2pz} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$. (Li_2^- , N_2)



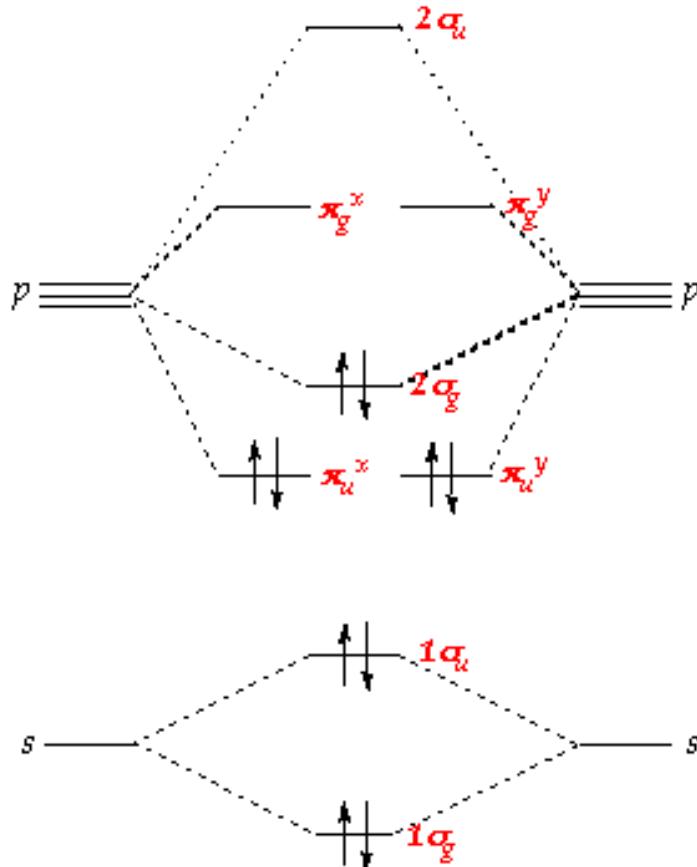
Molecular Orbital Diagram of N₂

Number of valence electrons two N atoms = 10

2s and 2p atomic orbitals of two N atoms give 8 MOs.

$$\text{B. O.} = (8-2)/2 = 3$$

Magnetic properties: Since all the electrons are paired up, so it is a diamagnetic compound.

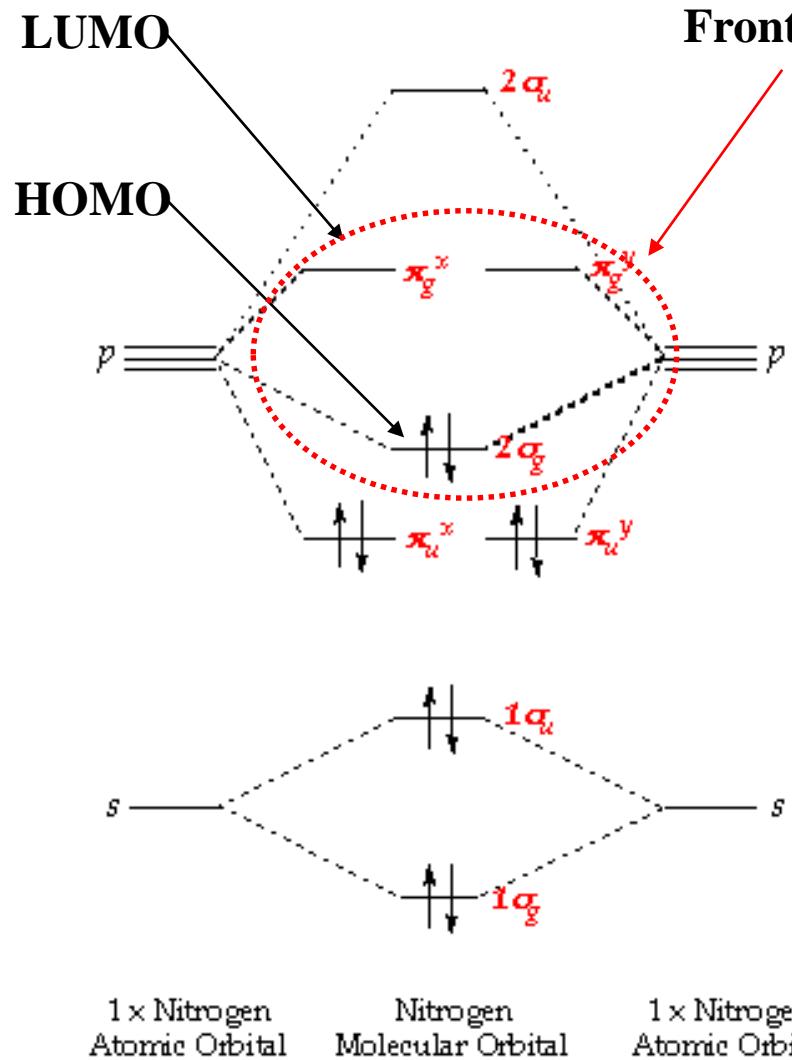


1 × Nitrogen
Atomic Orbital

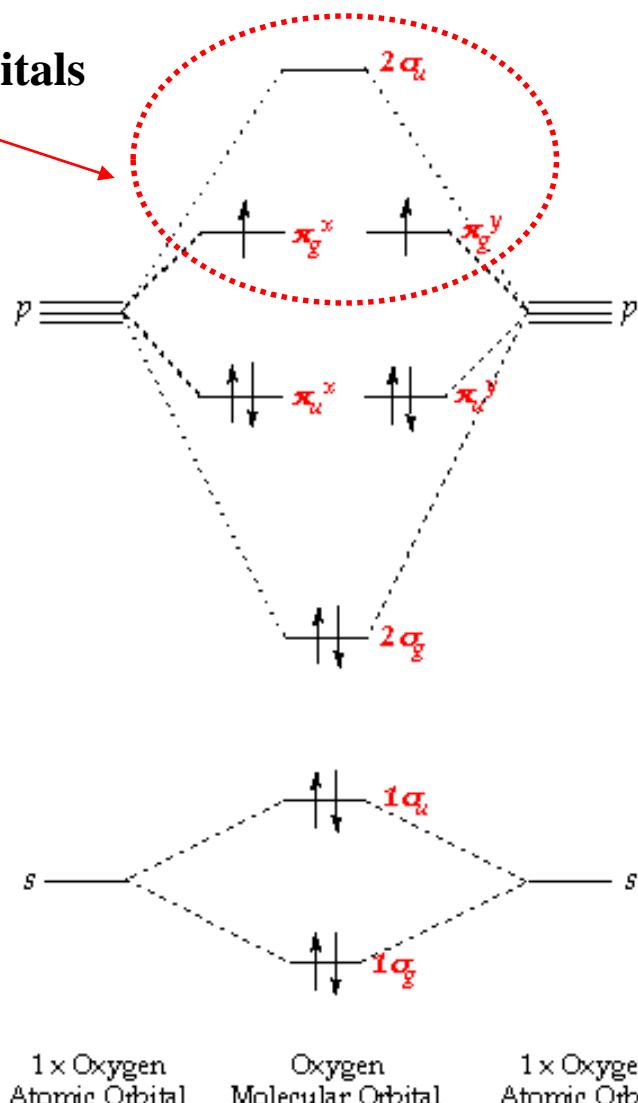
Nitrogen
Molecular Orbital

1 × Nitrogen
Atomic Orbital

N_2 molecule



O_2 molecule



1 x Nitrogen
Atomic Orbital

Nitrogen
Molecular Orbital

1 x Nitrogen
Atomic Orbital

1 x Oxygen
Atomic Orbital

Oxygen
Molecular Orbital

1 x Oxygen
Atomic Orbital

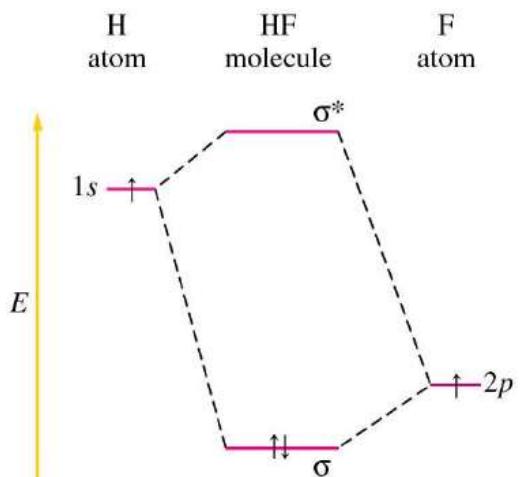


Heteronuclear diatomic molecule

In heteronuclear diatomic molecule, the atomic orbital have different energy and hence their contribution to MO will be unequal.

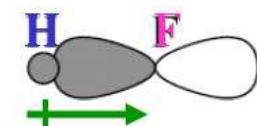
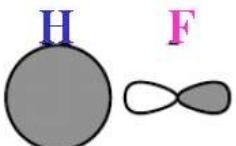
The AO closer in energy to a MO contribute more to that MO and its coefficient is large.

HF molecule



$$\text{B.O} = 1$$

**σ Antibonding (σ^*)
Mostly H(1s)**



**σ Bonding
Mostly F(2p)**

atom	orbital	$-\epsilon_i^{\text{TS}}$	$-H$ (eV)
H	1s	12.565	13.6
Li	2s	5.439	5.4
	2p	3.610	3.5
Be	2s	9.663	10.0
	2p	6.072	6.0
B	2s	14.440	15.2
	2p	8.438	8.5
C	2s	19.654	21.4
	2p	11.129	11.4
N	2s	25.366	26.0
	2p	13.900	13.4
O	2s	31.600	32.3
	2p	16.776	14.8
F	2s	38.373	40.0
	2p	19.769	18.1
Na	3s	5.331	5.1
	3p	3.178	3.0



Molecular orbital diagram of CO

Total no. of electrons = 14 (isoelectronic to N₂)

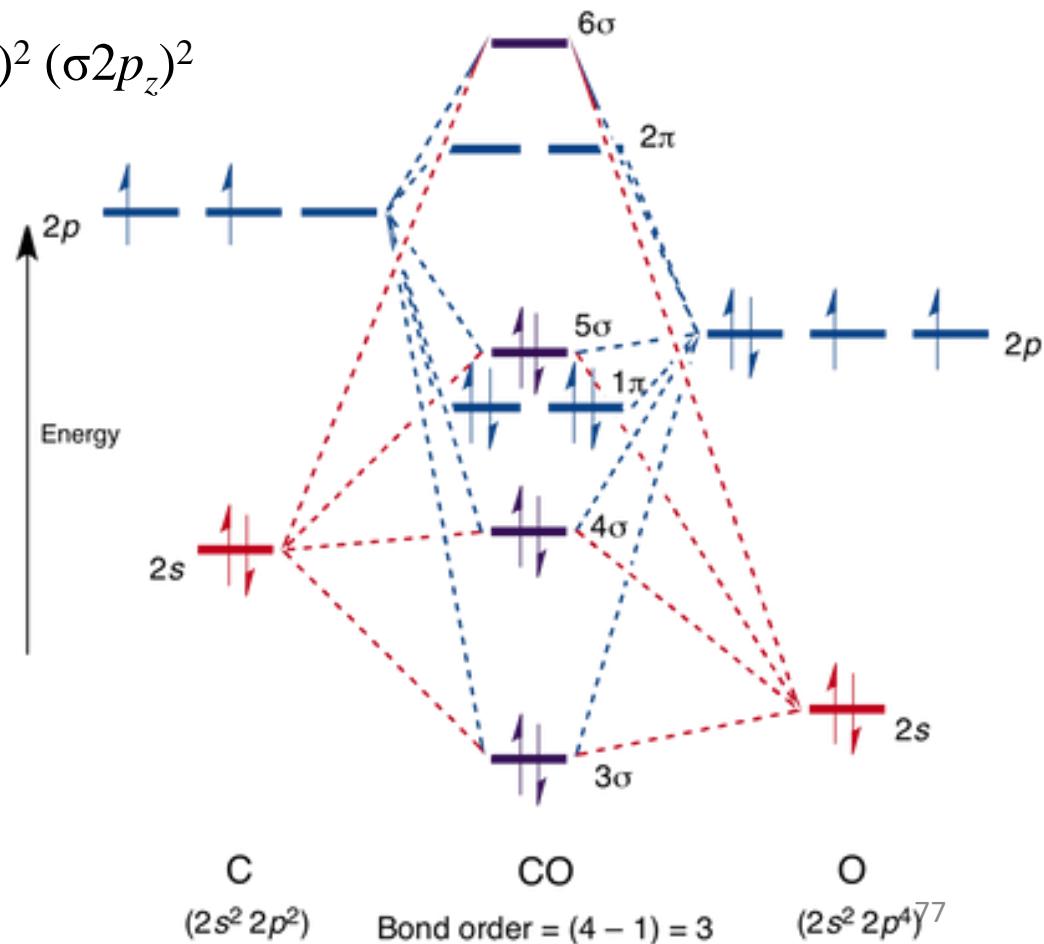
Total valence electrons = 10

So the electronic configuration is:

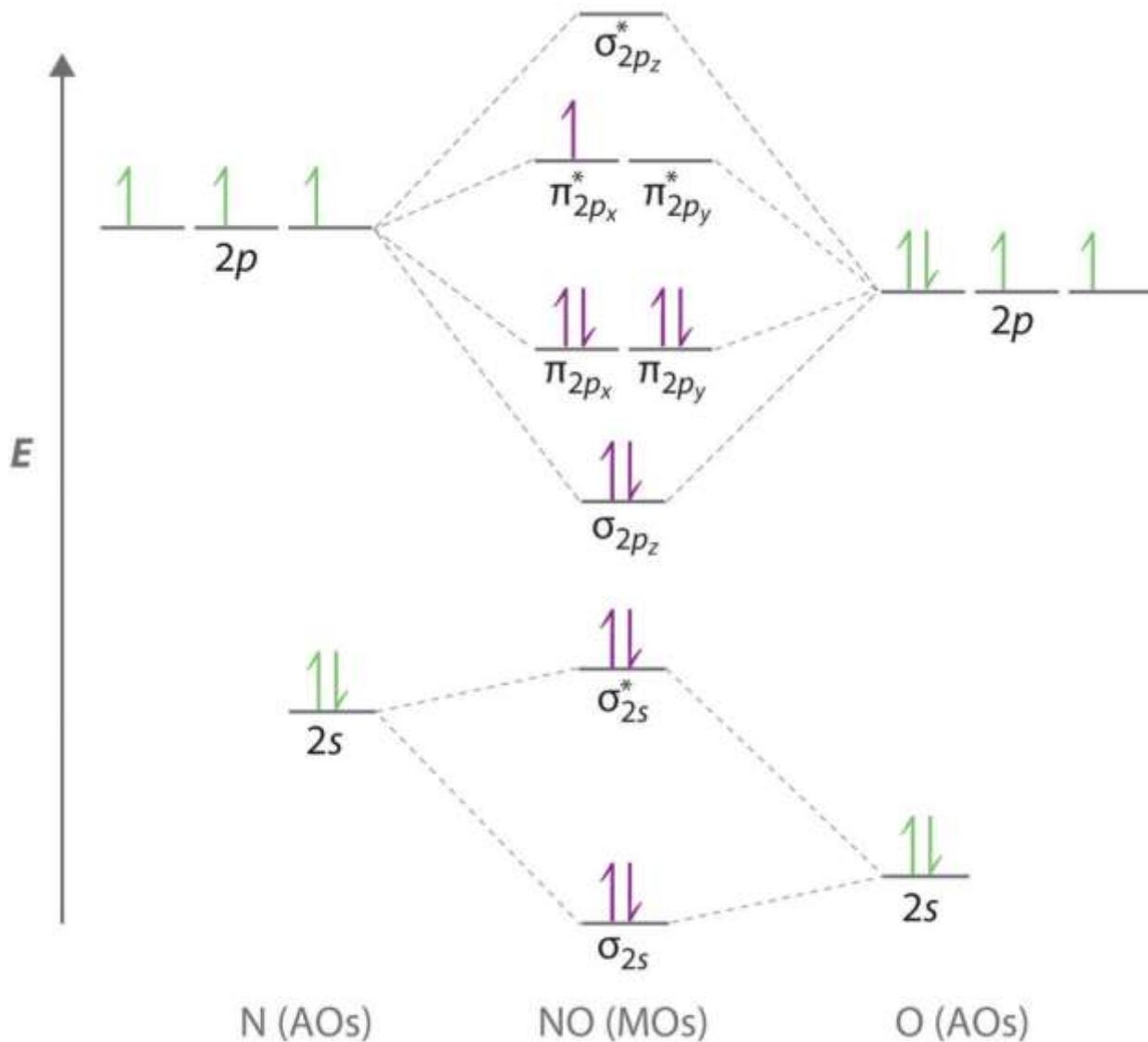
$$(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma 2p_z)^2$$

Oxygen has more electronegativity, so the atomic orbitals are lower lying compared to carbon.

$$\text{B.O} = 3$$



Q. Draw the MO diagram for NO. Find out the B.O.? Predict the magnetism in it.



What we learn from chemical bonding



- Prediction of geometry of molecule using VSEPR theory. Effect of lone pairs, electronegativity and multiple bonds.
- Application of VBT to diatomic and polyatomic compounds. Concept of hybridization.
- How to draw molecular orbital diagram of any homonuclear diatomic molecule.
- Symmetry of molecular orbital based on inversion center.
- s-p mixing observed in Li₂, Be₂, B₂, C₂, and N₂ molecules and heteronuclear compounds having VE ≤ 10)
- Molecular orbital diagram of heteronuclear diatomic molecules.

Tutorial

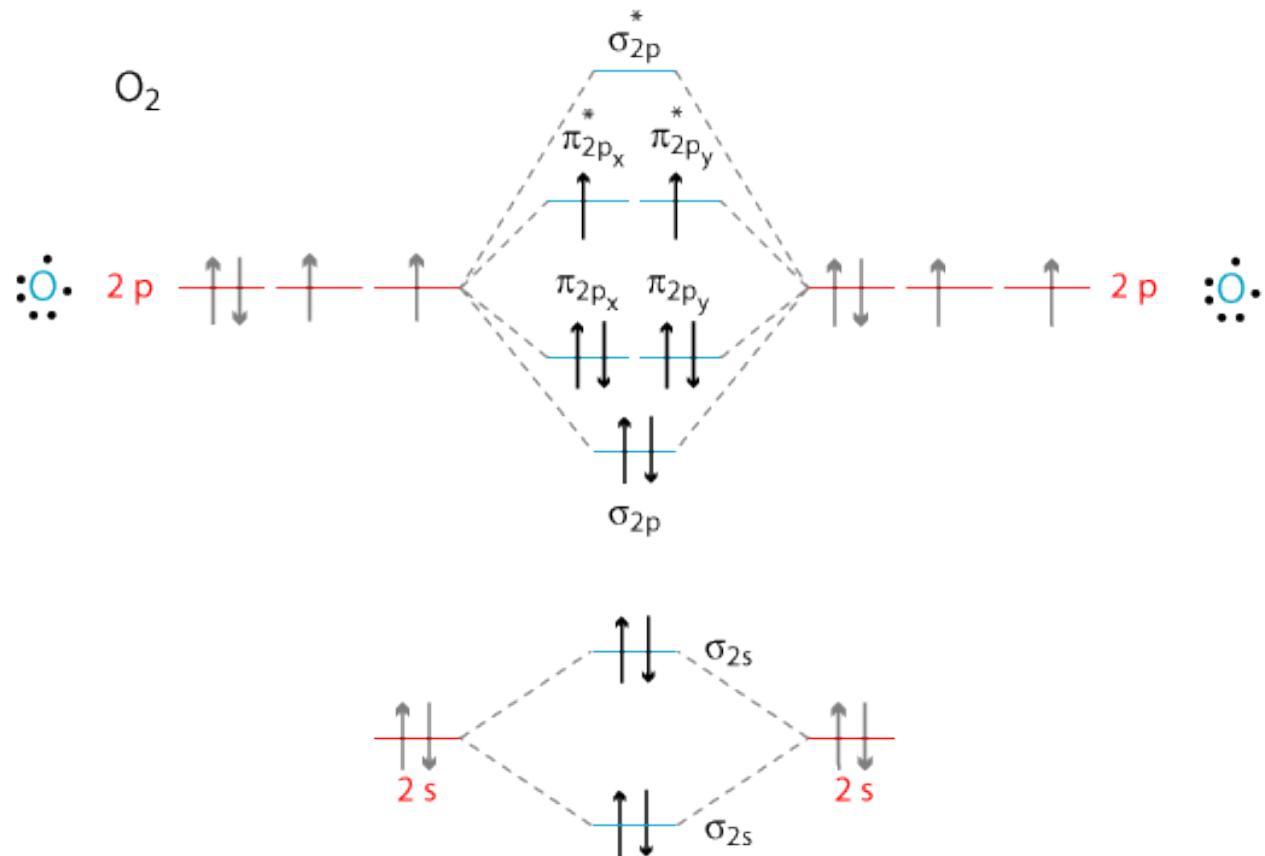
Chemical Bonding

1. Using VSEPR theory, predict the geometries of the following compounds (derive each step and draw the final structure):

- a) SCl_2 , b) Cl_2O , c) I_3^+ d) $\text{S}\text{O}\text{Cl}_2$, e) SO_3^{2-} , f) XeO_3 ,
- g) IO_2F_2^- , h) SbF_4^-

Bent structure (a-c); Pyramidal structure (d-f); See-saw (g-h)

2. Draw the molecular orbital diagram of O_2^+ . What are the expected changes in bond order and bond distances that accompany $O_2 \rightarrow O_2^+ + e^-$ ionization processes?



B.O of $O_2 = 2$, B.O of $O_2^+ = 2.5$

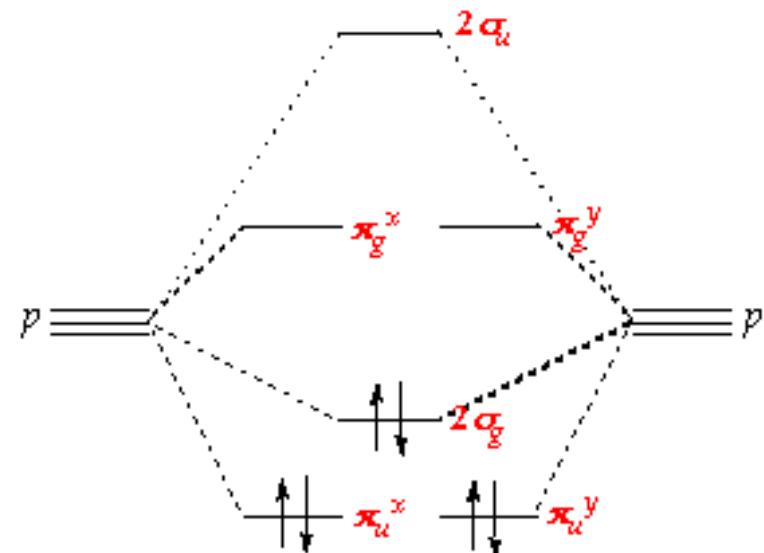
Bond distance of $O_2 >$ Bond distance of O_2^+



Basic Principles of VBT

- A covalent bond forms when the orbitals from two atoms overlap and a pair of electrons occupies the region between the nuclei.
- The greater the orbital overlap, the stronger the bond.
- The two electrons in the overlap region occupy the same space and hence must have opposite spins.
- To explain the geometry of molecule, it was proposed that the valence atomic orbitals in a molecule are different from isolated atoms.
- The valence orbitals undergo hybridization before making chemical bond.

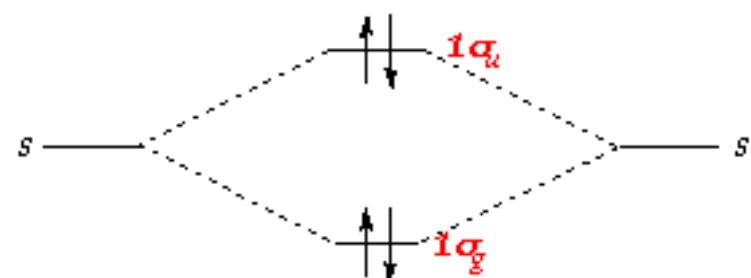
3. Draw the molecular orbital diagram of N_2^- . What are the expected changes in bond order and bond distances that accompany with $\text{N}_2 + \text{e}^- \rightarrow \text{N}_2^-$ process?



$$\text{B.O of } \text{N}_2 = 3$$

$$\text{B.O of } \text{N}_2^- = 2.5$$

Bond distance of $\text{N}_2 <$ Bond distance of N_2^-

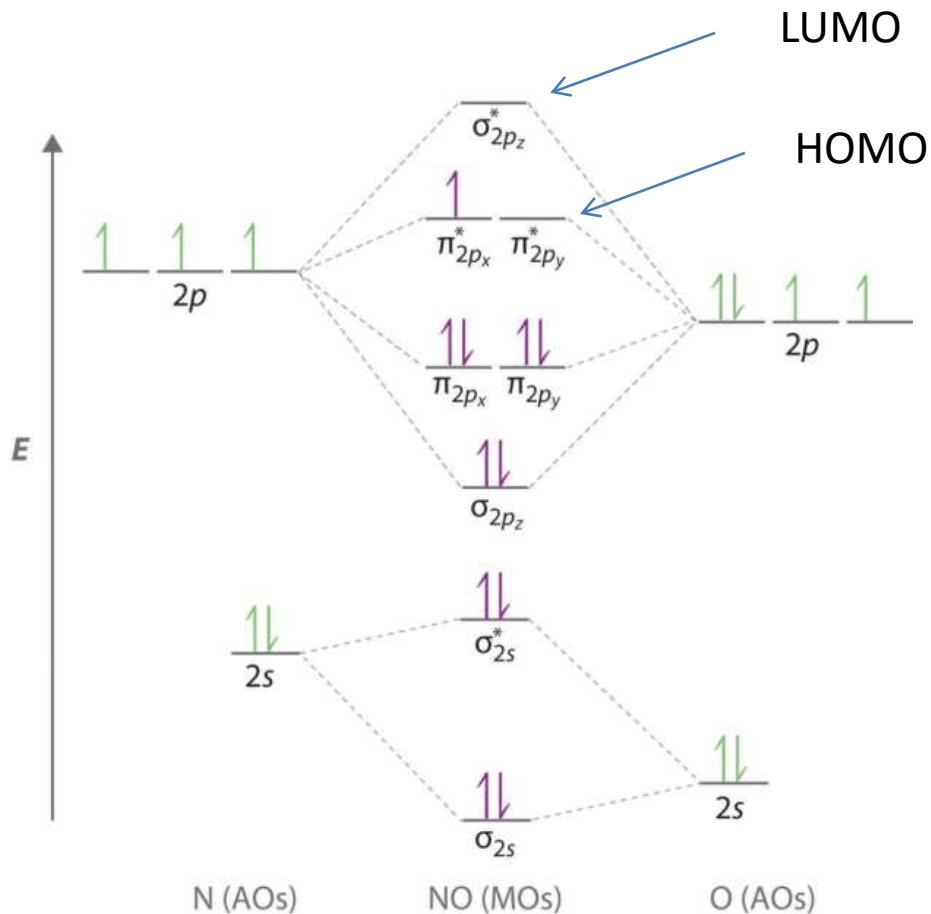


1 × Nitrogen
Atomic Orbital

Nitrogen
Molecular Orbital

1 × Nitrogen
Atomic Orbital

4. Draw the molecular orbital diagram of NO. Find out the bond order. Show the HOMO and LUMO molecular orbitals in the MO diagram of NO.



CY1101 (General Chemistry)



Dr. Vaidyanathan Sivakumar

Associate Professor

Department of chemistry

NIT Rourkela

vsiva@nitrkl.ac.in

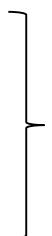
Welcome to CY1101 (general chemistry)



Scope and Objective

The course provides a comprehensive survey of the concepts involved in the study of the

- Electronic structure of atoms
- Chemical bonding
- Coordination chemistry



Inorganic Prof. V. Sivakumar

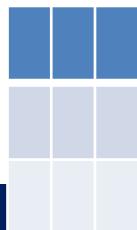
- Spectroscopy
- Thermodynamics
- Electrochemistry
- Chemical kinetics



Physical Prof (Mrs). Usharani Subuddhi

- Organic Chemistry (Stereochemistry).

Organic Prof (Mrs). Sabita Patel





Books:

1. *Inorganic Chemistry* by Gary L. Miessler and Donald A. Tarr
2. *Atkins' Physical Chemistry* by Peter Atkins and Julio de Paula
3. *Fundamentals of molecular spectroscopy*, C. N. Banwell, E. N. McCash, 1994.
4. *Organic Chemistry*, Clayden, Greeves, Warren and Wothers, Oxford, 2001.
5. *Principles of physical Chemistry*, B. R. Puri, L. R. Sharma, M. S. Pathania, 2001.

Coordination Chemistry



Coordination chemistry deals with the science concerned with the interactions of ligands with metal centers.

Coordination compounds include compounds of metal atom or ion and one or more ligands that formally donate electrons to the metal.

► Example

- * [Co(NH₃)₆]Cl₃
- * [Cu(NH₃)₄][PtCl₄]
- * [Pt(NH₃)₂Cl₂]

Metals = usually transition metals (Lewis acid)

Ligands = Molecules/ions capable of donating a pair of electron to metal (Lewis base)

Coordination Complex

Species where transition metal ion is surrounded by a certain number of *ligands* (ligare is Latin, to bind)

Metal-Ligand bond: Coordinate covalent bond

Coordination Compounds: retain their identity in solution



In solution exists as K^+ , Mg^{2+} and Cl^- :**Double Salt**



tetrammine copper (II) sulphate monohydrate

CuSO_4 Exists as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (**Pale Blue**) in water

In aq. Ammonia Exists as $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ (**Deep Blue**)

Metal-Ligand Bond is formed between a Lewis acid and a Lewis base

Transition metal ion: *empty orbitals*: **Lewis acid**

Ligands: *electrons rich*: **Lewis bases**

Coordination Compounds



- **Ligands**
 - classified according to the number of donor atoms

- Examples
 - monodentate = 1
 - polydentate
 - bidentate = 2
 - Tridentate = 3
 - tetradentate = 4
 - Pentadentate = 5
 - hexadentate = 6

chelating agents
(dent → teeth)

Ligands (ligare is Latin, to bind)

Classified according to the number of donor atoms

Monodentate: one bond to metal ion

Bidentate: two bonds to metal ion

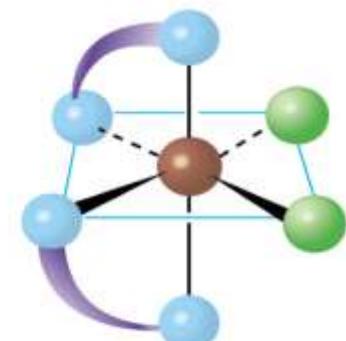
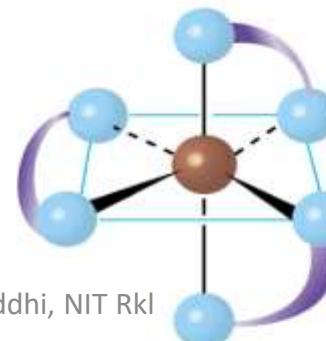
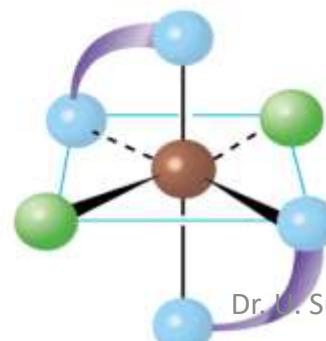
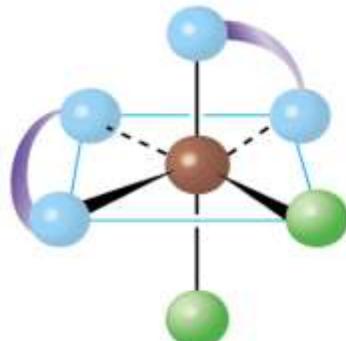
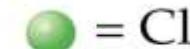
Polydentate: more than two bonds to a metal ion possible

Latin: “dent” → tooth

Chelate (crab like): Greek *chelos*: “crab”

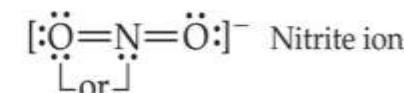
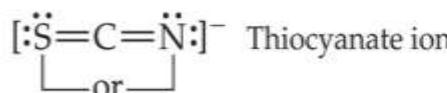
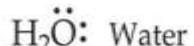
When more than one atom of the ligand is bonded to the central metal atom, ring structures are formed.

Such ring structures are called chelates.

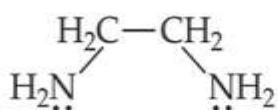


Ligand Type Examples

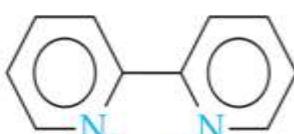
Monodentate



Bidentate



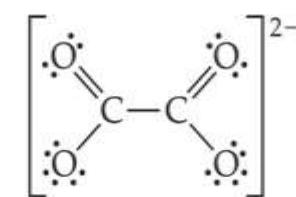
Ethylenediamine (en)



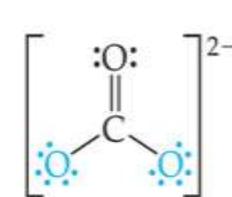
Bipyridine (bipy)



Ortho-phenanthroline (o-phen)

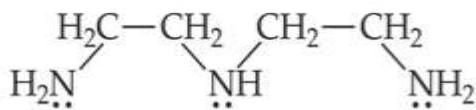


Oxalate ion

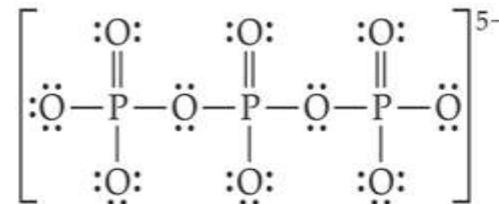


Carbonate ion

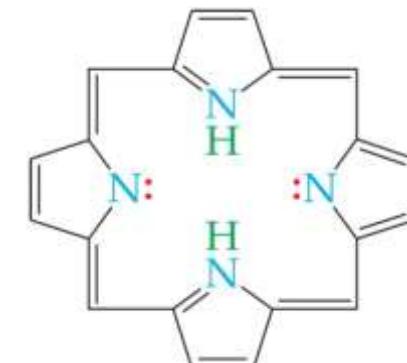
Polydentate



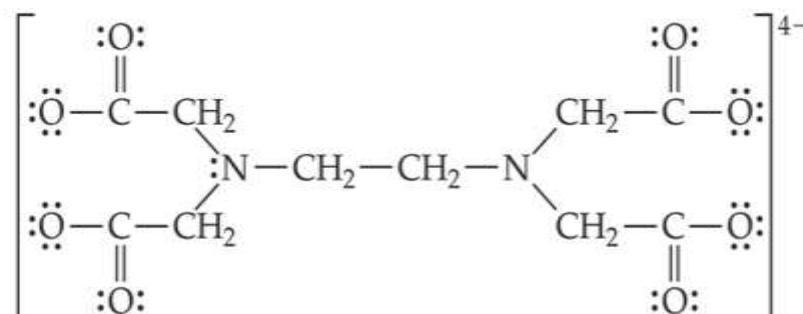
Diethylenetriamine



Triphosphate ion



Porphyrin



Dr. U. Subuddhi, NIT Rkl
 Ethylenediaminetetraacetate ion (EDTA^{4-})



Werner's coordination theory (Nobel prize in 1913)

Werner's experiment



AgNO₃ is used to determine quantitatively the amount of chloride.

Q. Why does a stable salt react with varying number of NH₃ to give several new compounds?

Q. What are their structures?

Correct formula:

1. $[\text{Co}(\text{NH}_3)_6]^{3+}(\text{Cl}^-)_3$
2. $[\text{Co}(\text{NH}_3)_6]^{3+}(\text{Cl}^-)_3$
3. $[\text{Co}(\text{NH}_3)_6]^{3+}(\text{Cl}^-)_3$
4. $[\text{Co}(\text{NH}_3)_6]^{3+}(\text{Cl}^-)_3$



Werner's coordination theory

Werner explained the nature of chemical bonding in these complexes assuming two kinds of valence /bonding (primary valence and secondary valence) of metal atom or ion.

Primary Valence

The number of charges on the complex ion.

These are non directional.

Ex: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ Primary valence of Co is +2.

Secondary Valence

The number of ligand atoms coordinated to the metal.

This is also known as coordination number.

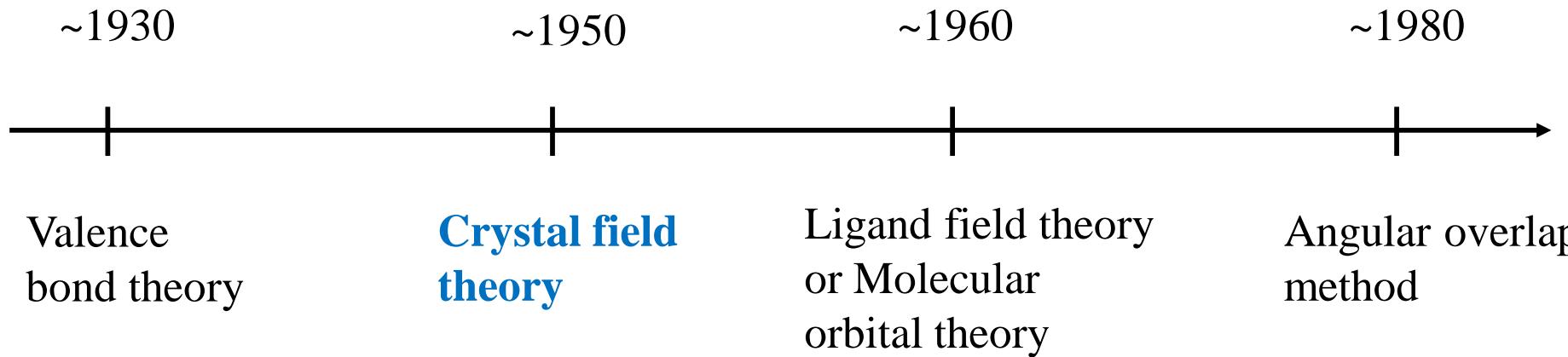
These bonds are directional.

Ex: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ Coordination number of Co is 6.

Bonding in coordination compounds



To explain nature of bonding in coordination compounds, several theories developed.



- Werner's coordination theory- Alfred Werner-1893 (Noble prize in 1913)
(before the discovery of electron in 1896 by Sir J.J. Thomson)
- Valence Bond Theory-Linus Pauling
- Crystal Field Theory (CFT)-Bethe and van Vleck
- Modified CFT, known as Ligand Field Theory
- Molecular Orbital Theory

Crystal Field Theory



It was proposed by Hans Bethe in 1929 and further developed by Van Vleck.

CFT-Assumptions

J. H. van Vleck



- The interaction between the metal ion and the ligands are purely electrostatic (ionic).
- The ligands are regarded as point charges or dipoles
- CFT does not allow ligand electrons to enter metal orbital. Thus the metal and ligand do not share their electrons.
- Electrons on the metal are under repulsive from those on ligands.

Subsequent modifications were proposed by J. H. van Vleck in 1935 to allow for some covalency in the interactions.

Hans Bethe

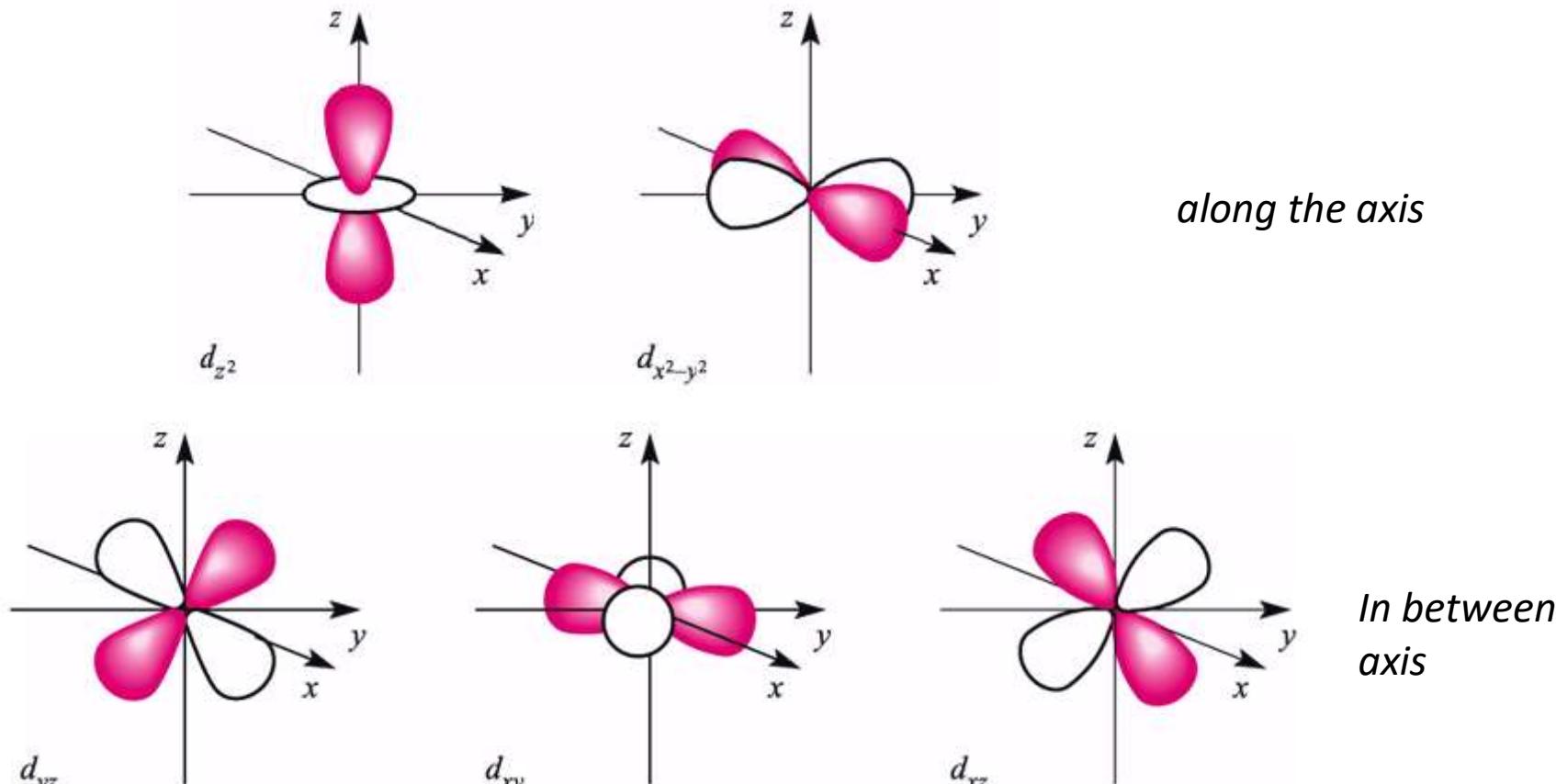


These modifications are often referred to as Ligand Field Theory

Crystal Field Theory



In order to understand the interaction of crystal or ligand field with valence orbitals (d-orbitals) of transition metal in complexes, it is necessary to understand the geometrical relationship of d-orbitals in different geometry of ligands.



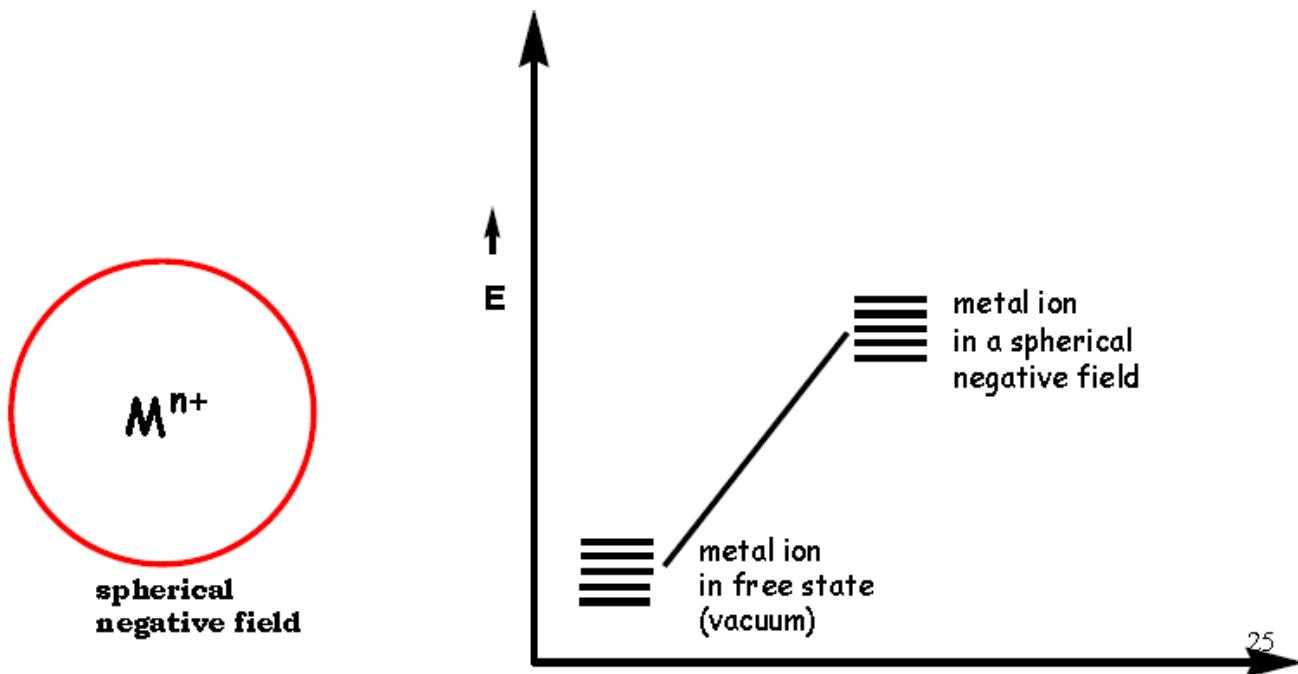
Pink color = positive sign; white = negative sign



Spherical symmetric field

Five d-orbitals of an isolated gaseous transition metal ion are degenerate.

If a spherical symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them raised in energy as a result of repulsion between the negative charge on the ligand and electron(s) in d-orbital.



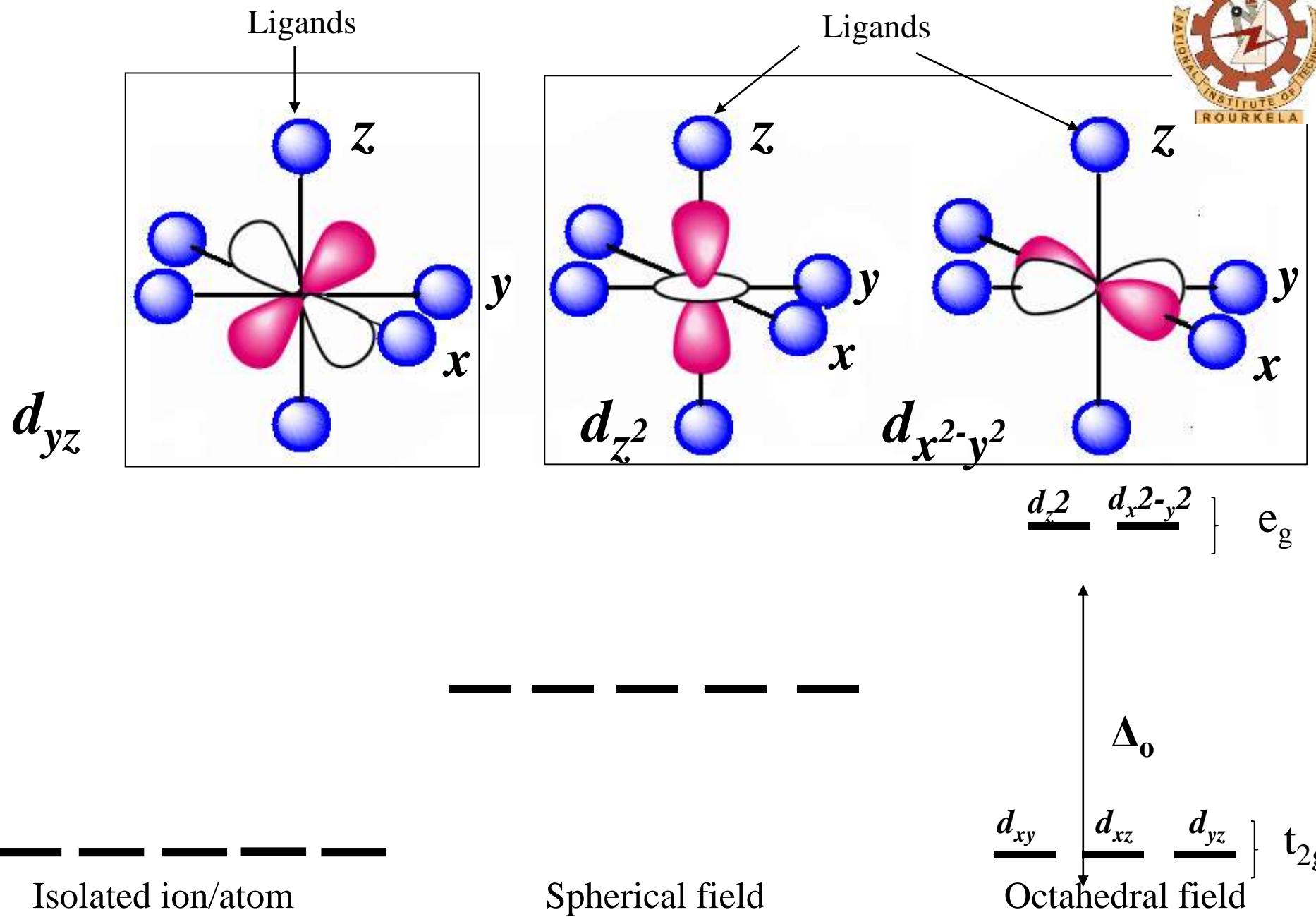
Crystal field effect in octahedral symmetry



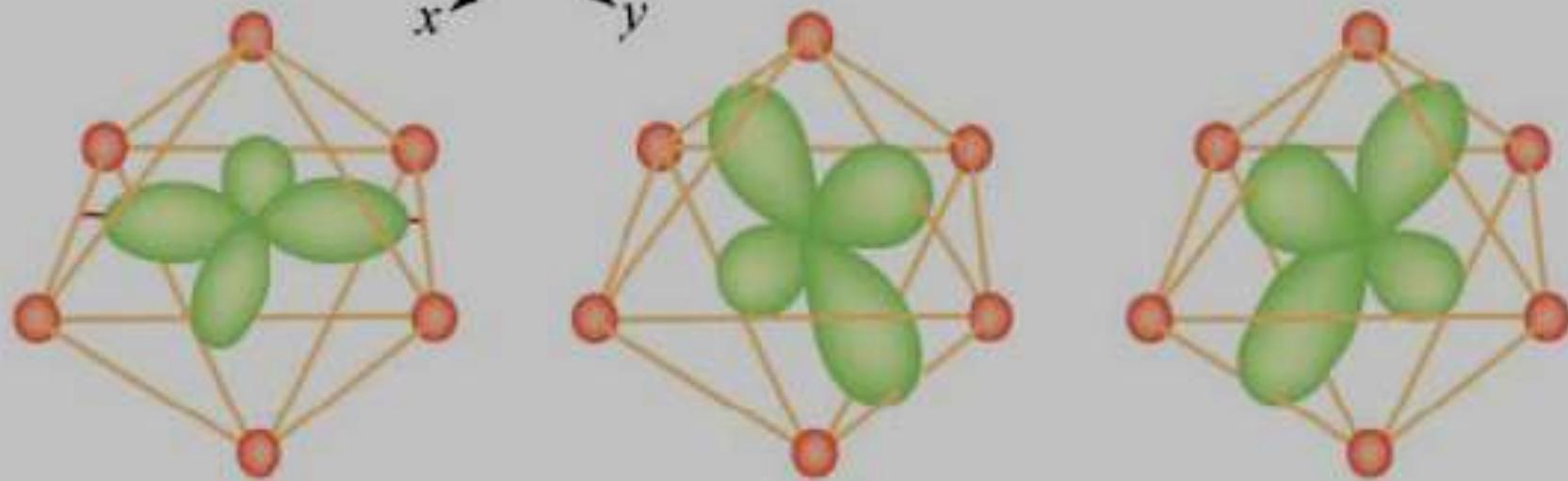
Q. How the six d-electrons are filled in the d-orbitals of Co^{3+} ion in presence of six NH_3 ligands in $[\text{Co}(\text{NH}_3)_6]^{3+}$?

Energy level diagram of d-orbitals in presence of ligands in octahedral geometry

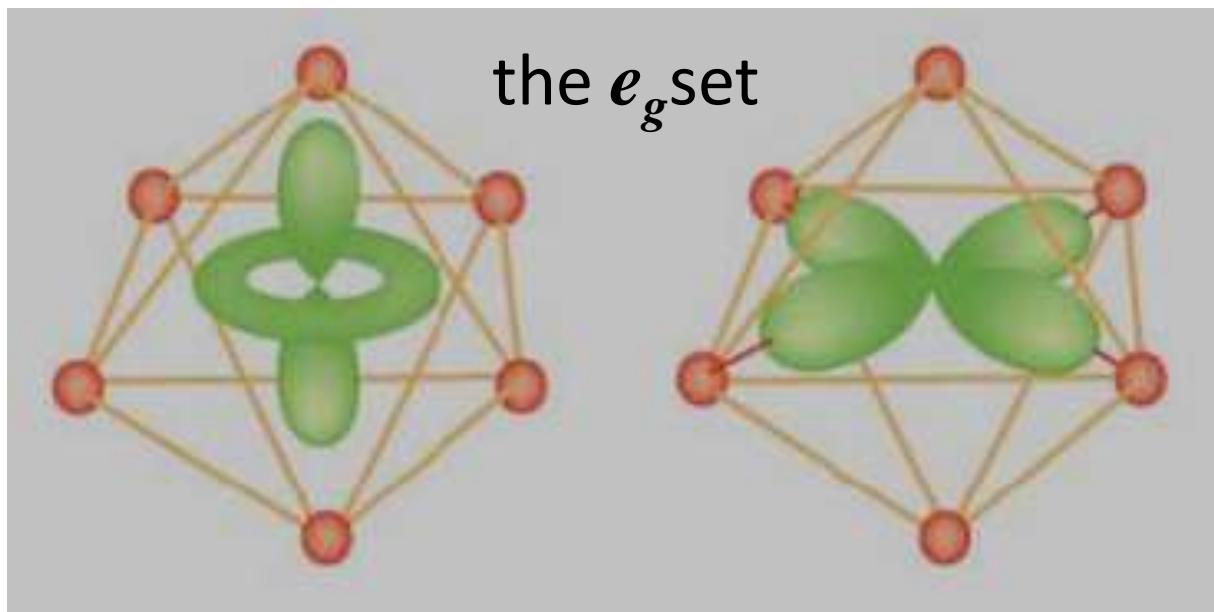
- If we have an electron in each d-orbital, then how much repulsion each d-orbital feels, by ligands in octahedral geometry (octahedral field), decide its relative energy.
- If the d-orbital feels more repulsion, then its energy will be higher.
- Since dx^2-y^2 and dz^2 orbitals directed along axial directions and the ligands come along the axial directions, so these orbitals feel more repulsion and hence have higher energy.
- d_{xy} , d_{xz} , d_{yz} orbitals directed in between axes and the ligands come along the axial directions, so these orbitals feel less repulsion and hence have lower energy.



the t_{2g} set

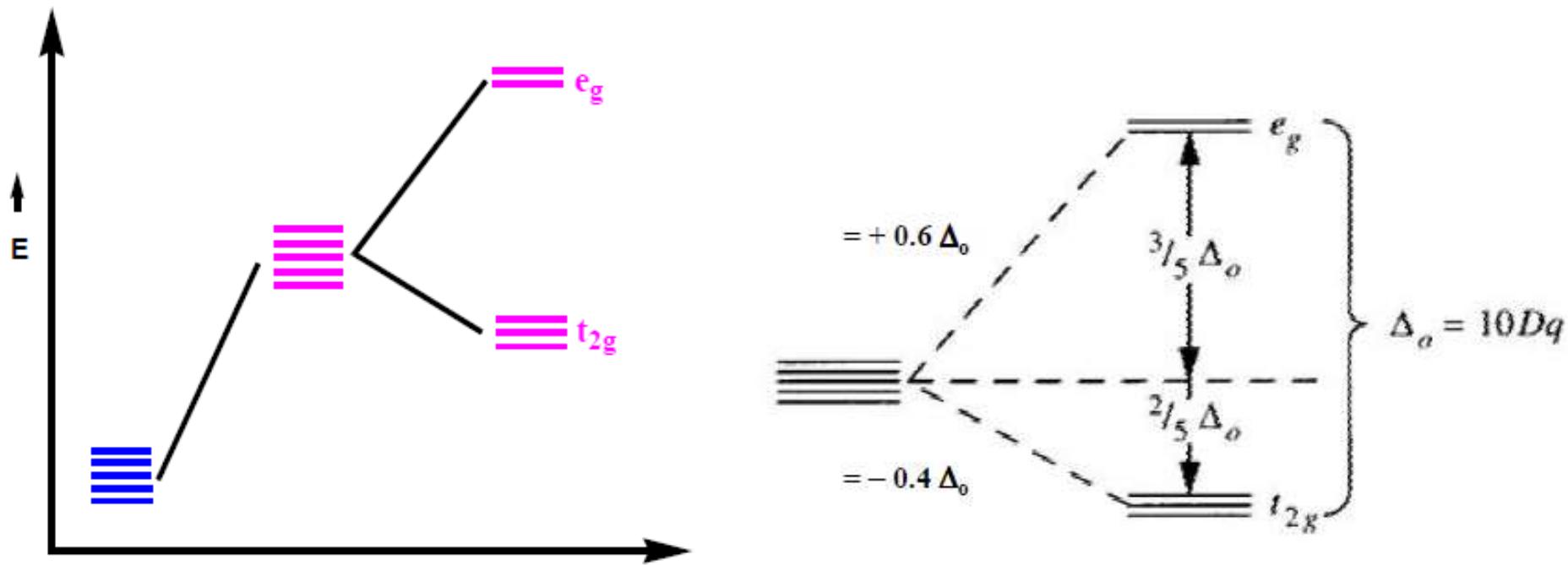


the e_g set



The extent to which these two sets of orbitals are split is denoted by Δ_o or $10Dq$.

As the **Bari center** must be conserved on going from a spherical field to an octahedral field, the t_{2g} set must be stabilized as much as the e_g set is destabilized.

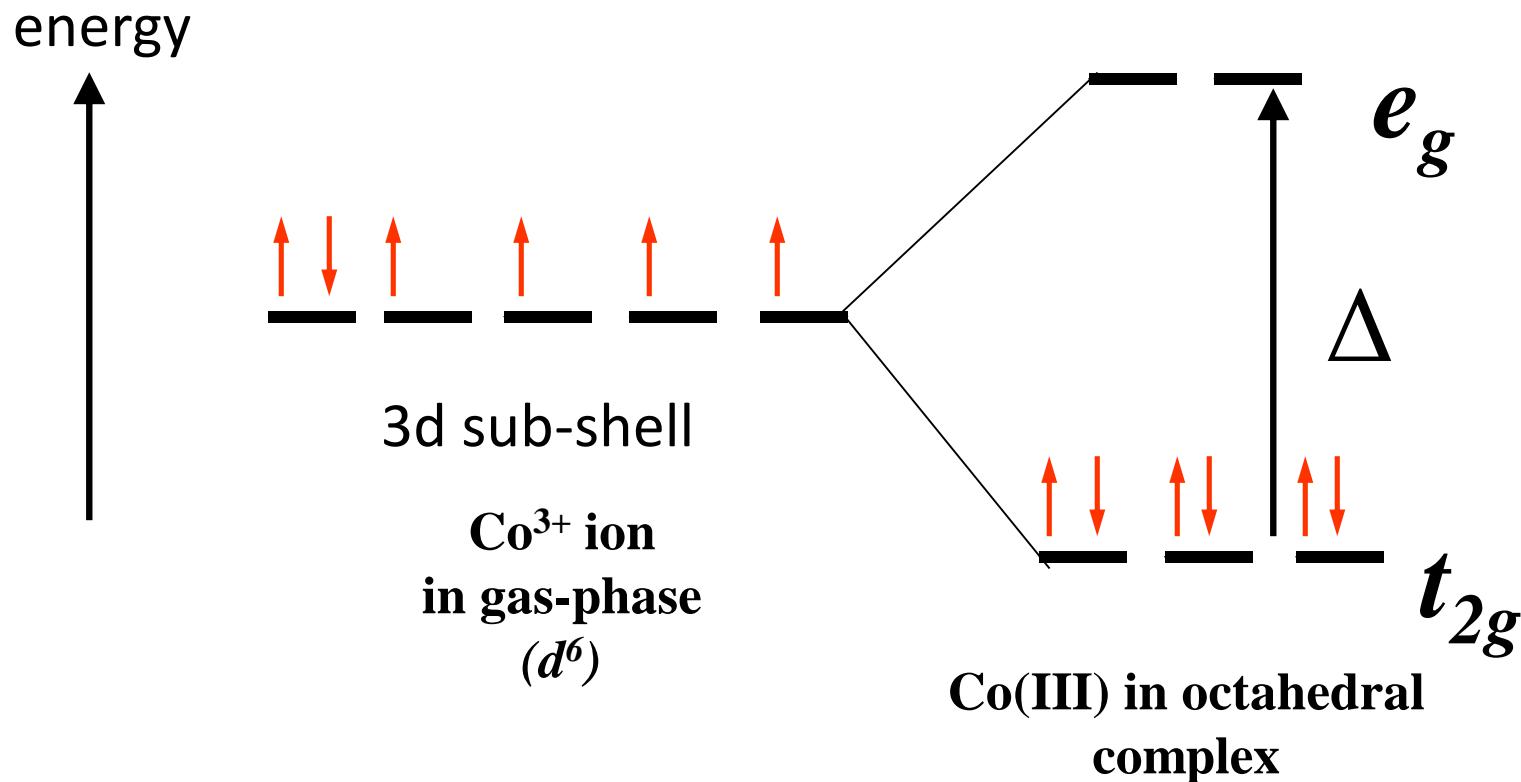


Crystal field effect in octahedral symmetry



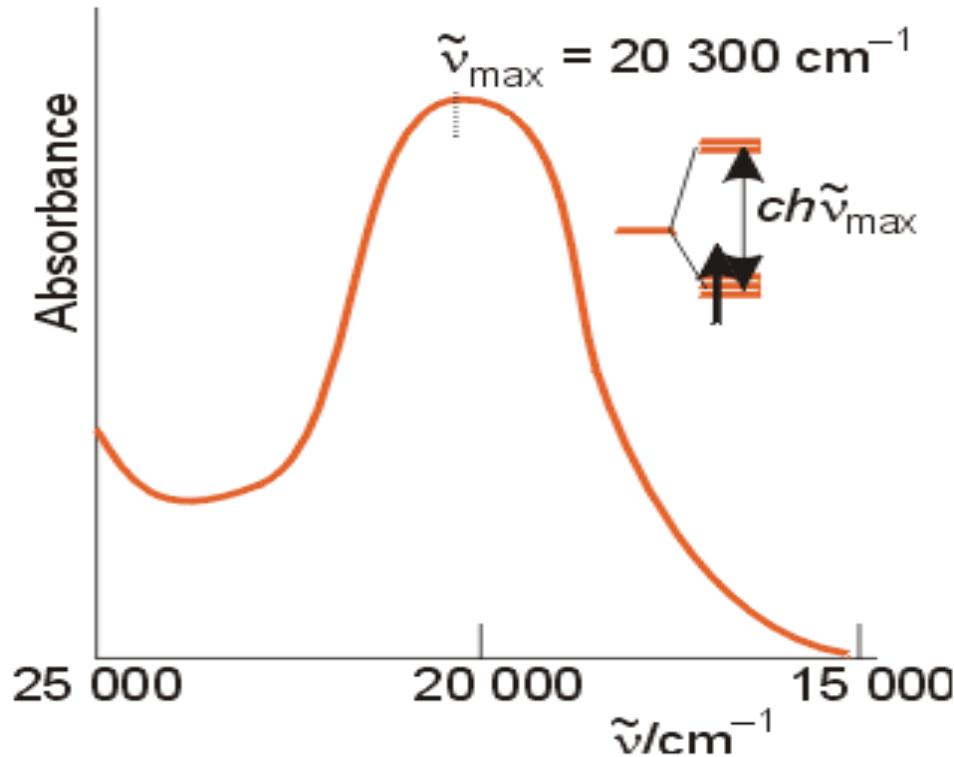
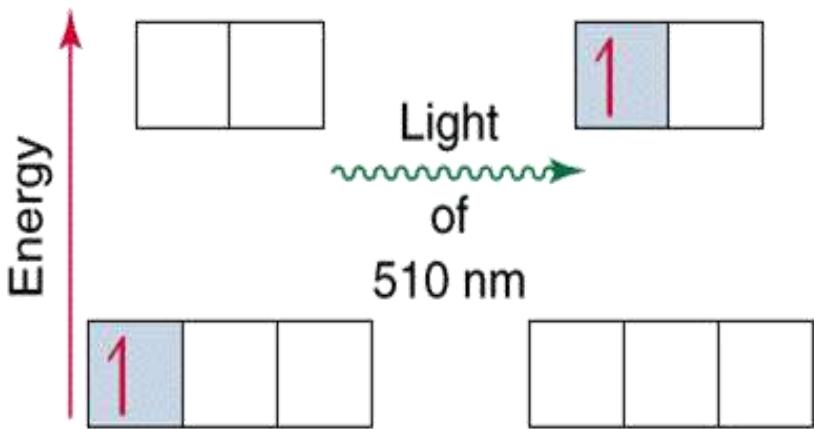
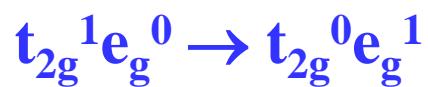
In presence of ligands in octahedral geometry, the d-orbitals split into two sets, e_g and t_{2g} . The energy difference between e_g and t_{2g} set of orbitals is the crystal field splitting energy (Δ_o).

d-electrons filling in $[\text{Co}(\text{NH}_3)_6]^{3+}$



The size of the energy gap Δ_o between t_{2g} and e_g levels can be measured easily by recording UV-Vis spectrum of the complex.

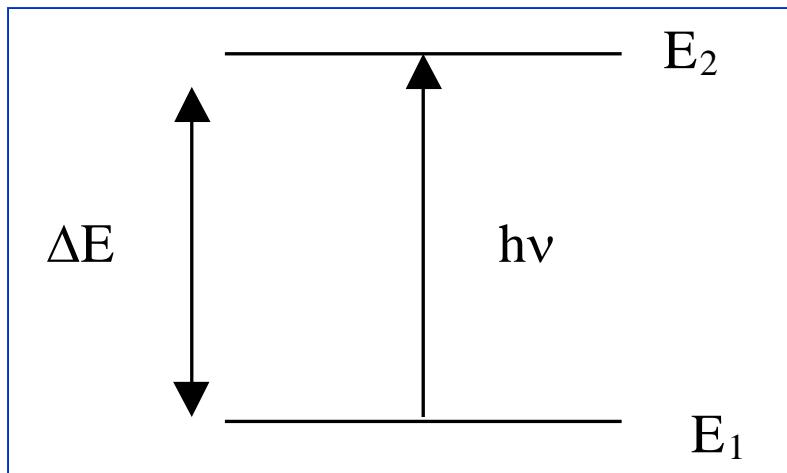
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$: a d¹ complex and the e⁻ occupies the lowest energy orbital, i.e. one of the three degenerate t_{2g} orbitals. On absorption of light, it excites to the higher energy excited state.



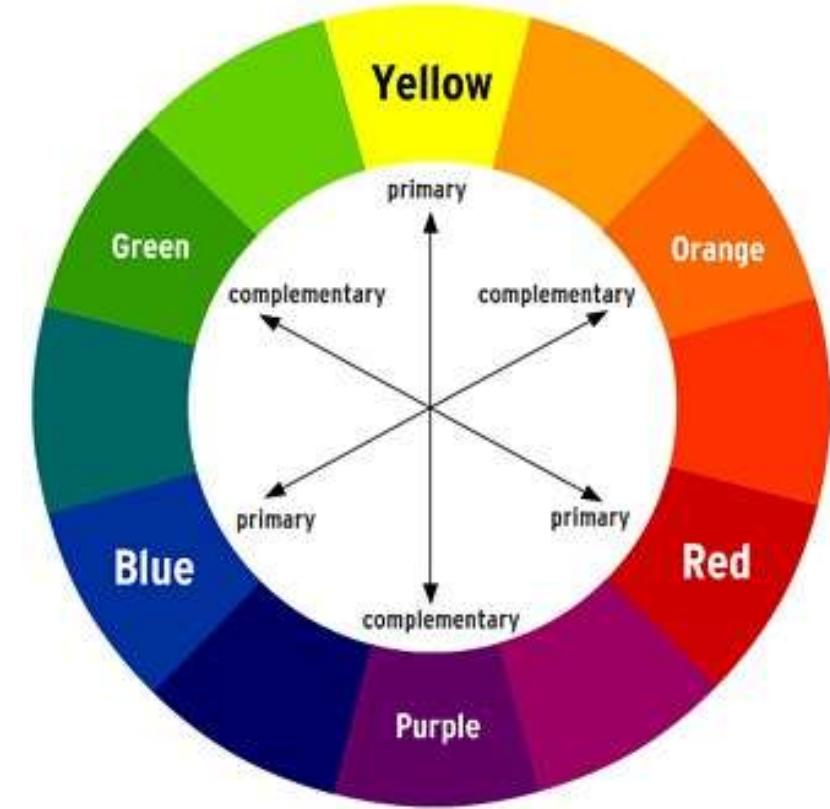
The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at $20300\ \text{cm}^{-1}$ which corresponds to $\Delta_o = 243\ \text{kJ/mol}$.

$$(1000\ \text{cm}^{-1} = 11.96\ \text{kJ/mol} \text{ or } 2.86\ \text{kcal/mol} \text{ or } 0.124\ \text{eV})$$

The origin of the color of the transition metal compounds



$$\Delta E = E_2 - E_1 = h\nu$$



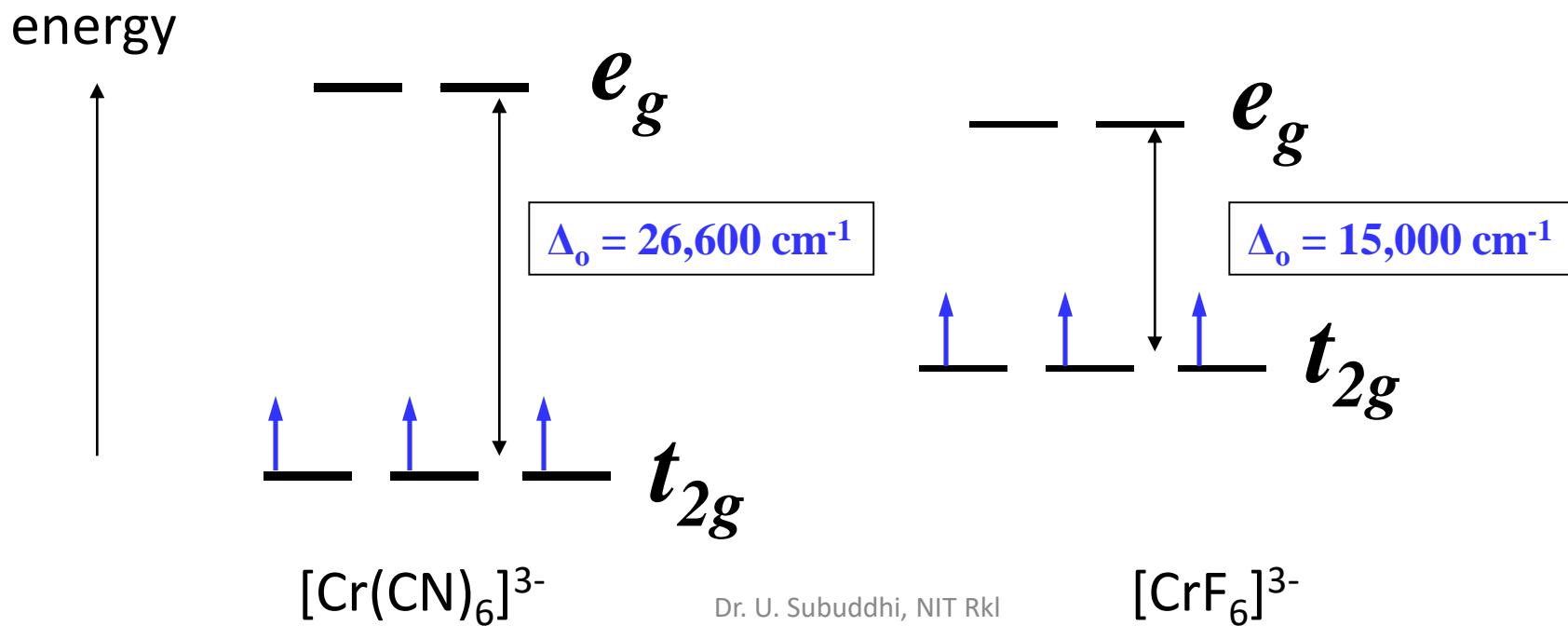
Ligands influence Δ_o , therefore the colour

The purple colour of the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ d^1 complex is a result of the absorption of its complementary yellow-green light.

The crystal field splitting parameter (Δ_o)

Different ligands produce different extents of splitting between the e_g and the t_{2g} levels.

This energy difference is the crystal field splitting parameter Δ_o , also known as $10Dq$, and has units of cm^{-1} .



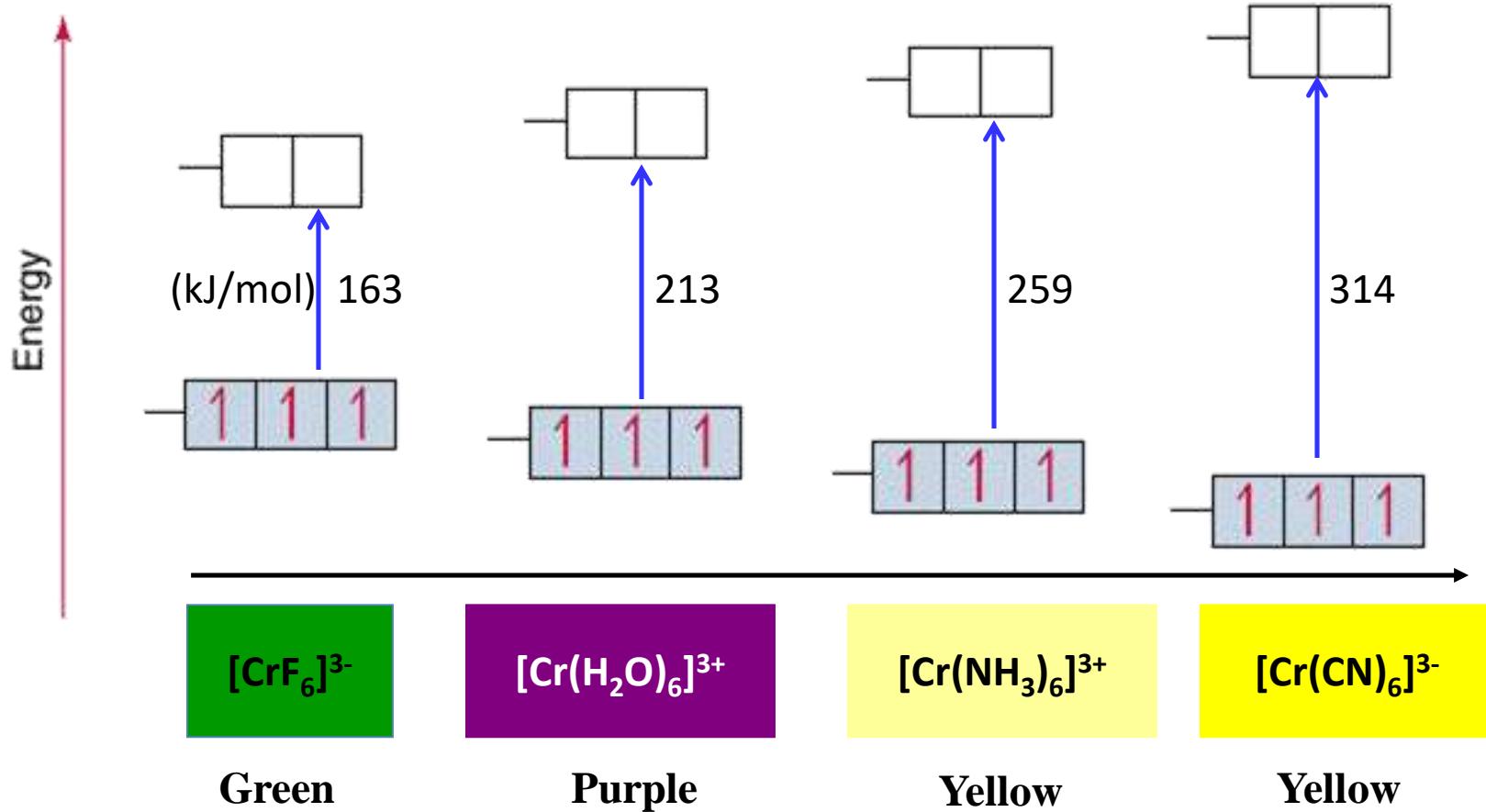
Spectrochemical series (experimentally determined)

$I^- < Br^- < S_2^- < SCN^- < Cl^- < N_3^-$, $F^- <$ urea, $OH^- <$ ox, $O_2^- < H_2O < NCS^- < py$, $NH_3 < en < bpy$, phen $< NO_2^- < CH_3^-$, $C_6H_5^- < CN^- < CO$

There is no visible pattern; No charge or size correlation

Actually both the sigma and pi bonding nature along with electrostatic attractions determine the crystal field splitting Δ

Color of the Complex depends on magnitude of Δ



Spectrochemical series: Increasing Δ

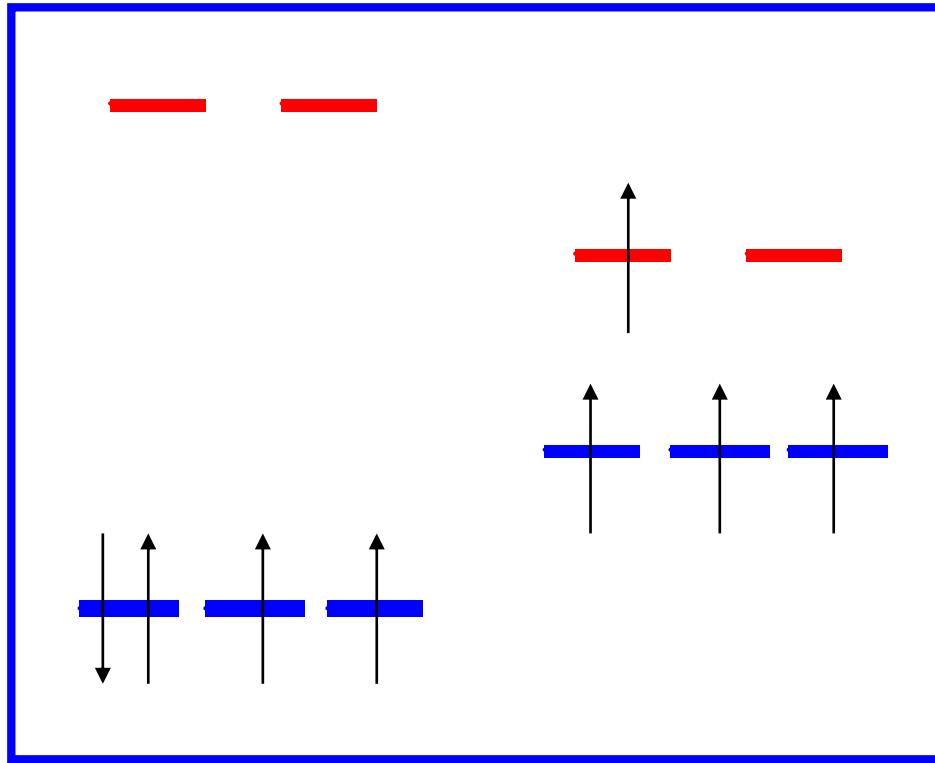
Electron Configuration in Octahedral Field

What happens for more than 1 electron in d orbitals?

- The electron-electron interactions must be taken into account.
- For d^1-d^3 systems: electrons will not pair and occupy the t_{2g} set (Hund's rule)
- For d^4-d^7 systems:
 - electrons in the t_{2g} set and therefore pair the electrons (low spin case or strong field situation).
 - electrons in the e_g set, which lies higher in energy, but the electrons do not pair (high spin case or weak field situation).
- Therefore, there are two important parameters to consider: The Pairing energy (P), and the $e_g - t_{2g}$ Splitting (referred to as Δ_o , $10Dq$, CFSE)
- For both the high spin (HS) and low spin (LS) situations, it is possible to compute the CFSE.

When the 4th electron is assigned it will either go into the higher energy e_g orbital at an energy cost of Δ_o or be paired at an energy cost of P, the pairing energy

Strong field
=
Low spin
(2
unpaired)

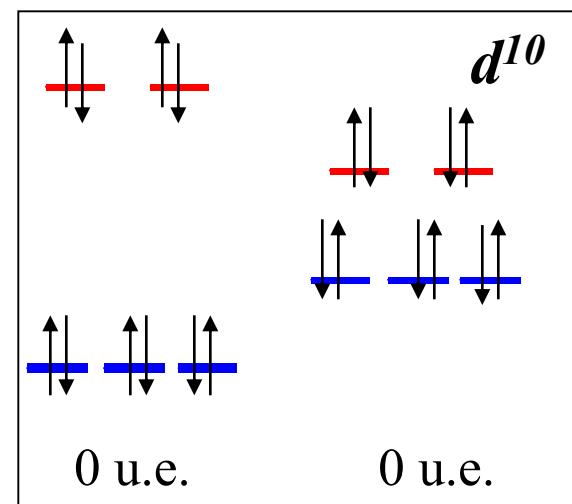
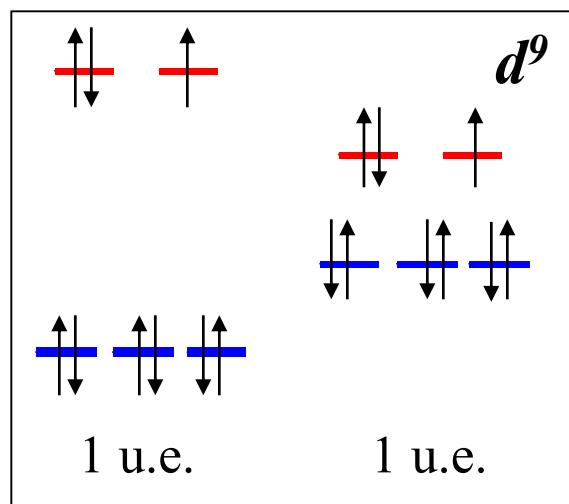
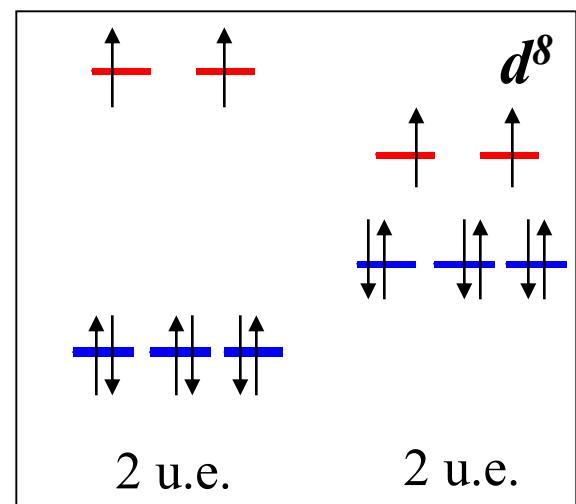
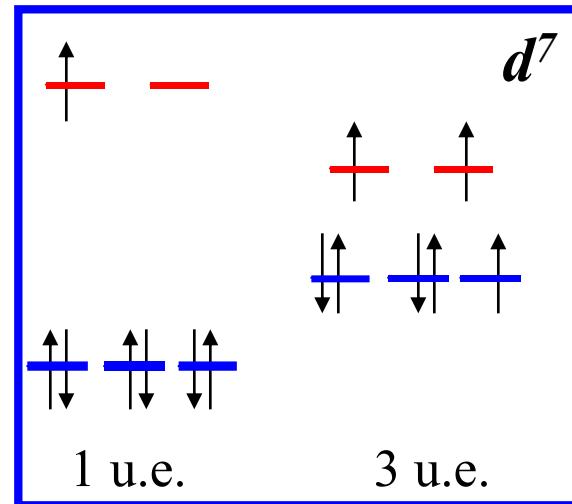
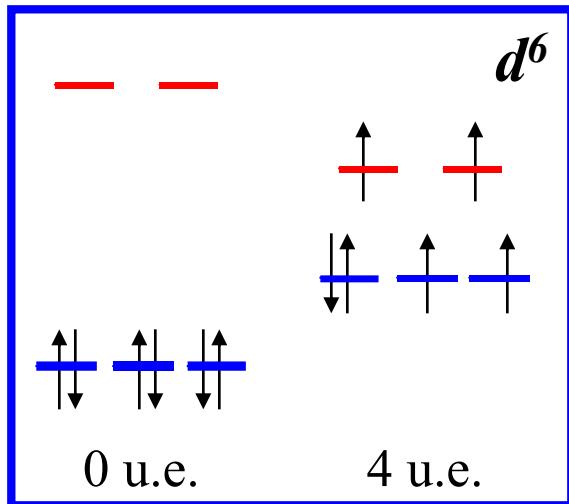
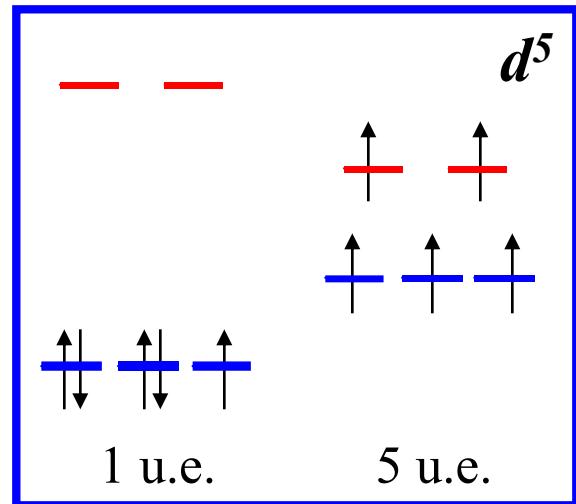


$[\text{Mn}(\text{CN})_6]^{3-}$
Strong field Complex
total spin is $2 \times \frac{1}{2} = 1$
Low Spin Complex

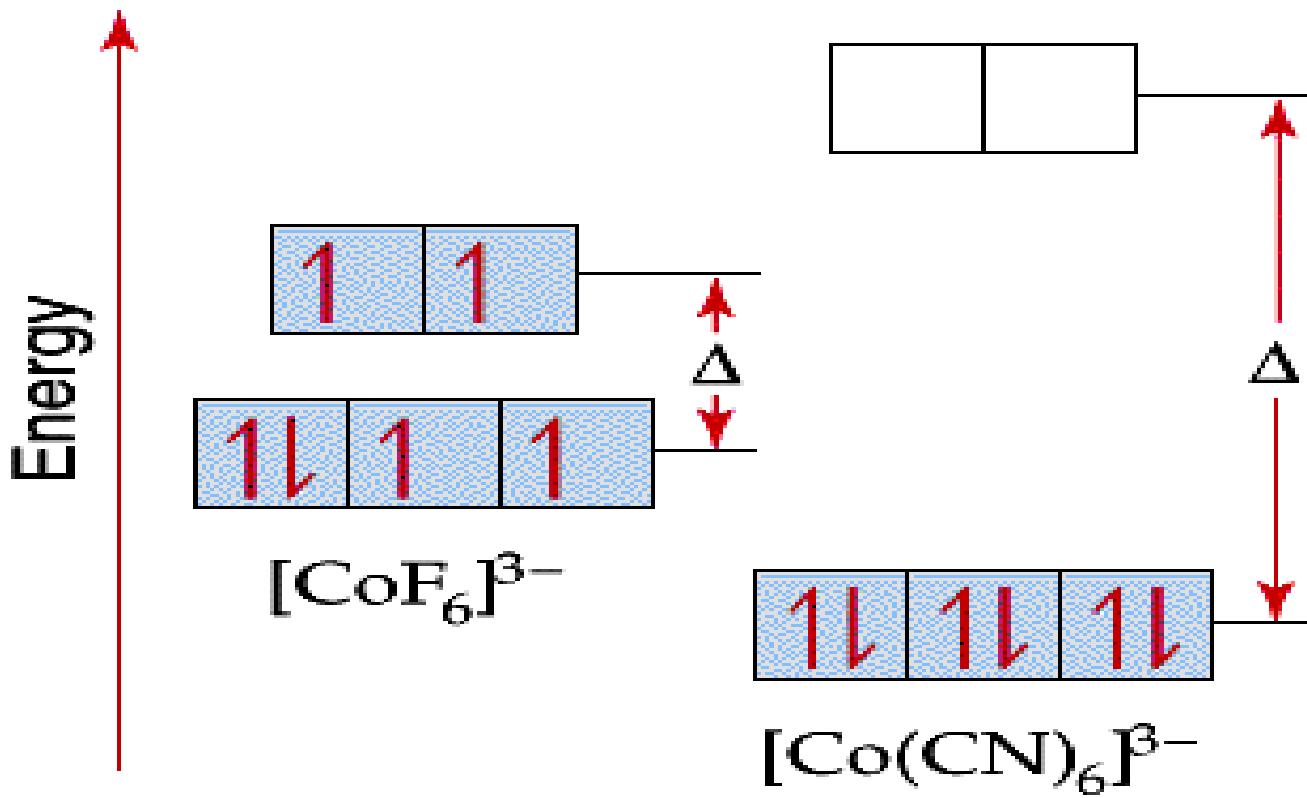
$$P > \Delta_o$$

$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$
Weak Field Complex
total spin is $4 \times \frac{1}{2} = 2$
High Spin Complex

Placing electrons in d orbitals



Only the d^4 through d^7 cases have both high-spin and low-spin configurations.



Weak field ligands
Small Δ , High spin complex

$$[\text{CoF}_6]^{3-} \Delta = 13,100 \text{ cm}^{-1}$$

$$P = 21,000 \text{ cm}^{-1}$$

Strong field Ligands
Large Δ , Low spin complex

$$[\text{Co}(\text{CN})_6]^{3-} \Delta = 34,800 \text{ cm}^{-1}$$

$$P = 21,000 \text{ cm}^{-1}$$

Magnetic properties of metal complexes

- Magnetism is caused by moving charged particles.
- Spinning electrons generate the bulk of the magnetism in an atom.
- Electrons with opposite spins pair together, resulting in no net magnetic field.
- Only unpaired electrons lead to magnetic moment.
- The spin-only magnetic moment (μ_s)

$$\mu_s = \sqrt{n(n+2)} \mu_B$$

$$\mu_B = \text{Bohr magneton} = eh/4\pi m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$$

The spin-only formula (μ_s) applies reasonably well to metal ions from the first row of transition metals

Magnetic properties: Spin only and effective

Metal ion	d ⁿ configuration	μ_s (calculated)	μ_{eff} (observed)
Ca ²⁺ , Sc ³⁺	d ⁰	0	0
Ti ³⁺	d ¹	1.73	1.7-1.8
V ³⁺	d ²	2.83	2.8-3.1
V ²⁺ , Cr ³⁺	d ³	3.87	3.7-3.9
Cr ²⁺ , Mn ³⁺	d ⁴	4.90	4.8-4.9
Mn ²⁺ , Fe ³⁺	d ⁵	5.92	5.7-6.0
Fe ²⁺ , Co ³⁺	d ⁶	4.90	5.0-5.6
Co ²⁺	d ⁷	3.87	4.3-5.2
Ni ²⁺	d ⁸	2.83	2.9-3.9
Cu ²⁺	d ⁹	1.73	1.9-2.1
Zn ²⁺ , Ga ³⁺	d ¹⁰	0	0

Crystal field effect in square planar symmetry

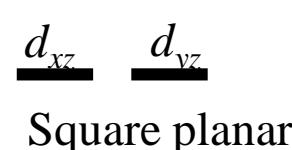
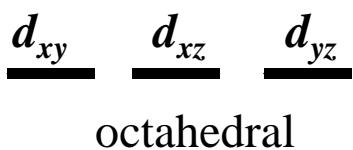
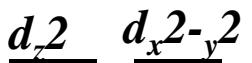


If one removes the ligands along z-direction, it gives square planar geometry.

In square planar field, the ligands approach the metal ion along x and y-directions.

So the $d_{x^2-y^2}$ orbital feels more repulsion energy and hence highest energy.

Orbitals having z-component will experience less repulsions from the ligands and hence be stabilized.

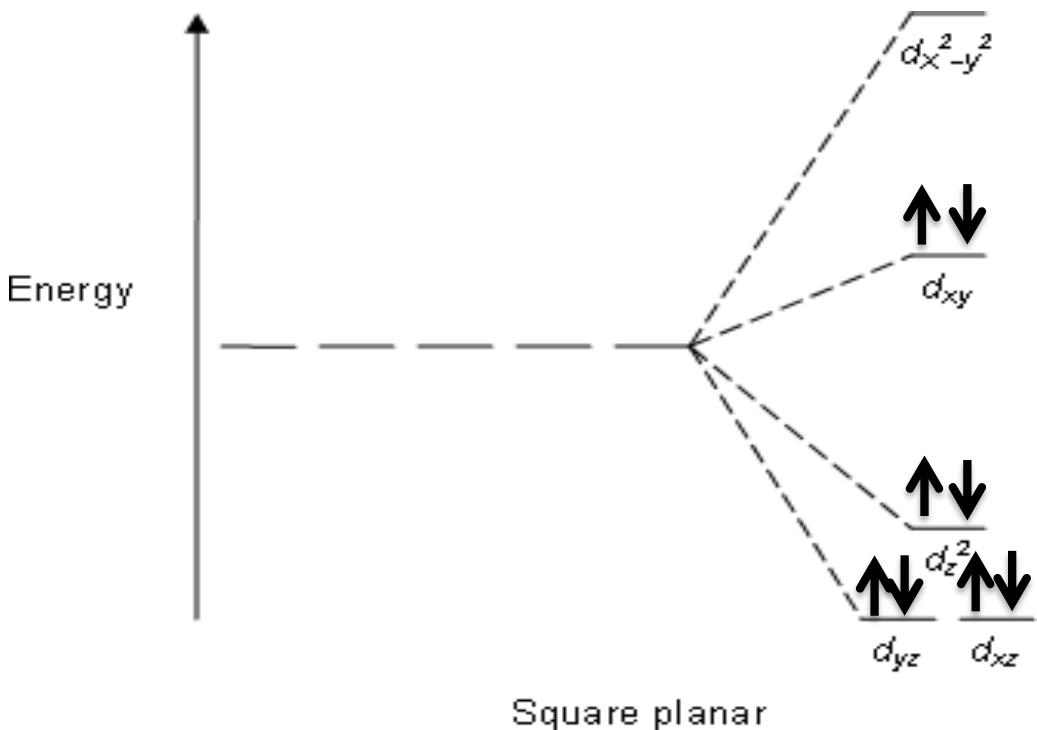


Crystal field effect in square planar symmetry



Square planar geometry is favored by metal having d⁸ electronic configuration in the presence of a strong field ligand.

Example: [Ni(CN)₄]²⁻

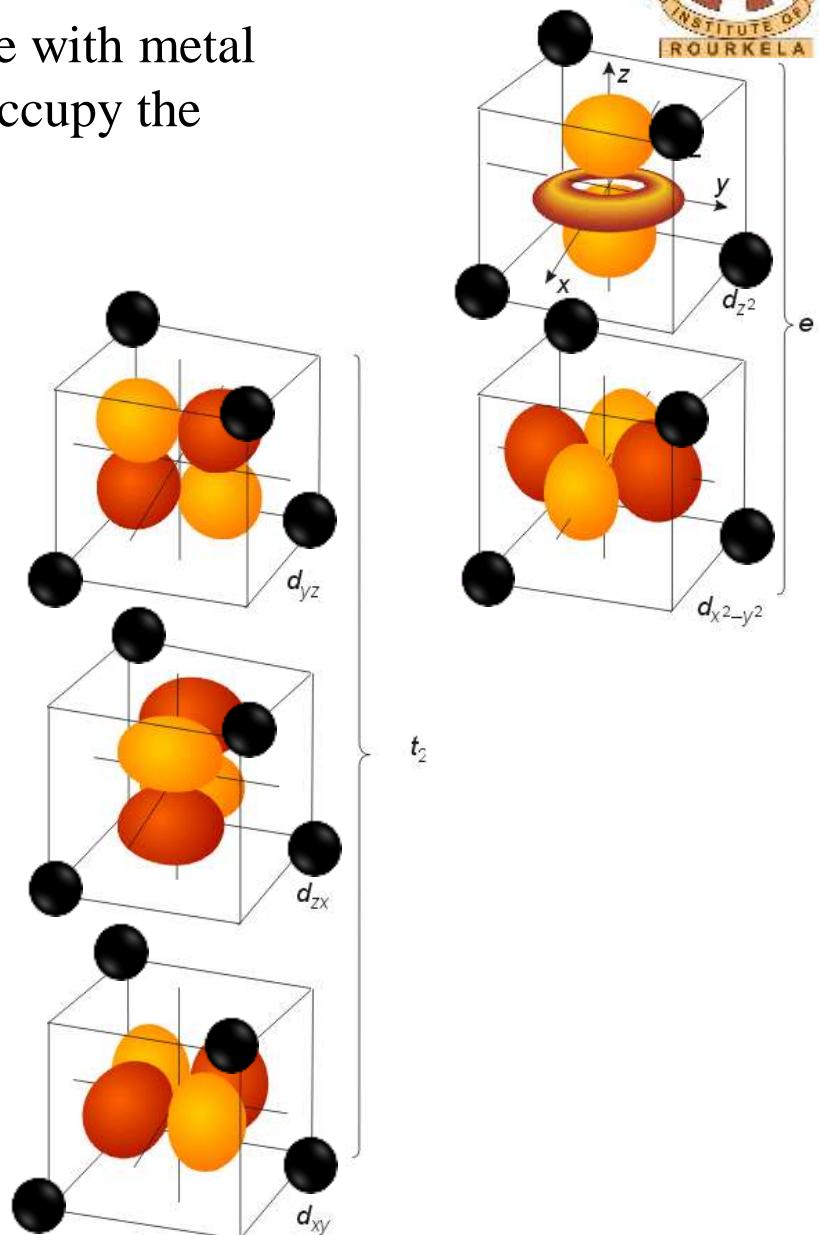


Ni⁺² (d⁸ system)

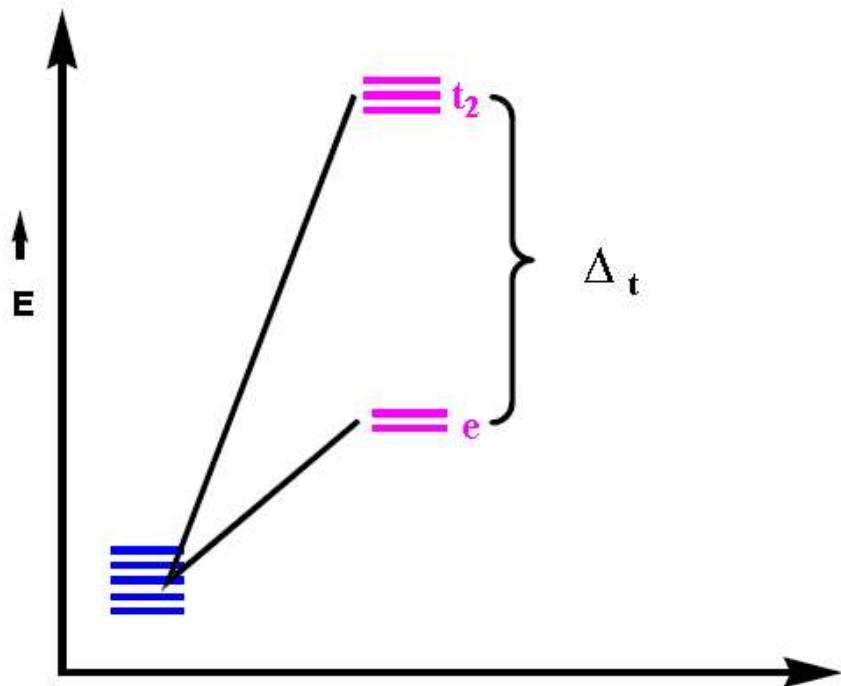
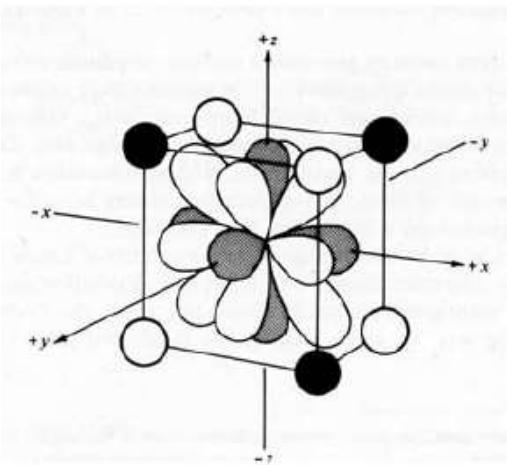
Crystal field effect in tetrahedral symmetry



- Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube.
- The two e-orbitals (d_{z^2} and $d_{x^2-y^2}$) point to the center of the face of the cube. The three t_2 -orbitals point to the center of edges of the cube.
- Therefore the t_2 -orbitals are nearer to the ligands than e-orbitals.
- Hence t_2 -orbitals have higher energy compared to e-orbitals.



Tetrahedral Field



$$\Delta_t < \Delta_o$$

$$\Delta_t = 4/9 \Delta_o$$



Factors affecting the magnitude of Δ

Number of factors that affect the extent to which d-orbitals split by surround ligands:

1. Oxidation state of the metal ion

The magnitude of Δ increases with increasing oxidation state on the central metal ion.

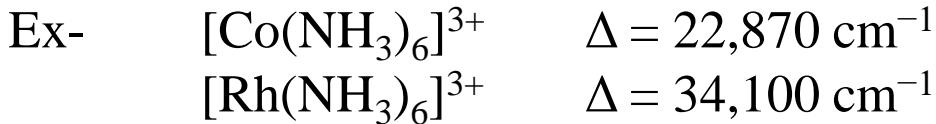
Complex	Δ (cm $^{-1}$)
$[\text{CrF}_6]^{2-}$	22,000
$[\text{CrF}_6]^{3-}$	15,060
$[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$	28,600
$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$	19,800



Factors affecting the magnitude of Δ

2. Nature of metal ion

The magnitude of Δ increases from 3d to 4d and to 5d transition elements.

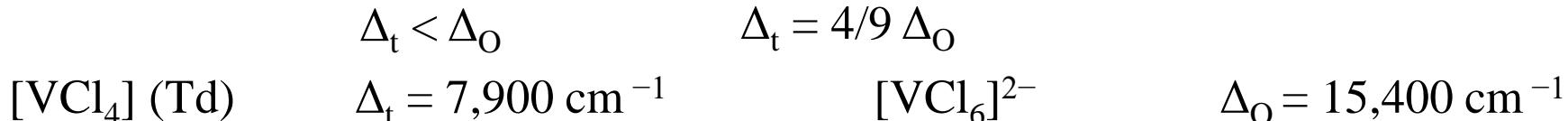


The pairing energy decreases as we go from 3d to 4d and to 5d transition elements.



3. Number and geometry of ligands

If there are more number of ligands then there is larger splitting of d-orbitals.





4. Effect of type of ligand

Different ligands split the d-orbitals of the metal atom/ion to different extent.

Complex	Δ (cm $^{-1}$)
$[\text{VCl}_6]^{3-}$	~12,000
$[\text{VF}_6]^{3-}$	~16,000
$[\text{V}(\text{Urea})_6]^{3+}$	~17,000
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	~18,000
$[\text{V}(\text{CN})_6]^{3+}$	~23,000

Spectrochemical series:

Organization of ligands according to the magnitude of (Δ) crystal field splitting energy exerted.



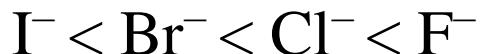
Increasing order of Δ

Weak field ligands: Ligands cause small splitting of d-orbitals.

Strong field ligands: Ligands cause larger splitting of d-orbitals.



Qualitative explanation:

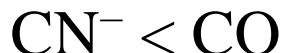


Smaller the ligand, the closer it comes to the metal ion, thus greater the repulsion.



F^- , OH^- can donate a pair of electrons from their p-orbital to d-orbital of metal forming a π bond. F^- , OH^- are π donor ligands but H_2O is not.

This reduces the charge on both ligand and metal resulting less repulsion on d-orbitals and hence less splitting.



Metal donate electrons to empty atomic orbital or low lying antibonding MO of ligand, resulting a π bond. PPh_3^- , CN^- , CO are π acceptor ligands.

When a bond forms by donation of electron from metal to ligand, it is called as back bonding.

Combination of bonding and back bonding creates strong bonding in complexes containing PPh_3^- , CN^- , CO ligands.



Crystal Field Stabilization Energy (CFSE)

Occupation of the

lower energy d-orbitals by electrons causes a stabilization of the complex.
higher energy d-orbitals causes a rise in energy of the complex.

In octahedral field

$$\text{CFSE} = [-0.4 n(t_{2g}) + 0.6 n(e_g)] \Delta_o$$

In tetrahedral field

$$\text{CFSE} = [-0.6 n(e) + 0.4 n(t_2)] \Delta_t$$

where $n(t_{2g})$ and $n(e_g)$ are the numbers of electrons in the t_{2g} and e_g levels respectively in octahedral complex.

And $n(t_2)$ and $n(e)$ are the numbers of electrons in the t_2 and e levels respectively in octahedral complex.



CFSE in octahedral field

d¹-d³

If there are one to three valence electrons present in metal ion, the t_{2g} orbitals are filled in an octahedral geometry of ligands.

So the CFSE will be $-0.4\Delta_o$, $-0.8\Delta_o$ and $-1.2\Delta_o$ for d1, d2 and d3 electronic configuration, respectively.



d⁴-d⁷



Two possibilities.

The electron may enter the higher energy, eg, level.

(High spin complexes, seen in weak field ligands.

Or, it may pair up with another electron in one of the t_{2g} orbital.

Low spin complexes, observed in strong field ligands.



CFSE in octahedral field

d^4-d^7

The actual configuration depends on the relative magnitude of Δ_o and P (pairing energy).

Pairing energy is the amount of energy needed to pair up d-electron.

For $\Delta_o < P$, the fourth electron enters one of the eg orbital. **High spin complex**

For $\Delta_o > P$, the fourth electron pair up with one in t_{2g} orbital. **Low spin complex**

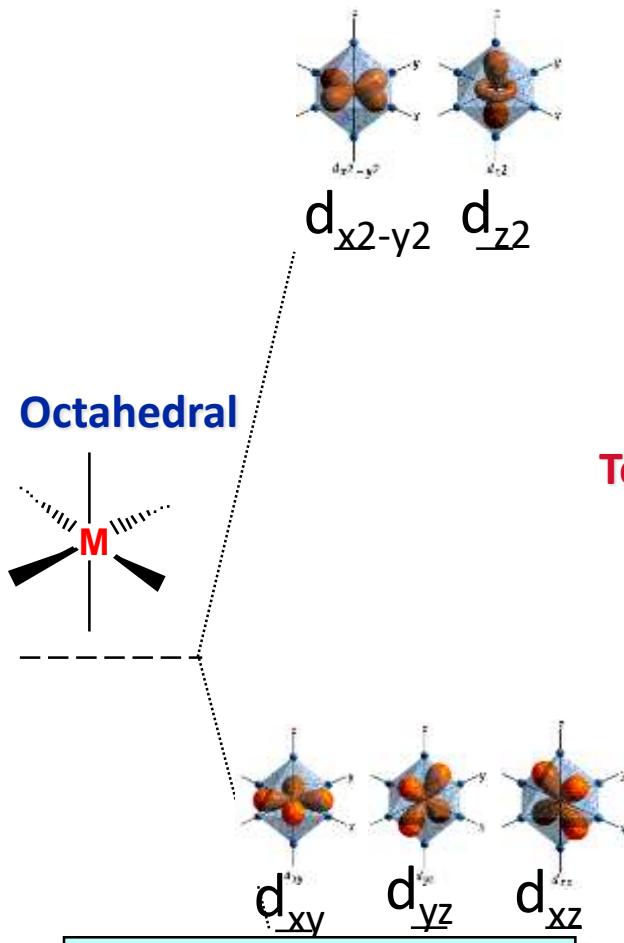
Weak field ligand \Rightarrow smaller $\Delta_o \Rightarrow$ High spin complex

strong field ligand \Rightarrow larger $\Delta_o \Rightarrow$ Low spin complex

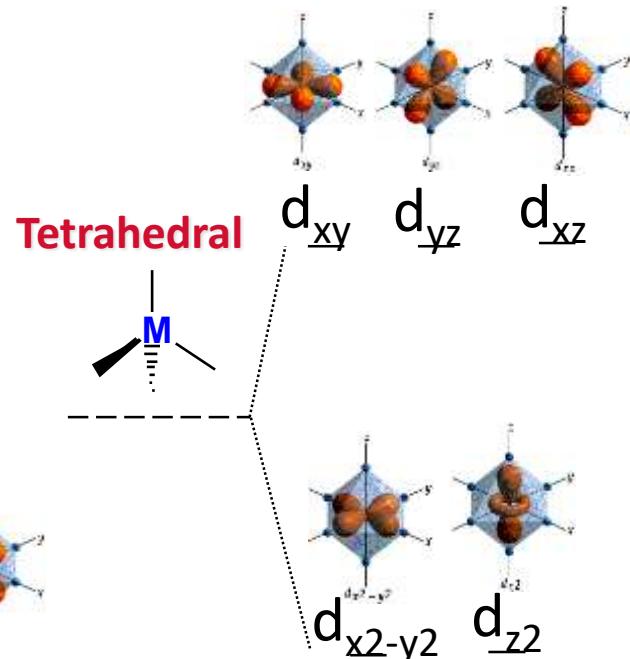
Since $\Delta_t = 4/9 \Delta_o$, all the tetrahedral complexes are high spin complexes.

Q. Calculate the CFSE for d^5 , d^6 , d^7 metal ions in both high spin and low spin octahedral complex.

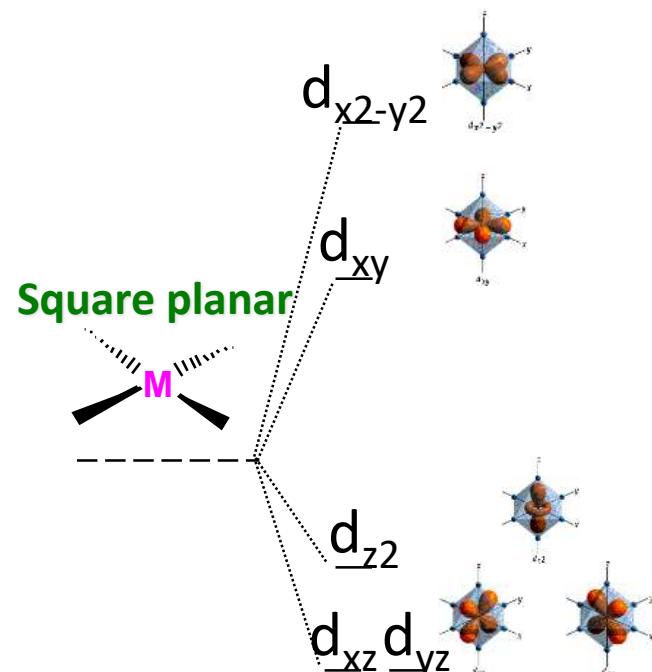
Octahedral, Tetrahedral & Square Planar



Pairing energy Vs. Δ
 Weak field $\Delta < P$
 Strong field $\Delta > P$



Small $\Delta \rightarrow$ High Spin

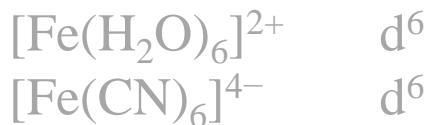


Mostly d^8
 (Majority Low spin)
 Strong field ligands
 i.e., Pd^{2+} , Pt^{2+} , Ir^{+} , Au^{3+}



Q1. Among $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, explain which forms low spin complex.

Ans. $[\text{Fe}(\text{CN})_6]^{4-}$



$$\begin{array}{ll} \Delta_o = 10,400 \text{ cm}^{-1} & P = 17,600 \text{ cm}^{-1} \\ \Delta_o = 10,400 \text{ cm}^{-1} & P = 17,600 \text{ cm}^{-1} \end{array}$$

Q2. Among $[\text{Co}(\text{F})_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$, explain which forms low spin complex.

Q3. $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is a strong oxidizing agent, but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is stable in aqueous solution. Explain.

Q4. Calculate the CFSE of tetrahedral complex $[\text{Fe}(\text{Cl})_4]^{2-}$ in the unit of Δ_t and Δ_o .



Chelating Ligands

Ligands with two or more points of attachment to the metal atom/ion are called as chelating ligands.

The complex compounds containing such type of ligands are called as chelates.

Common multidentate (chelating) ligands

Name of Ligand ^b	Abbreviation	Formula ^a
Ethylenediamine	en	H ₂ NCH ₂ CH ₂ NH ₂
Oxalato	ox	[OOCOO] ²⁻
Ethylenediaminetetraacetato	EDTA	[(OOCCH ₂) ₂ NCH ₂ CH ₂ N(CH ₂ COO) ₂] ⁴⁻
Acetylacetonato	acac	CH ₃ COCHCOCH ₃ ⁻
Bypyridine	bipy	C ₁₀ H ₈ N ₂
triethyltetraamine	trien	NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂
glycine	gly	NH ₂ -CH ₂ -CO-O ⁻

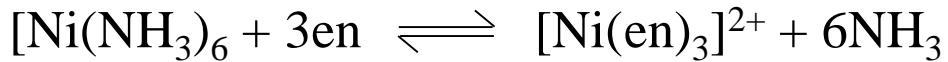


Application of chelation

- (1) Used to remove unwanted metal ions in water.
- (2) Selective removal of Hg^{2+} and Pb^{2+} from body when poisoned.
- (3) Prevent blood clots.
- (4) Solubilizing iron in plant fertilizer.
- (5) Separation of Lanthanides.

Chelates have enhanced stability.

Entropy increases in chelation and hence complex containing chelate ligands are more stable.



Metal Carbonyls



In metal carbonyl, CO binds to the metal through its C-donor. Usually the metals in metal carbonyl are zero-valent

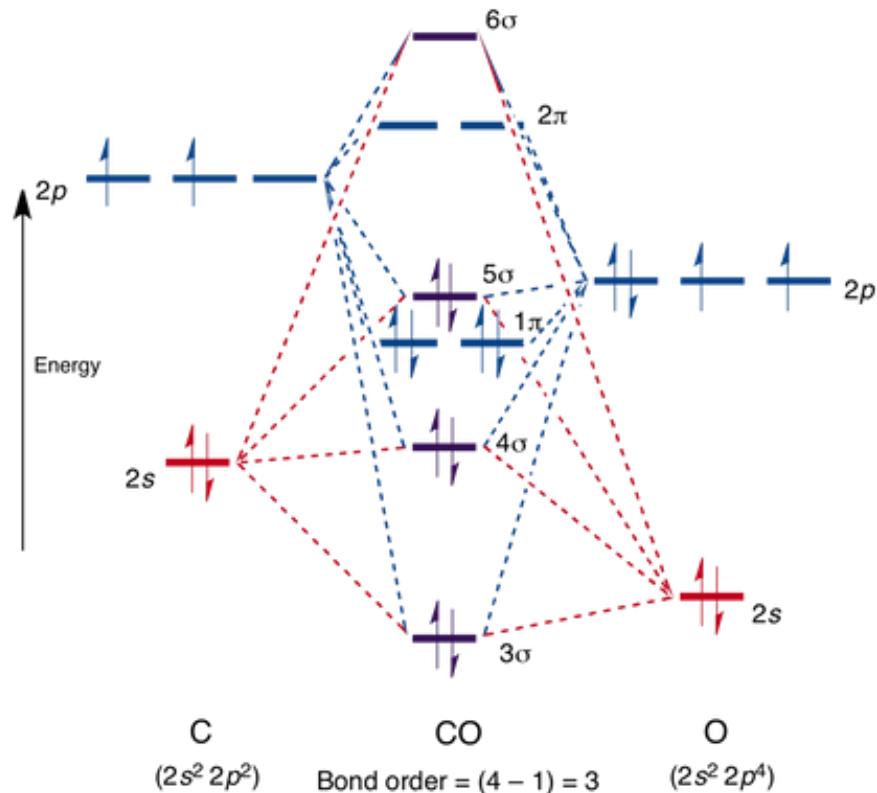
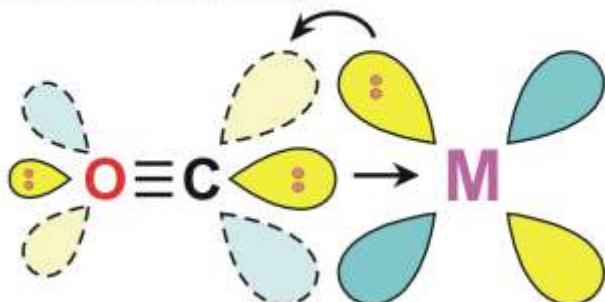
Example:



CO is a powerful π -acceptor ligand.

Both bonding and back bonding makes strong bonding in metal carbonyl compounds.

empty π^ -acceptor orbitals on carbonyl*



Why in CO, carbon atom participate in bonding with metal

MOT can explain this

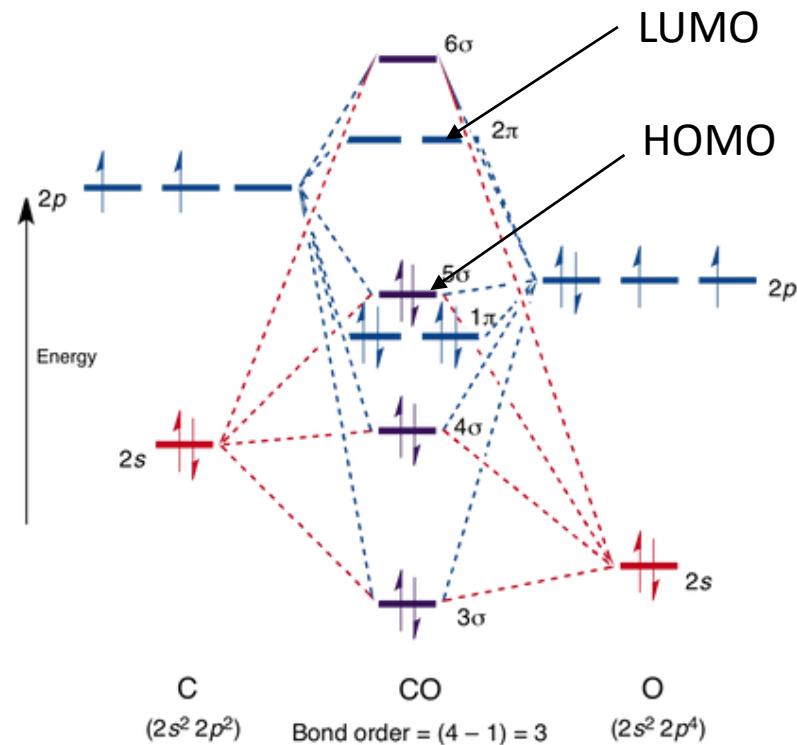
In metal carbonyl, the **bonding** occurs by **transfer of electrons from HOMO of CO to metal** atom.

Back bonding occurs by transfer of e- from **metal to LUMO** of CO.

2_{pz} atomic orbital of oxygen has contributions to σ^*_{2s} , σ_{2pz} and σ^*_{2pz}

2_{pz} atomic orbital of carbon has contributions to σ_{2pz} and σ^*_{2pz}

So, the contribution of carbon atom to σ_{2pz} (HOMO) of CO molecule is large.



The LUMO ($\pi^*_{2px} = \pi^*_{2py}$) orbitals have more carbon $2p_x$ and $2p_y$ character.



18 Electron "Rule"

Electron counting is the process of determining the number of valence electrons about a metal/atom center in a molecule.

Simple compounds from elements in 1st and 2nd period follow octet or 8-electron (ns^2+np^6) rule.

Transition metal complexes follow 18-electron ($ns^2+(n-1)d^{10} + np^6$) rule.

the sum of the d-electrons possessed by the metal plus those donated by the ligands (Ex-2 per C≡O) must total eighteen

To determine the electron count for a metal complex:

1. Determine the oxidation state of the transition metal center(s) and count the number of *d*-electrons.
2. Count the number of electrons being donated to the metal center from each ligand
3. Add up the electron counts for the metal center and ligands

Complexes with 18 e- counts are referred to as *saturated* compounds and are more stable.

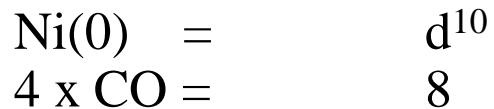
Complexes with counts lower than 18e- are called *unsaturated* and can electronically bind additional ligands.



Why electron count rule

- Basic tool to understand structure stability
- Predicting reactivity and type of reaction

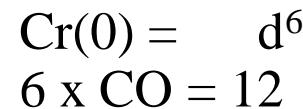
Basic tool to understand structure stability



18 e



18e



18e.



Strong reducing agent.



Very reactive (unstable compound)

Stable compounds.



More examples



$$V(0) = d^5$$

$$6 \text{ CO} = 12e$$

$$\overline{1-} = +1e$$

$$= 18e$$



$$Mn(0) = d^7$$

$$6 \text{ CO} = 12e$$

$$\overline{1+} = -1e$$

$$= 18 e$$



$$Fe(0) = d^8$$

$$4 \text{ CO} = 8e$$

$$\overline{2-} = 2e$$

$$= 18e$$

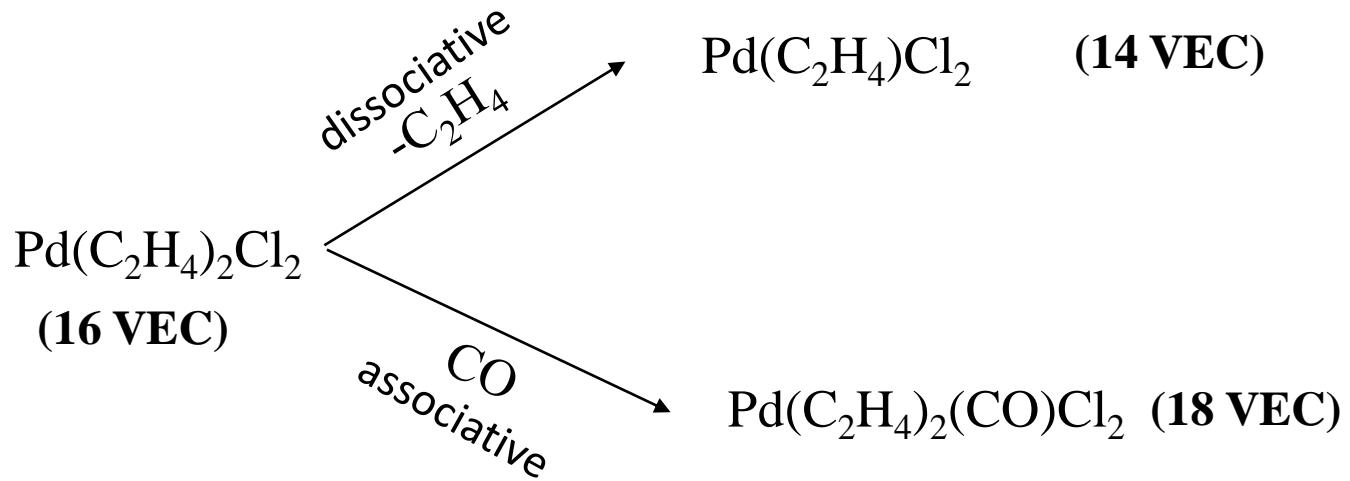
Formal oxidation state = V(-I)

Formal oxidation state = Mn(I)

Formal oxidation state = Fe(-II)



Predicting reactivity and type of reaction



Associative reaction favors.

Metal ions in biological system



Periodic Distribution of Biologically Important Elements

IA	IIA	III A	IV A	V A	VI A	VII A	VIII	VIII	IB	IIB	IIIB	IVB	VB	VIB	VII B	O	
H																He	
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

Bulk biological elements

Trace elements believed to be essential
for plants or animals

Possibly essential trace elements

The role of the metal center in biomolecules

- Metal ions can have structural roles, catalytic roles, or both.
- Metals that have catalytic roles will be present at the *active site* of the biomolecule which will likely be a **metalloprotein** (a metalloenzyme).
- The reactivity of a metalloprotein is defined by the nature of the metal, particularly its electronic structure and oxidation state.
- The electronic structure and spin state of a metal center defines its **chemical reactivity**
 - as a **redox center** (*i.e.* it controls its efficiency at accepting or donating electrons)
 - as a **Lewis acid** (electron-pair acceptor) which enables it to bind ligands (O₂, N₂, CO ..) for transport, activation and reaction.

Biological Roles of Metallic Elements

Structural

Skeletal roles via *biomineralization*

Ca^{2+} , Mg^{2+} , P, O, C, Si, S, F as anions, e.g. PO_4^{3-} , CO_3^{2-} .

Charge neutralization.

Mg^{2+} , Ca^{2+} to offset charge on DNA^- phosphate anions

Charge carriers:

Na^+ , K^+ , Ca^{2+}

Transmembrane concentration gradients ("ion-pumps and channels")

Trigger mechanisms in muscle contraction (Ca). Electrical impulses in nerves (Na, K), Heart rhythm (K).

Biological Roles of Metallic Elements

Hydrolytic Catalysts: Zn²⁺, Mg²⁺

Lewis acid/Lewis base Catalytic roles. Small labile metals.

Redox Catalysts: Fe(II)/Fe(III)/Fe(IV), Cu(I)/Cu(II), Mn(II)/Mn(III)/(Mn(IV)),
Mo(IV)/Mo(V)/Mo(VI), Co(I)/Co(II)/Co(III)

Transition metals with multiple oxidation states facilitate electron transfer - energy transfer. Biological ligands can stabilize metals in unusual oxidation states and fine tune redox potentials.

Activators of small molecules.

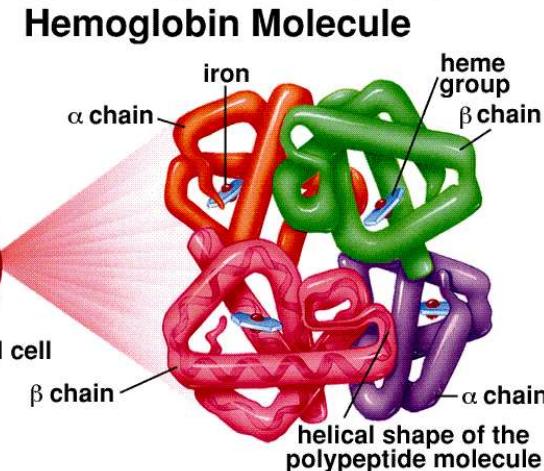
Transport and storage of O₂ (Fe, Cu), Fixation of nitrogen (Mo, Fe, V)
Reduction of CO₂ (Ni, Fe)

Fe

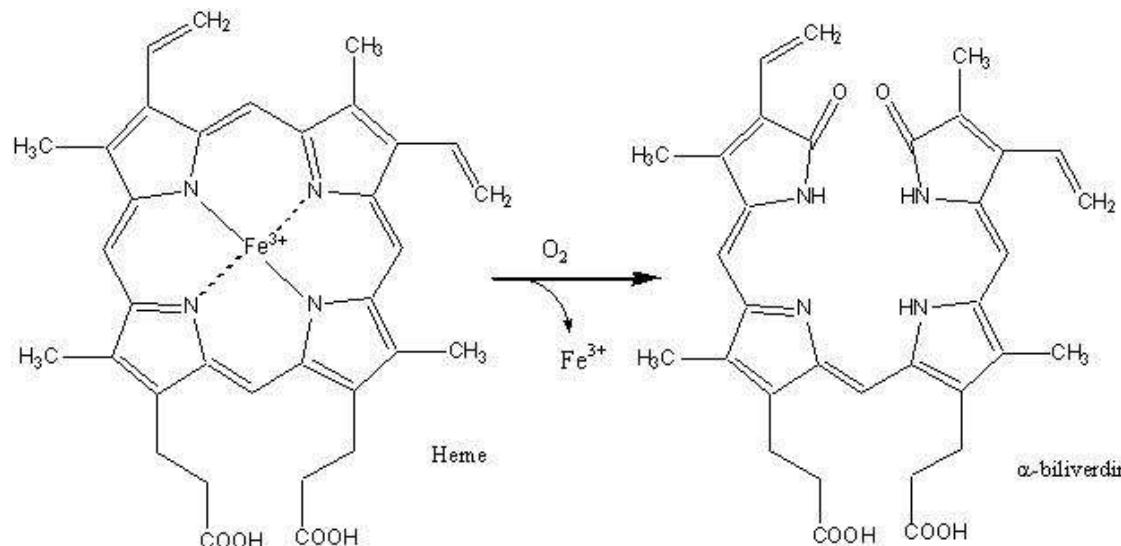
Transition Metals in Biomolecules

- O₂ uptake proteins (i.e hemoglobin, myoglobin, hemerythrin);

Sylvia S. Mader, *Inquiry into Life*, 8th edition. Copyright © 1997 The McGraw-Hill Companies, Inc. All rights reserved.



- *Oxygenase enzymes;*
 - *Catalase, peroxidase, cytochrome P-450;*
 - *Aconitase, in cytochrome c oxidase (also cu);*
 - **Nitrogenase (also Mo), in hydrogenase;**
 - Electron transport proteins like Fe-s protein, cytochromes;
 - In storage protein ferritin; about 70 Fe-proteins are well knownA diagram of a red blood cell, represented as a red sphere with a smaller white sphere inside representing the nucleus. A horizontal line extends from the bottom right of the cell, labeled "β chain", which then branches into two diagonal lines forming a triangular shape.



Transition Metals in Biomolecules

Iron.

Most abundant transition element. Serves more biological role than any other metal. Used by all plants and animals including bacteria.

Transport of iron

In higher animals iron is carried in the bloodstream by the **transferrins** (iron binding proteins).

In aerobic microorganism iron is carried by **siderophores**.

In both transferrins and siderophores, iron is present in the **+3 oxidation state**.

However, in hemoglobin, myoglobin, cytochromes, ferredoxins, iron present in **+2 oxidation state**.

Transferrins in general have larger stability constant towards iron (III) than do the various siderophores.

So they act as antibacterial agents.

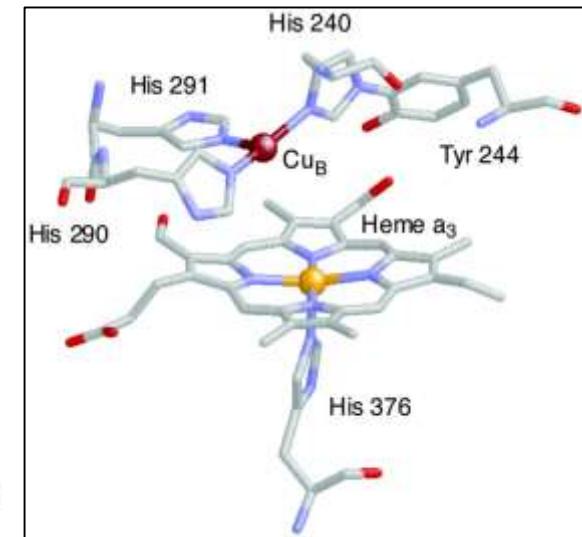
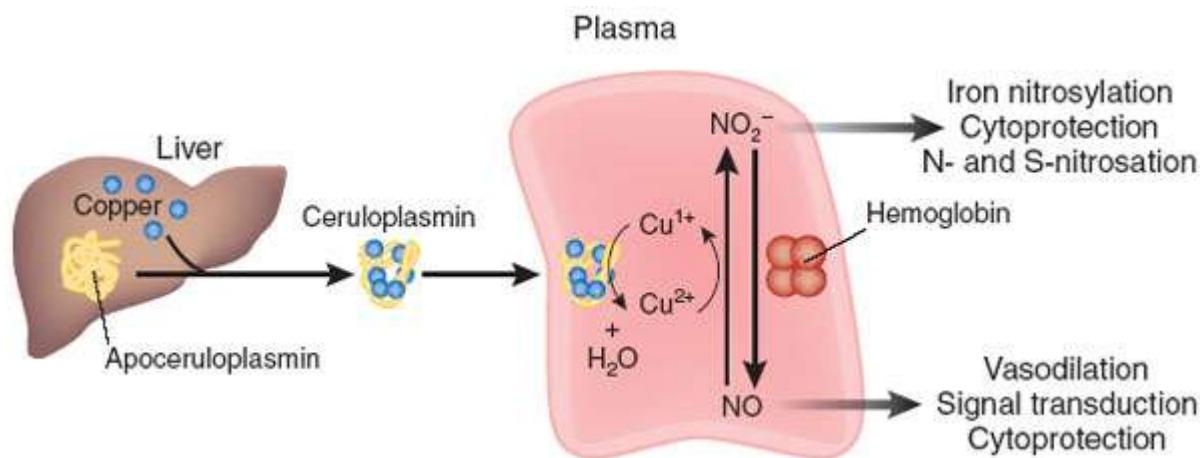
Storage of iron

In higher animals iron is stored as ferritin. In lower organism it stored in ferrichrome.

Cu

Transition Metals in Biomolecules

- Enzymes like *cytochrome c oxidase* (also fe), *amine oxidase*, *ascorbic acid oxidase*, *tyrosinase*
- Electron transport proteins like *plastocyanin*, *azurin*, *stellacyanin*
- Oxygen transport protein *hemocyanin* (in lower forms of life)
- Storage protein *ceruloplasmin*.



Transition Metals in Biomolecules

Copper

Often participatse together with Fe in proteins or has equivalent redox roles in same biological reactions.

Reversible O₂ binding, O₂ activation, electron transfer, O₂⁻ dismutation (SOD).

- Enzymes like *cytochrome c oxidase* (also *Fe*), *amine oxidase*, *ascorbic acid oxidase*, *tyrosinase*
- Electron transport proteins like *plastocyanin*, *azurin*, *stellacyanin*
- Oxygen transport protein **hemocyanin** (in lower forms of life)
- Storage protein *ceruloplasmin*.

Chromium, Vanadium and Nickel

Small quantities, uncertain biological roles. Sugar metabolism (Cr);

Ni only in plants and bacteria (role in CH₄ production) and SOD enzymes.

Zinc.

Relatively abundant metal. Major concentration in metallothionein (which also serves as a reservoir for other metals, e.g. Cd, Cu, Hg). Many well characterized Zn proteins, including redox proteins, hydrolases and nucleic acid binding proteins.

Cobalt.

Unique biological role in cobalamin (B_{12} -coenzymes) isomerization reactions.

Manganese

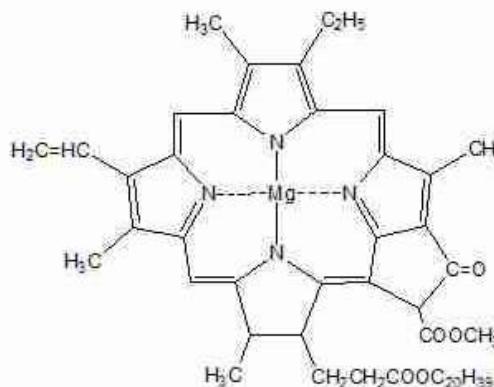
Critical role in photosynthetic reaction centers, and SOD enzymes.

Molybdenum

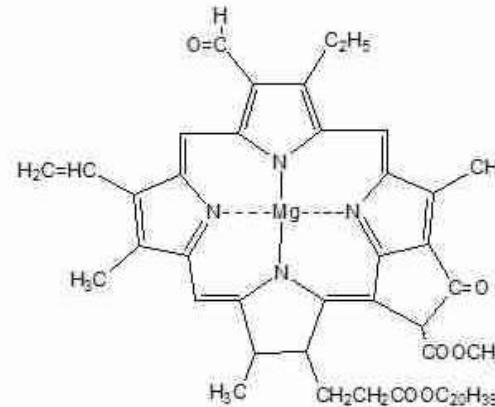
Central role in nitrogenase enzymes catalyzing $N_2 \rightarrow NH_3$, $NO_3^- \rightarrow NH_3$

Mg

- Photosynthesis,



Chlorophyll a



Chlorophyll b

- ATP hydrolysis,
- Phosphate group transfer reactions (i.e kinase reactions),
- Structure formation, stabilizing DNA and RNA, construction of cell membranes,
- DNA polymerase enzyme catalyzing the transcription of DNA.

What we learn in coordination chemistry?



Werner's theory

Crystal Field theory

d-orbital splitting energy in octahedral, tetrahedral and square planar geometry

Factors affecting the d-orbital splitting energy.

Crystal field stabilization energy. High spin and low spin complexes.

18- electron rule and stability of metal carbonyls.

Metals in biological system.

- *Lighter elements are more abundant in general and therefore utilized more.*
3d metals, rather than 4d, are used as catalytic centers in metalloenzymes.
- *Why has Mo (4d) rather than Cr (3d) been utilized more biologically?*
Although Mo is rare in the earth's crust, Mo is the most abundant transition metal in sea water as MoO_4^- has fairly high solubility in water.
Better correlation exists between the abundance of elements in in human body and in sea water than between the human body and the earth's crust.
Taken as evidence for the oceans as the site of evolution of life.
- *Despite the high abundance of Si, Al and Ti (the 2nd, 3rd and 10th most abundant elements on earth). Why are they are not utilized biologically?*
Because of the insolubility of their naturally occurring oxides (SiO_2 , Al_2O_3 , TiO_2) under physiological conditions. A lower oxidation state is unavailable for Si and Al and unstable for Ti in an aerobic environment and is readily

- Why has iron been used so widely in biology although Fe^{3+} , its most stable oxidation state, is highly insoluble at pH 7
Complex biological mechanisms have been developed to accommodate the low solubility of $Fe(OH)_3$ ($K_{sp} = 1 \times 10^{-38}$) ~ pH 7, and take advantage of its high "availability".
- Co^{2+} and Zn^{2+} have very similar coordination chemistry and ionic size and can be interchanged in many Zn enzymes without loss of activity. Why is Co not utilized more biologically?
Zn is much more abundant and therefore has been utilized more.
- Why has cobalt been given an essential role in cobalamins despite its very low availability?
- The unique properties of cobalt (e.g. its oxidation states, redox potentials and coordination chemistry) is needed to achieve essential functions of B_{12} coenzymes.

CHEMISTRY 1101 (CY 1101)



Dr. Usha Subuddhi
Assoc. Professor
Office: MN424
Dept. of Chemistry
subuddhiu@nitrkl.ac.in
Phone: 2662

Dr. U. Subuddhi, NITRkl

CHEMICAL KINETICS

- ✓ Empirical Chemical Kinetics (Rate equations)
- ✓ Methods of determination of order of a reaction
- ✓ Temp. dependence of reactions, Arrhenius theory
- ✓ Complex Reactions (Opposing, Consecutive, Parallel)
- ✓ Concept of Steady State and -equilibrium Approximation
- ✓ Chain Reaction (Free Radical)
- ✓ Enzymatic Catalysis (M Equation and Inhibition)
- ✓ Heterogeneous Catalysis (Simple surface reactions)

Book:

Atkin's Physical Chemistry by Peter Atkins and Julio D'aula

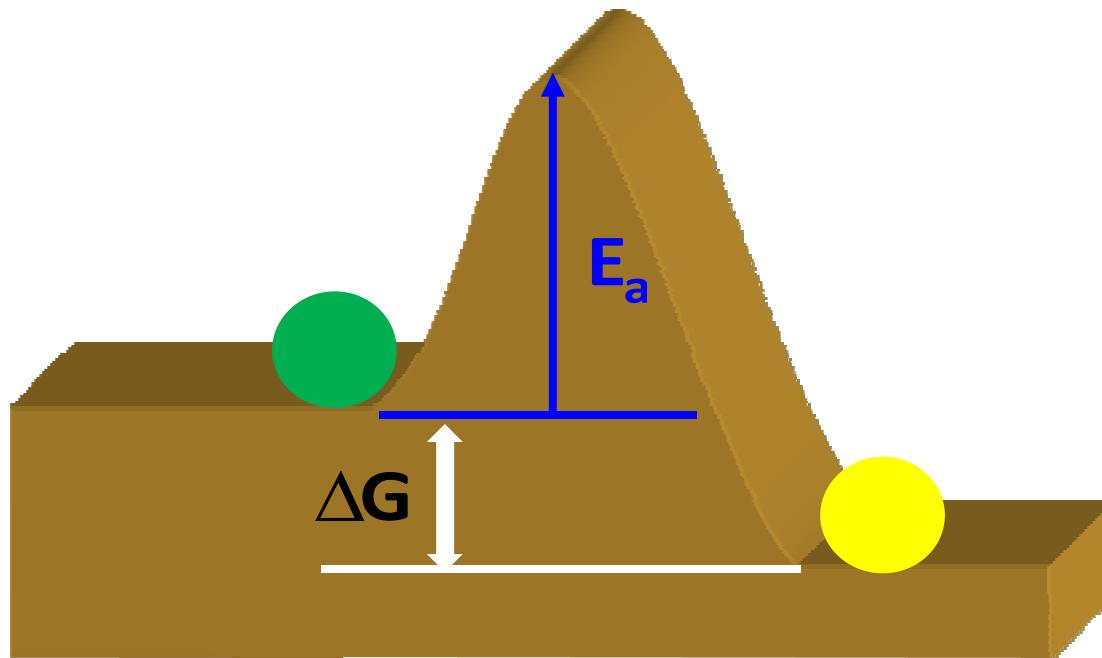
Dr. U. Subuddhi, NITRkl

Thermodynamics vs. Kinetics

Thermodynamics:

Is the reaction feasible ($\Delta_r G = -ve$)?

Which product is stable? (at equilibrium)



Kinetics:

How fast (rate) is the chemical process!

Mechanism of reaction! (any intermediate!)

Thermodynamics vs. Kinetics



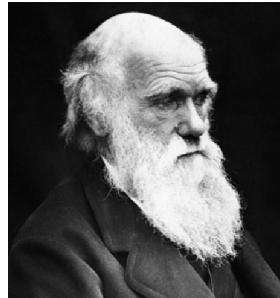
Thermodynamics favors the process $\Delta G < 0$
Kinetics makes this reaction nearly impossible
(Requires a very high pressure and temperature over long time)

Dr. U. Subuddhi, NITRkl

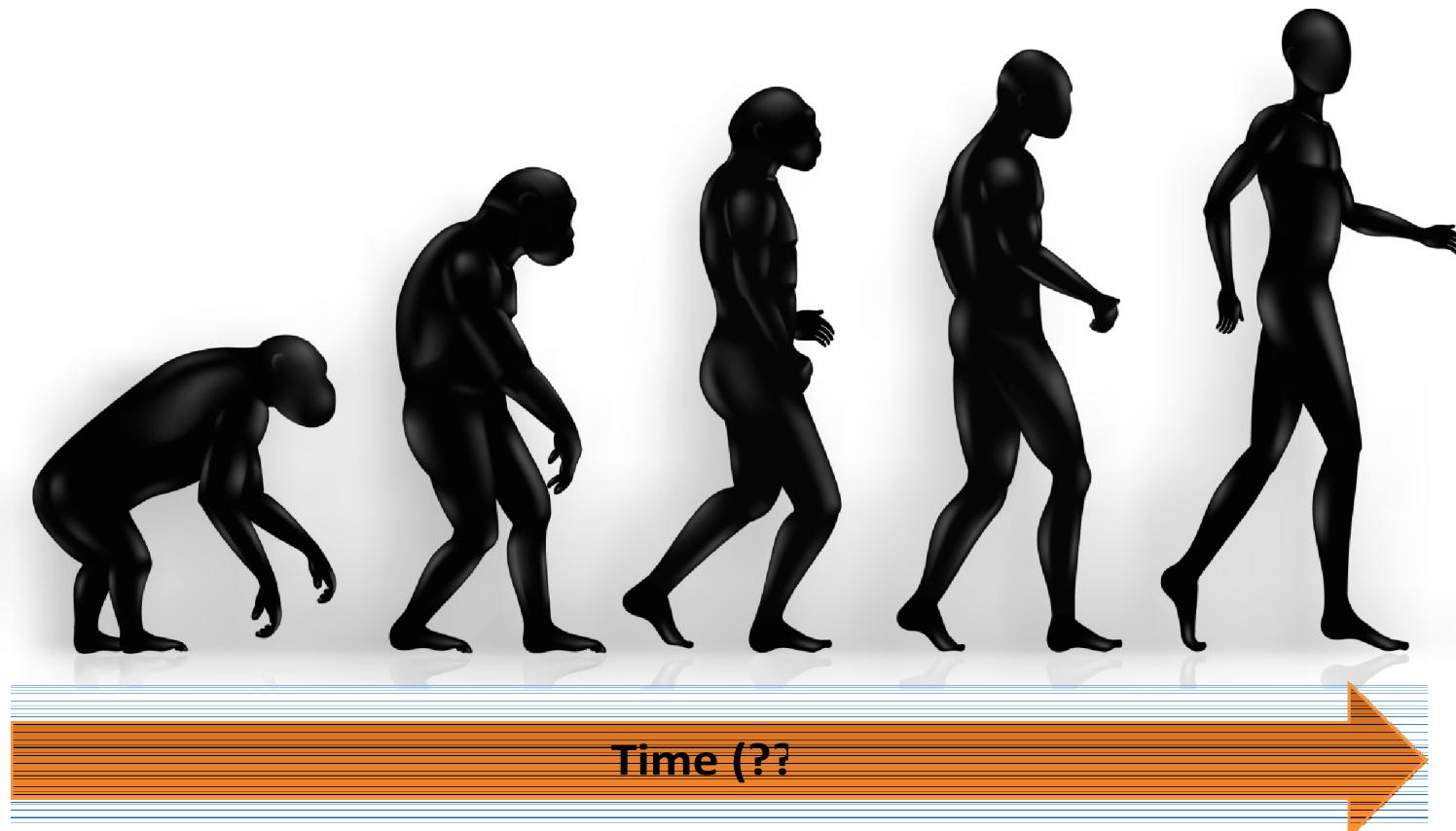
Kinetics (Ancient Greek: "kinesis", *movement* or *to move*)

- Chemical kinetics also known as Reaction dynamics is the study of rate of chemical processes.
- Helpful for understanding the mechanism of chemical reactions.
- A kinetic study can disprove a mechanism but it can't establish a mechanism with certainty.

What makes one reaction faster than another??

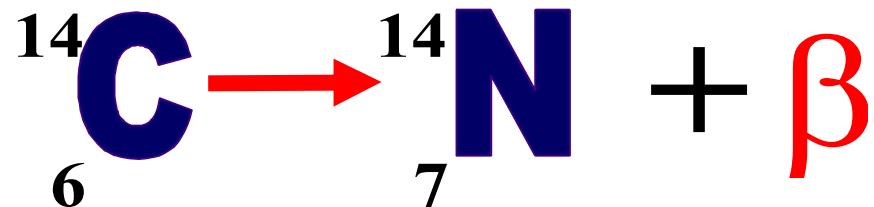


Evolution: Very Slo**P**rocess

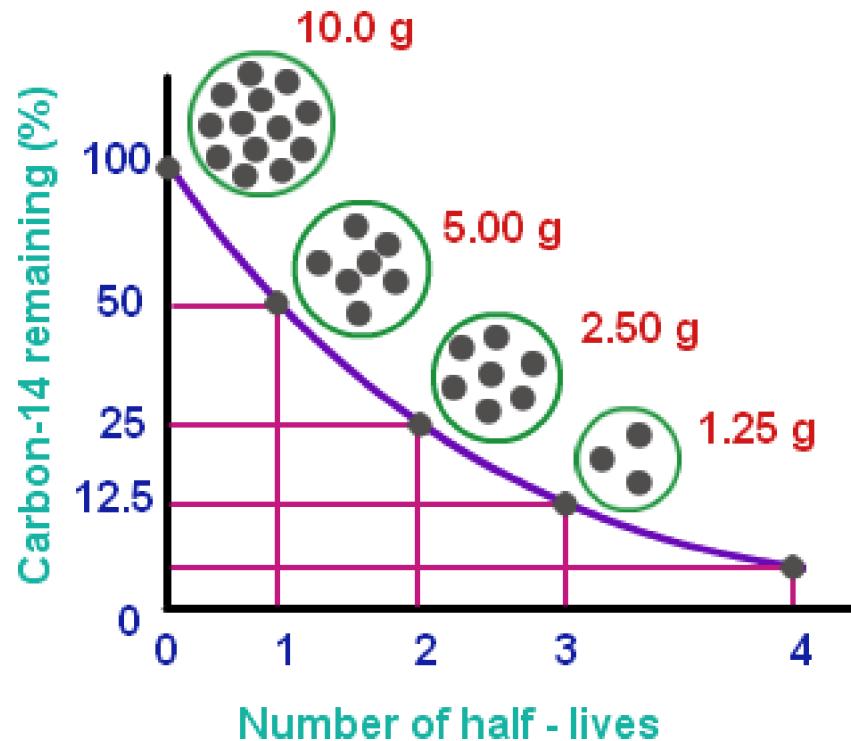


Dr. U. Subuddhi, NITRkl

Carbon14 Decay



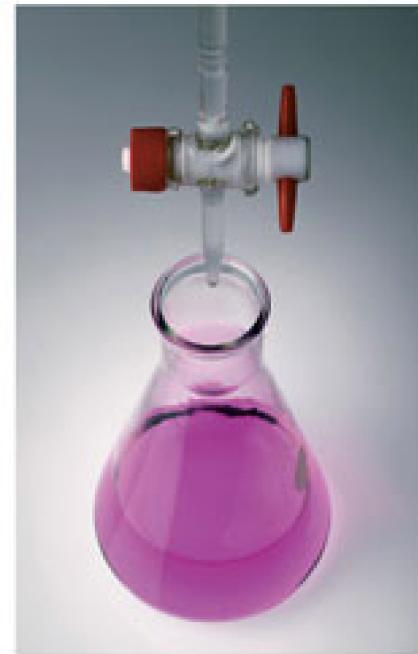
1 Halflife = 5730 Years!!



Dr. U. Subuddhi, NITRkl

Note: NOT all radioactive decays are so slow!

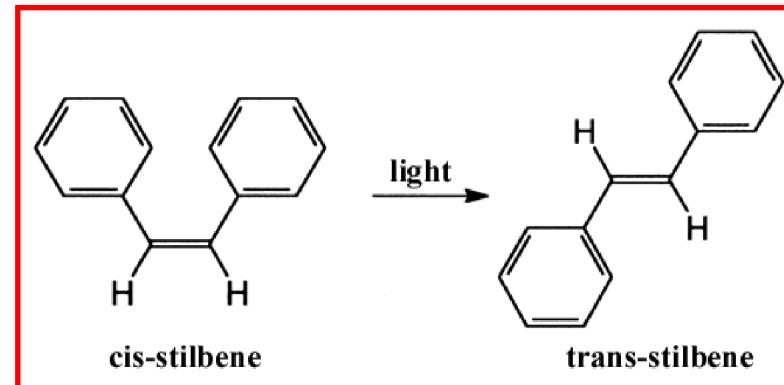
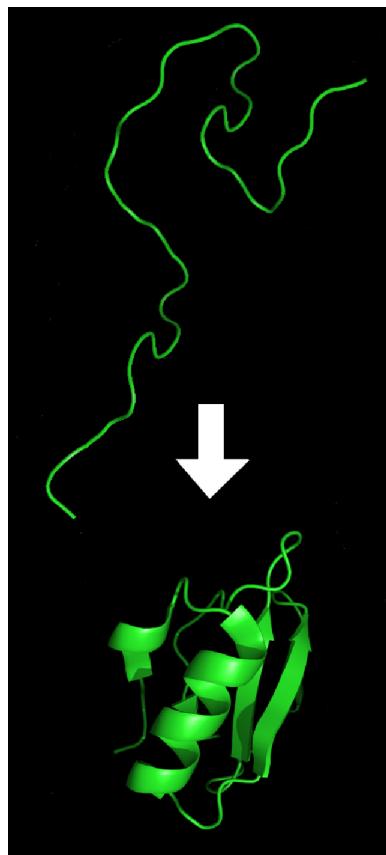
Titration of Any Kind: Reaction of Seconds to Minutes



Fast Reactions: 10^3 - 10^{15} s time scale

Protein Folding

nanosec(10^9 s) to sec



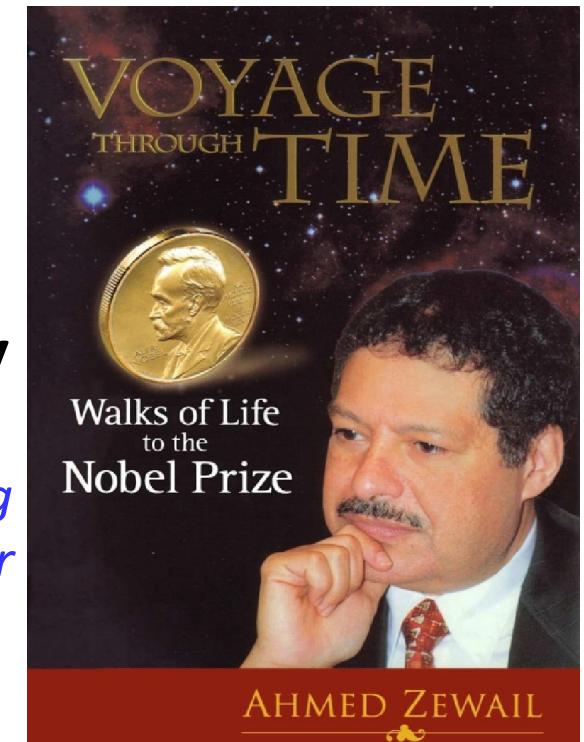
Femtosecond
(10^{15} s)

1999 Nobel Prize
In Chemistry

Ahmed Hassa~~z~~ewail
"father of femtochemistry"

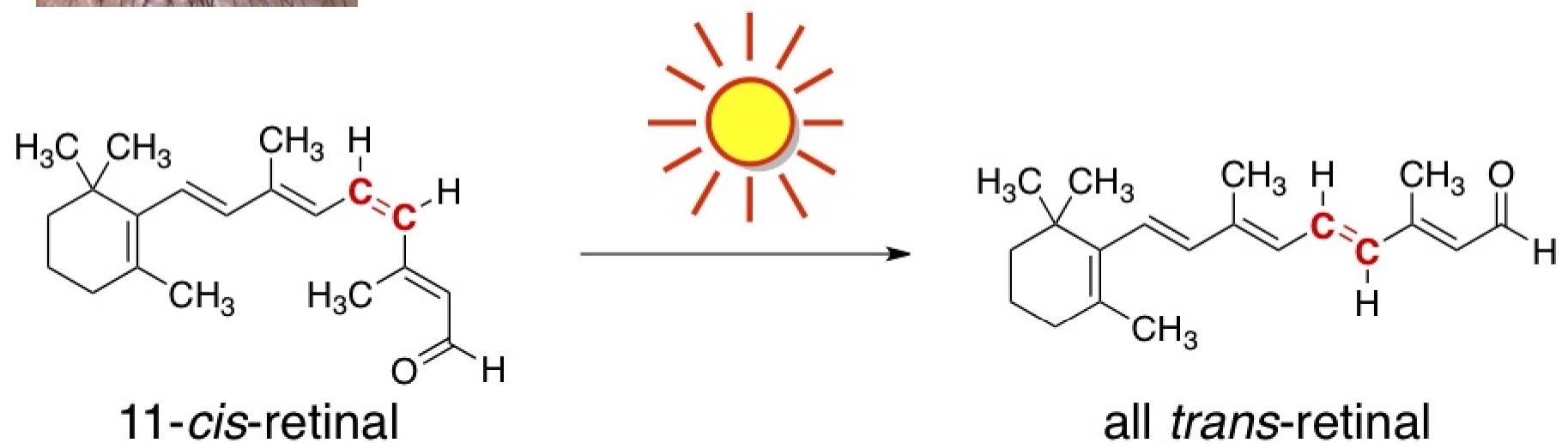
For his studies of the transition states of chemical reactions using femtosecond (ultrashort) laser spectroscopy

Dr. U. Subuddhi, NITRkl





Light Driven Femtochemistry : Reason for Vision

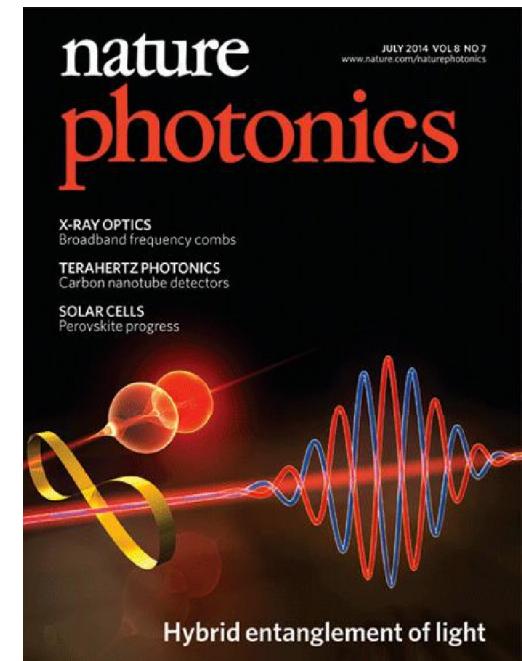


This **Isomerisation** sets off a cascade of chemical reactions that results in a signal to the brain, which is interpreted as vision

It takes about 0.15 second from the moment light hits the retina to when the earliest recognition of basic object identity can occur

How Fast is The Fastest Chemical Reaction?

Attosecond (10^{-18} s)
molecular dynamics:
fact or fiction



Nature Photonics, 195–204(2014)

Franck Lépine, Misha Y. Ivanov & Marc J. J. Vrakking

Dr. U. Subuddhi, NITRkl

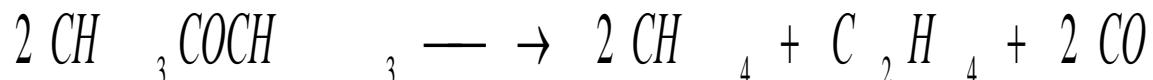
Macroscopic Kinetics Most rate measurements are made on systems that are in thermal equilibrium obeying Boltzmann distribution. Experiments of this kind are referred to as “bulk” experiments. Macroscopic kinetics describes this branch of kinetics since the results relate to the behavior of a very large group of molecules in thermal equilibrium.

Microscopic Kinetics Kinetic studies at the molecular level are referred to as microscopic kinetics. Here the reacting molecules are in well-defined states (velocity and internal energy). Crossed molecular beam experiments are used to investigate microscopic kinetics.

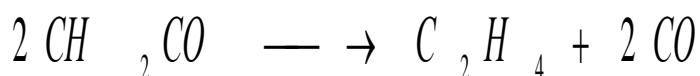
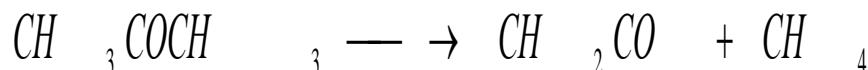
When substances react together, if an overall stoichiometry equation applies throughout the course of the reaction, the reaction is said to have **time independent stoichiometry**. $H_2 + Br_2 \longrightarrow 2 HBr$

Sometimes the stoichiometry changes throughout the course of the reaction, which is said to show **time - dependent stoichiometry**.

Thermal decomposition of acetone, the overall reaction is represented as



Appreciable amount of ketene is present during the course of the reaction, thus the amounts of products present during the course of reaction are not related by any stoichiometric relation to the amount of reactant that has been consumed.



In such case the correct relationships between the amounts of reactants and product must include time - dependent terms and therefore must be based on a knowledge of the kinetics of the reaction.

Extent and Rate of Reaction

For any reactant or product in a reaction having time - independent stoichiometry the extent of reaction is defined as

$$\xi = \frac{n_i - n_i^0}{v_i}$$

v_i : stoichiometric coefficient

It is convenient to define a rate that is same for all the species .

For a reaction showing time - independent stoichiometry this can be done in terms of the extent of reaction

The rate of reaction independent of the reactant and product species is defined as the time derivative of the extent of reaction divided by the volume

$$v = \frac{1}{Vdt} \frac{d\xi}{dV}$$

$$\dot{\xi} = \frac{1}{v_i} \frac{dn_i}{dt}$$

n_i : amount of i

v_i : stoichiometric coefficient

The rate of reaction is therefore

$$v = \frac{1}{\nu_i V} \frac{dn_i}{dt}$$



$$v = -\frac{1}{aV} \frac{dn_A}{dt} = -\frac{1}{bV} \frac{dn_B}{dt} = \frac{1}{cV} \frac{dn_C}{dt} = \frac{1}{dV} \frac{dn_D}{dt}$$

If the volume does not change during the course of the reaction we can replace $\frac{dn_i}{V}$ with dc_i

$$v = \frac{1}{\nu_i} \frac{dc_i}{dt}$$

$$\boxed{\text{Rate of the rx}^n = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}}$$

Volume change during reaction

If in a reaction the volume does not remain constant during the course of the reaction, a change in the volume will bring about a change in the concentration of a substance.

To remove the restriction of constant volume we also need to take care of the change in volume with time

$$n_A = [A]V$$

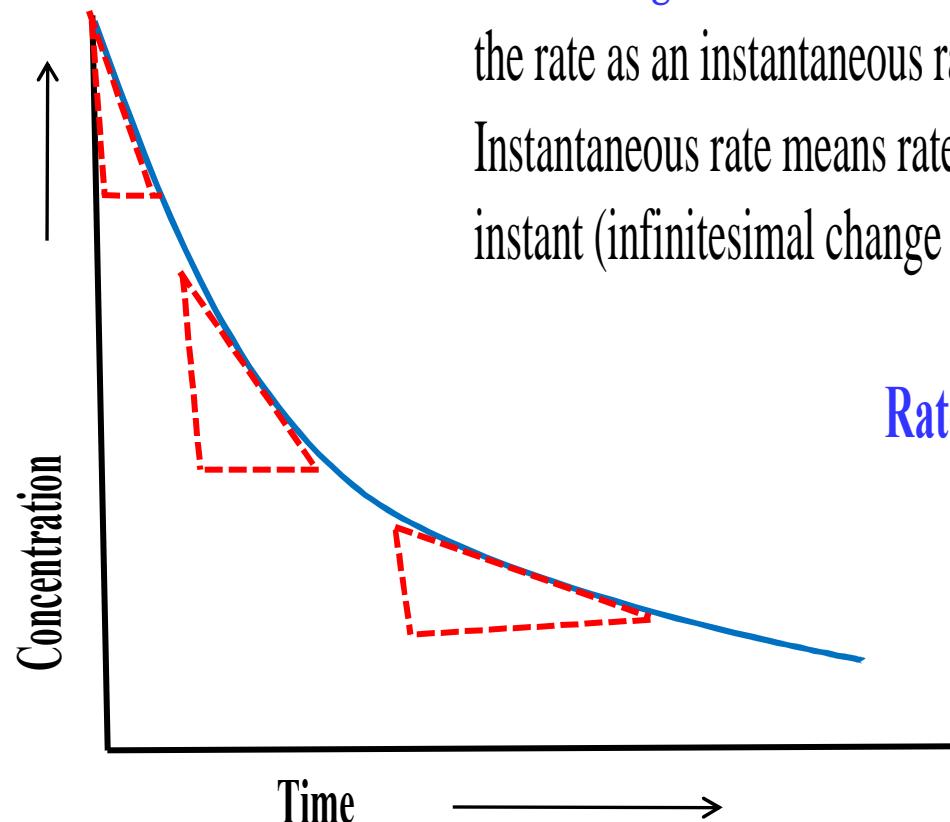
$$dn_A = Vd[A] + [A]dV$$

$$\nu = \frac{1}{\nu_A V} \frac{dn_A}{dt} = \frac{1}{\nu_A} \frac{d[A]}{dt} + \frac{[A]}{\nu_A V} \frac{dV}{dt}$$

The changes in volume usually are not needed for reaction in solution. However they become necessary for liquid phase reactions and for gas reactions in open systems e.g. reactions in flames

Rate can be expressed in three different ways

- (i) **Initial rate**
- (ii) **Average rate**
- (iii) **Instantaneous rate**



Rate changes with time

hence expressing

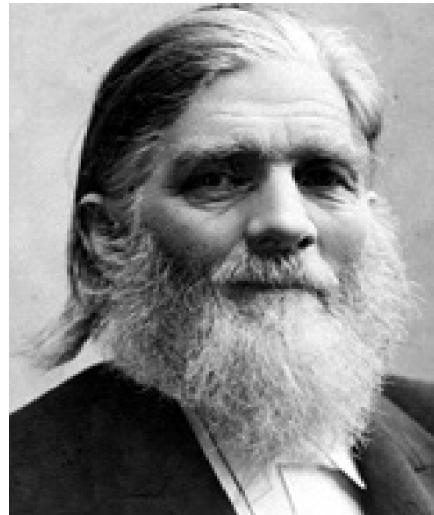
the rate as an instantaneous rate is preferable.

Instantaneous rate means rate at a particular instant (infinitesimal change in time)

i.e.

$$\text{Rate} = \frac{\pm d[\text{concentration}]}{dt}$$

In 1864 **Peter Waage** and **Cato Guldberg** pioneered the development of Chemical Kinetics by formulating the law of mass action



Peter Waage Guldberg

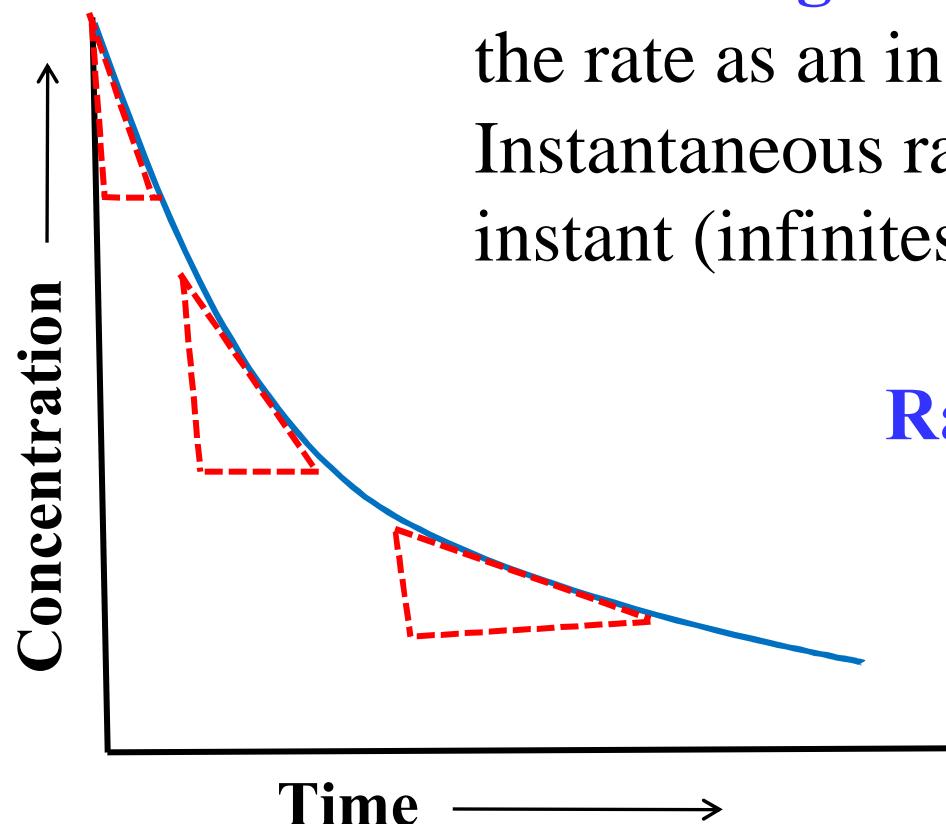
Law of Mass Action

The rate of an elementary reaction is proportional to the product of the concentrations (active mass) of the participating molecules

Dr. U. Subuddhi, NITRkl

Rate can be expressed in three different ways

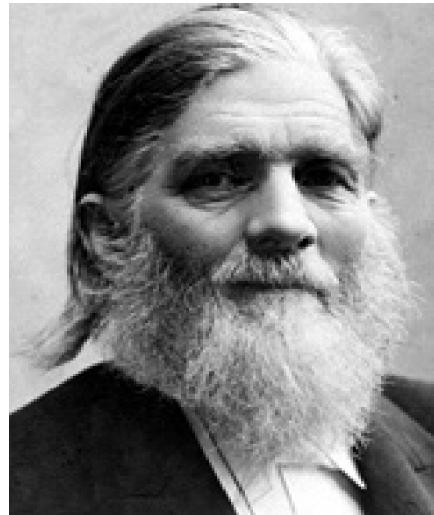
- (i) **Initial rate**
- (ii) **Average rate**
- (iii) **Instantaneous rate**



Rate changes with time hence expressing the rate as an instantaneous rate is preferable. Instantaneous rate means rate at a particular instant (infinitesimal change in time) *i.e.*

$$\text{Rate} = \frac{\pm d[\text{concentration}]}{dt}$$

In 1864 **Peter Waage** and **Cato Guldberg** pioneered the development of Chemical Kinetics by formulating the law of mass action



Peter Waage Guldberg

Law of Mass Action

The rate of an elementary reaction is proportional to the product of the concentrations (active mass) of the participating molecules

Dr. U. Subuddhi, NITRkl

RateLaw

The rate of a homogeneous reaction is proportional to the product of the concentrations of the reactants raised to some power

Thus for a general reaction $aA + bB \rightarrow cC + dD$

$$\text{Rate} \propto [A]^{\alpha} [B]^{\beta}$$

or

$$\text{Rate} = k [A]^{\alpha} [B]^{\beta}$$

- ‘k’ is the proportionality constant known as **rate constant** or **specific rate** or **velocity constant**.
- It is independent of concentration and time
- Has a **specific value at a given temperature**

Dr. U. Subuddhi, NITRkl

Order of a Reaction

- The sum of the powers of the concentration terms ($\alpha + \beta$) in the rate equation is known as the **overall order** of the reaction.
- α, β are called the **partial orders** w. r. t the reactants A and B respectively.
- The order of a reaction generally has a value 0 to 3.
- Order can also have **fractional value**. e.g. decomposition of acetaldehyde: $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$
rate = $k [\text{CH}_3\text{CHO}]^{3/2}$ order = 3/2 or 1
- Order is different from the stoichiometric coefficient and needs to be determined **experimentally**.

Dr. U. Subuddhi, NITRkl

Methods for Determination of Order of a Reaction

- 1. Differential Method**
- 2. Method of Integration**
- 3. Half-life Method**
- 4. Isolation Method**

Dr. U. Subuddhi, NITRkl

1. Differential Method

In this method rates are measured directly by determining the slopes of the conc. vs. time curves and the information is obtained on how the rate is related to conc.

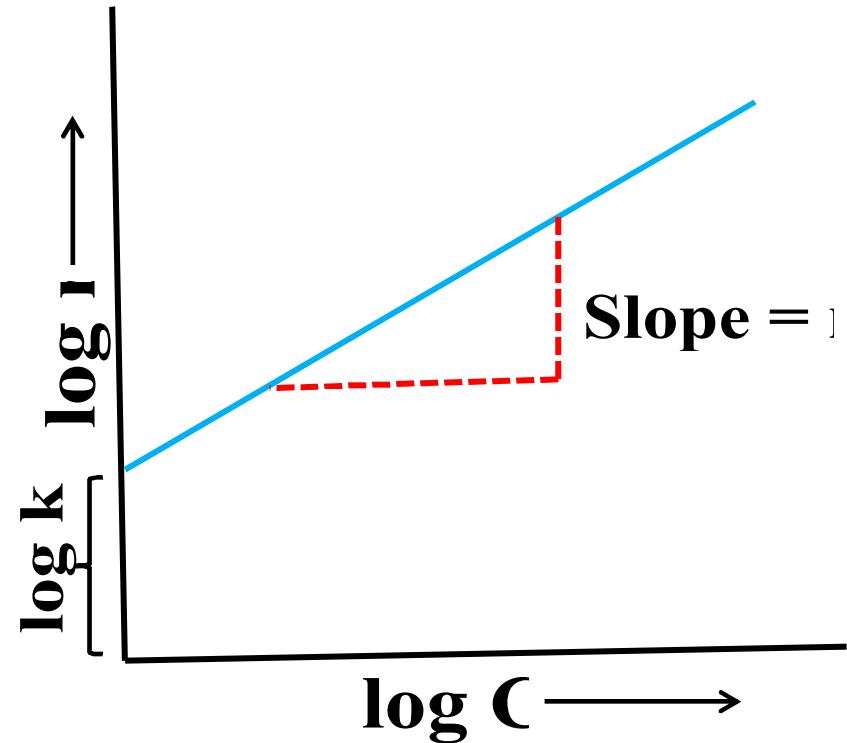
This method was first introduced van't Hoff in 1884
The rate of a 'thn' order reaction is given as

$$r = -\frac{dC}{dt} = k C^n, \text{ where } C = \text{conc. of the reactant}$$

$$\log r = \log k + n \log C$$

A double logarithmic plot $\log r$ vs. $\log C$ gives a straight line of slope 'n' (order) and intercept 'log k'

$$\log r = \log k + n \log C$$



If a straightline plot is not obtained then the rate cannot be expressed as above and the reaction does not have an order w. r. t. that particular reactant

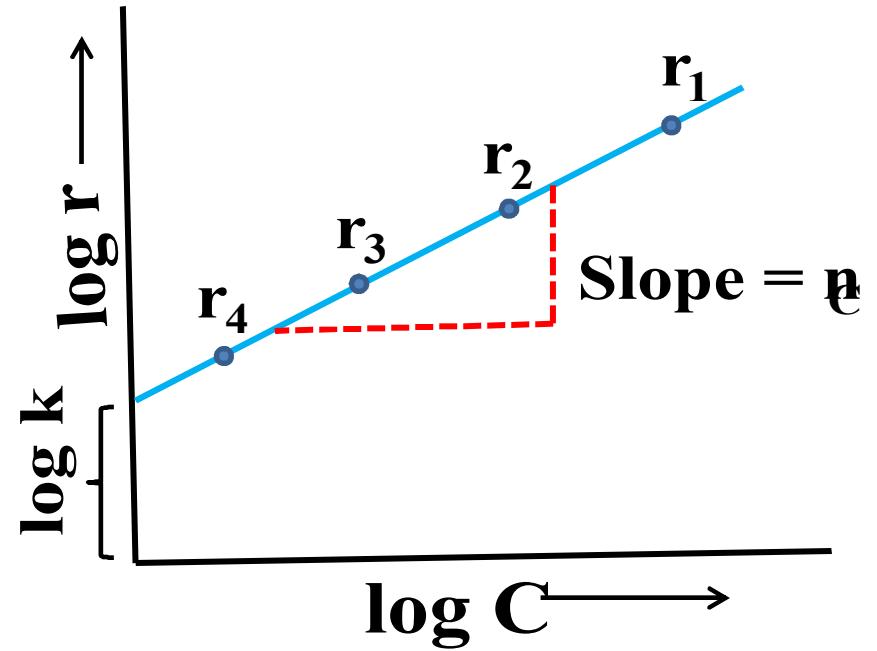
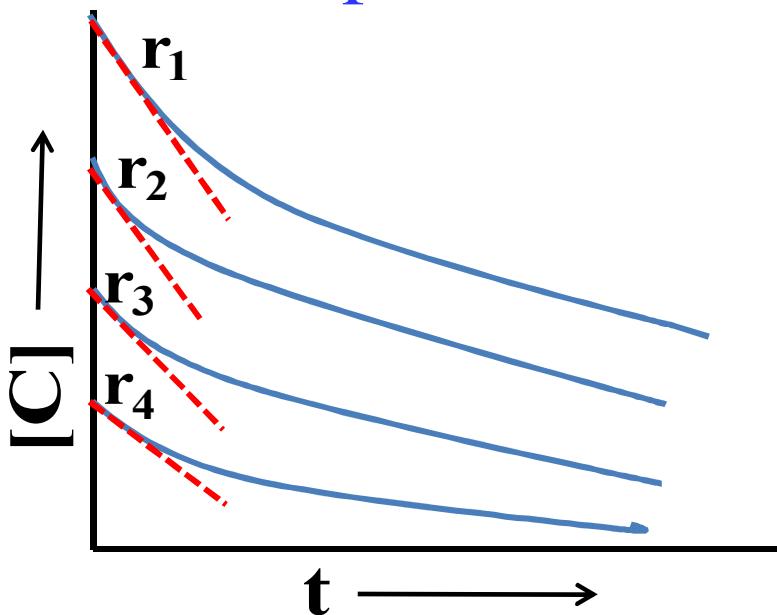
The rate can be measured in two different

1. By various runs at different initial concentrations
2. By single run but measuring the rate at different times

Dr. U. Subuddhi, NITRKL

1. With different initial concentrations

Various runs are carried out at different initial concentrations of the reactant and initial rates are measured by measuring the initial slope.



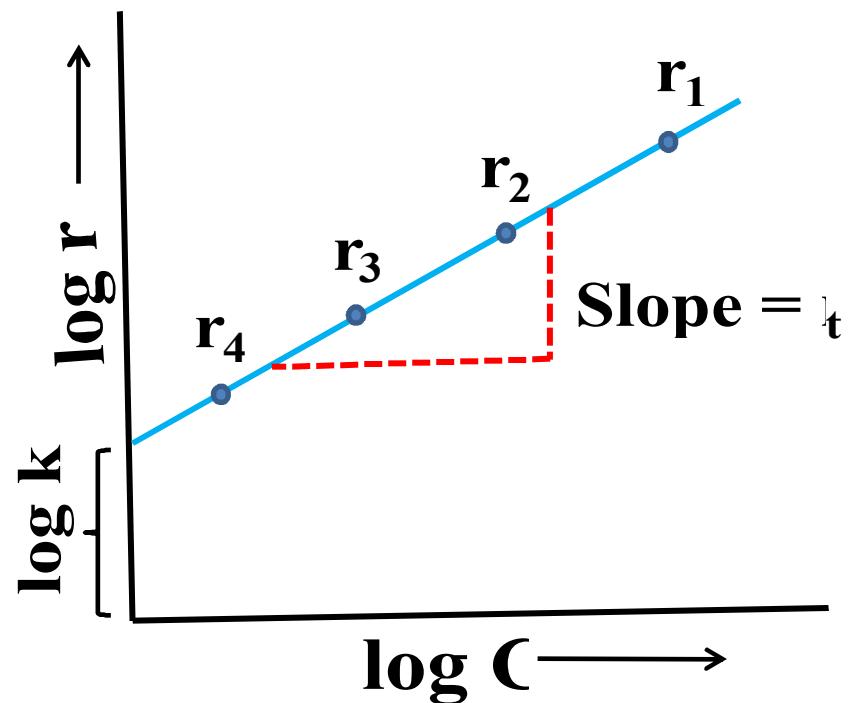
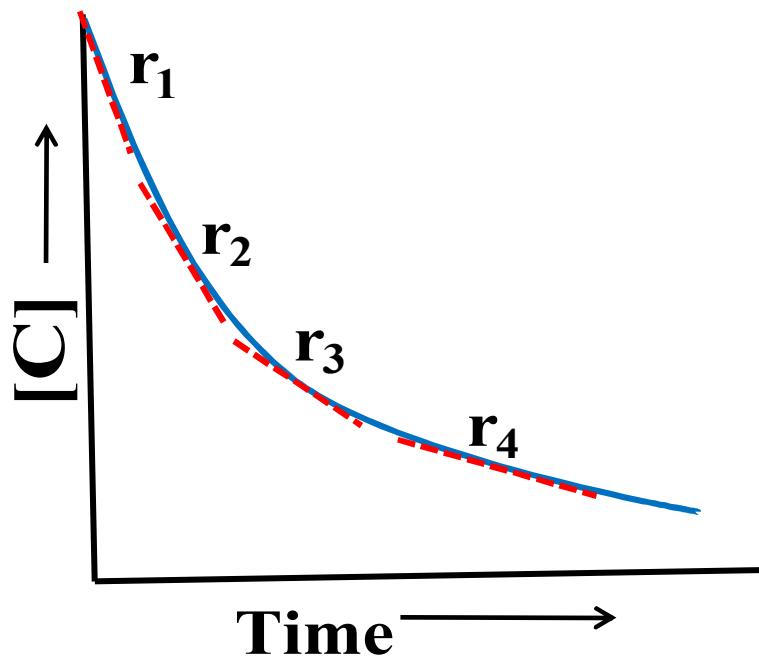
This procedure avoids the possible complications due to the interference by products (e.g. inhibition or autocatalysis).

The order thus determined is called **w.r.t conc. order n_C**

Dr. U. Subuddhi, NITRkl

2. At different time

In this procedure a single run is carried out and the slopes are measured at different times. So this variation of rate with respect to time



The order thus determined is called **order w.r.t time (t)**

If r_1 and r_2 are the rates at two different initial concentrations C_1 and C_2 then

$$r \propto C^n$$

$$\frac{r_1}{r_2} = \left(\frac{C_1}{C_2}\right)^n$$

$$\log \frac{r_1}{r_2} = n \log \frac{C_1}{C_2}$$

$$n = \frac{\log r_1/r_2}{\log C_1/C_2}$$

Dr. U. Subuddhi, NITRkl

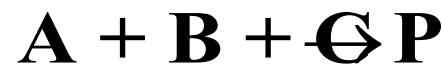
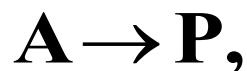
2. Method of Integration

This method needs to first make a tentative guess on what might be the order of the reaction and the corresponding differential equation is integrated. The constant value of 'k' if obtained suggests the correctness of the guess.

Disadvantage Since best fit would give the order, accuracy is a problem. For fractional order or complex reaction this method will fail.

1. First Order Reaction

The reaction can be of any type such as



$A \rightarrow P$

$$\frac{dx}{dt} = k (a_0 - x)$$

$$\frac{dx}{(a_0 - x)} = k dt$$

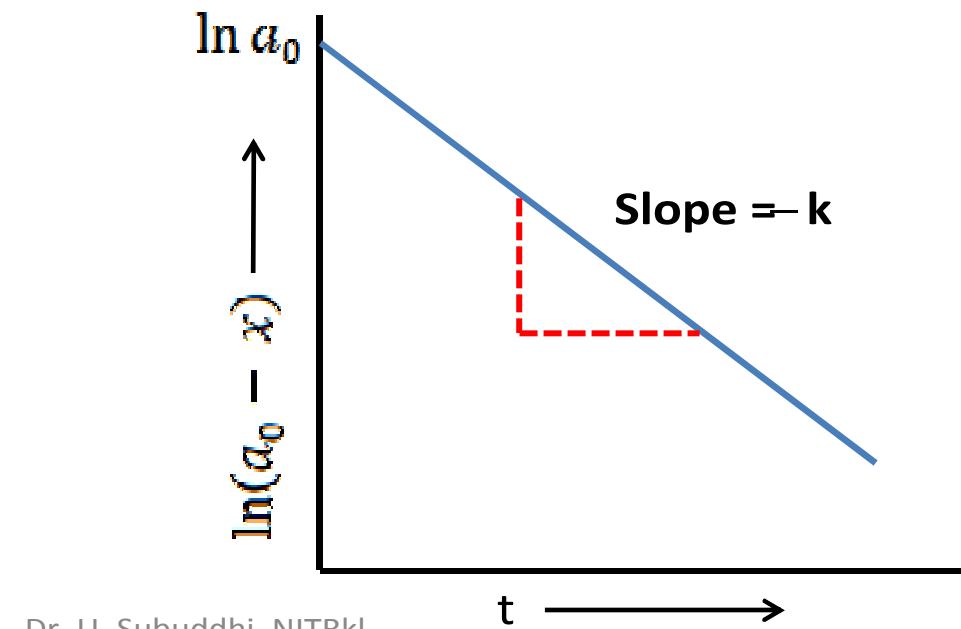
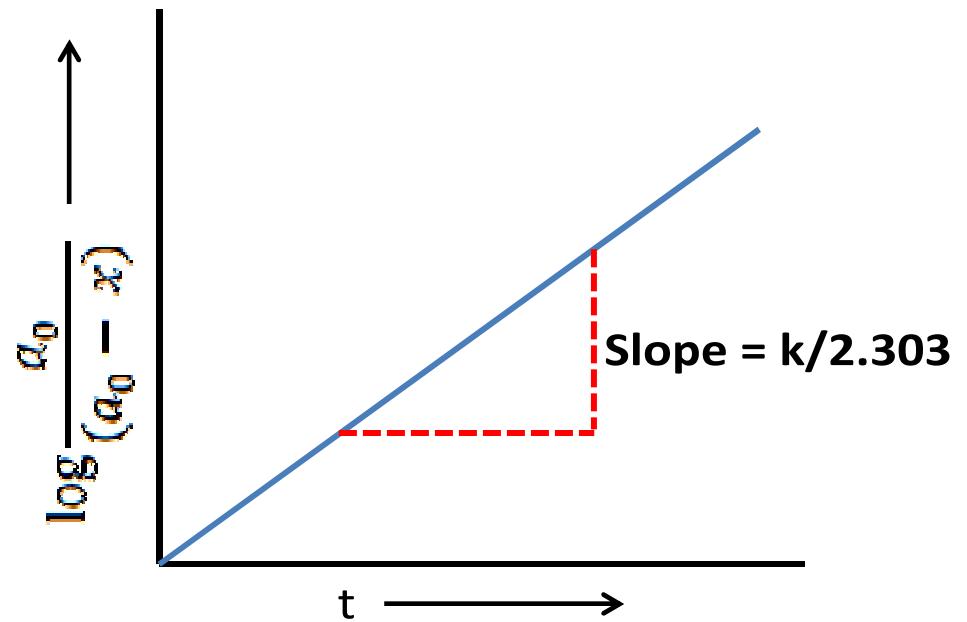
$$\int_0^x \frac{dx}{(a_0 - x)} = k \int_0^t dt$$

$$[-\ln(a_0 - x)]_0^x = k [t]_0^t$$

$$\ln \frac{a_0}{(a_0 - x)} = kt$$

$$2.303 \log \frac{a_0}{(a_0 - x)} = kt$$

$$\boxed{\log \frac{a_0}{(a_0 - x)} = \frac{k}{2.303} t}$$

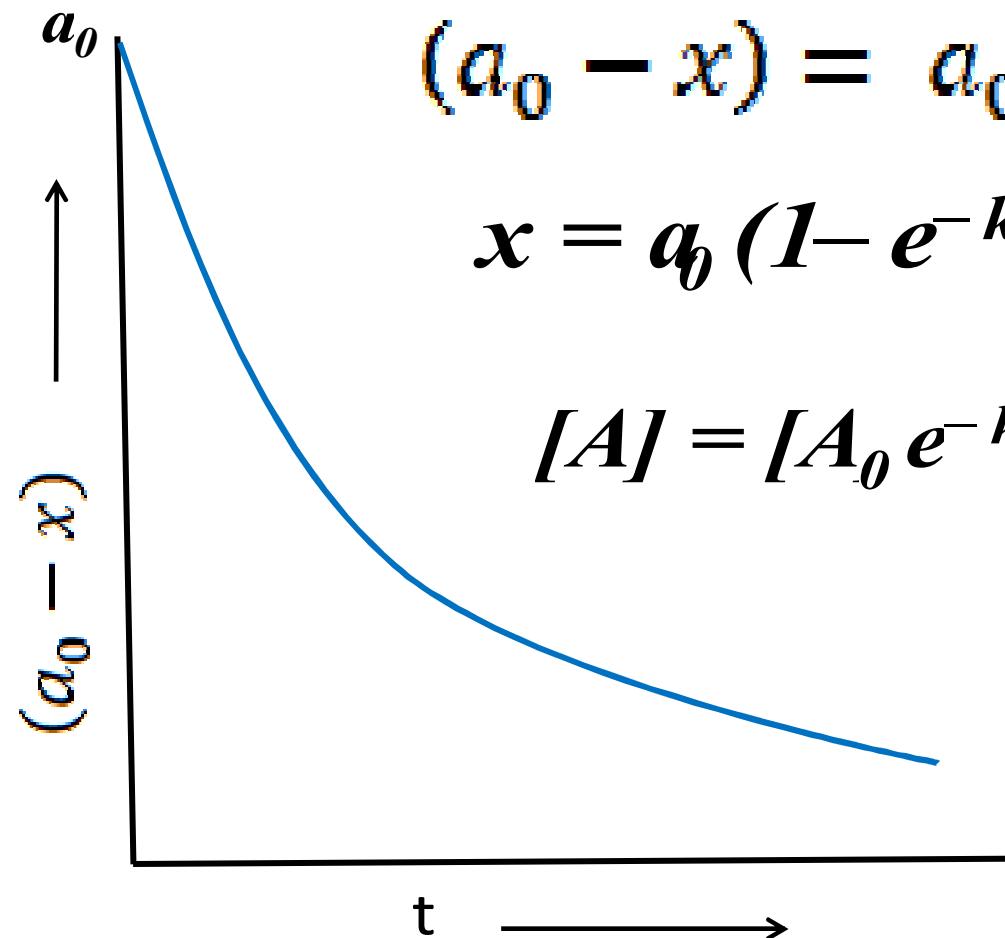


$$\ln \frac{a_0}{(a_0 - x)} = kt$$

$$(a_0 - x) = a_0 e^{-kt}$$

$$x = a_0 (1 - e^{-kt})$$

$$[A] = [A_0] e^{-kt}$$



2. Second-Order Reaction

The reaction can be any type such as



$$\text{Rate} = k(a_0 - x)^2$$

$$\frac{dx}{dt} = k(a_0 - x)^2$$

$$\frac{dx}{(a_0 - x)^2} = k dt$$

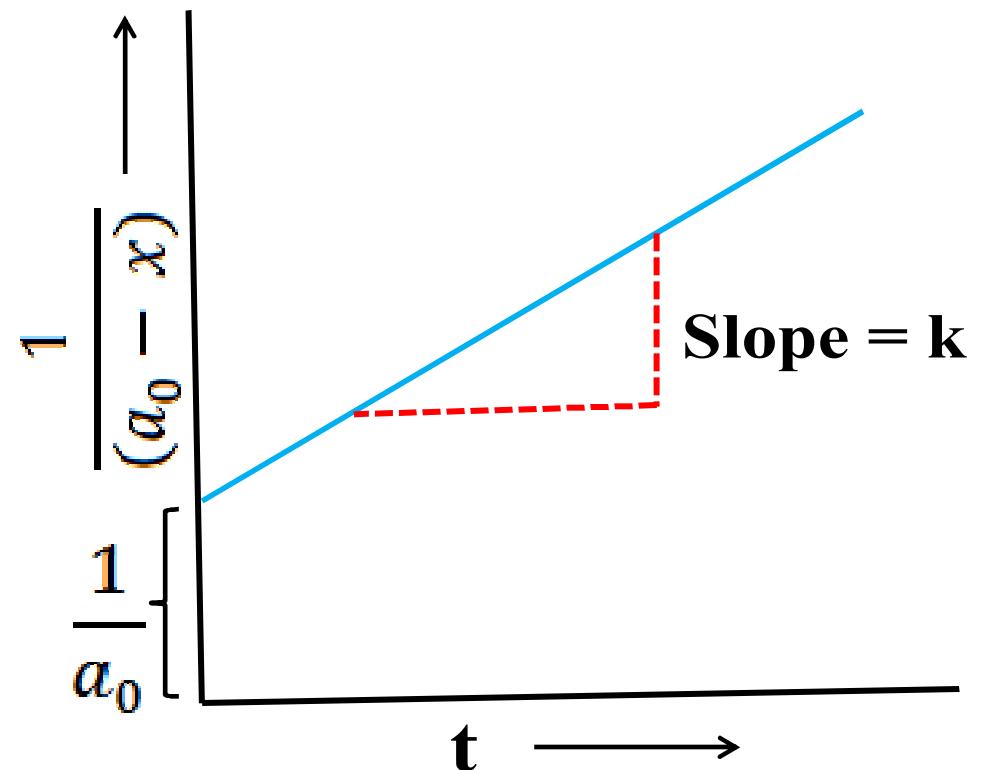
$$\int_0^x \frac{dx}{(a_0 - x)^2} = k \int_0^t dt$$

$$\frac{1}{(a_0 - x)} - \frac{1}{a_0} = kt$$



$$\text{Rate} = k(a_0 - x)^2 \text{ if } a_0 = t_0$$

$$\text{Rate} = k(a_0 - x)(b_0 - x)$$



$$\frac{dx}{dt} = k (a_0 - x)(b_0 - x)$$

$$\int_0^x \frac{dx}{(a_0 - x)(b_0 - x)} = k \int_0^t dt$$

$$\frac{1}{(a_0 - x)(b_0 - x)} = \frac{1}{(a_0 - b_0)} \left[\frac{1}{(b_0 - x)} - \frac{1}{(a_0 - x)} \right]$$

$$\frac{1}{(a_0 - b_0)} \left[\int_0^x \frac{dx}{(b_0 - x)} - \int_0^x \frac{dx}{(a_0 - x)} \right] = k \int_0^t dt$$

$$\frac{1}{(a_0 - b_0)} \ln \frac{b_0(a_0 - x)}{a_0(b_0 - x)} = kt$$

Dr. U. Subuddhi, NITRkl

3. ZeroOrder Reaction

Catalytic decomposition of phosphine (PH_3)
on hot tungsten at high pressures

Let's consider the reaction



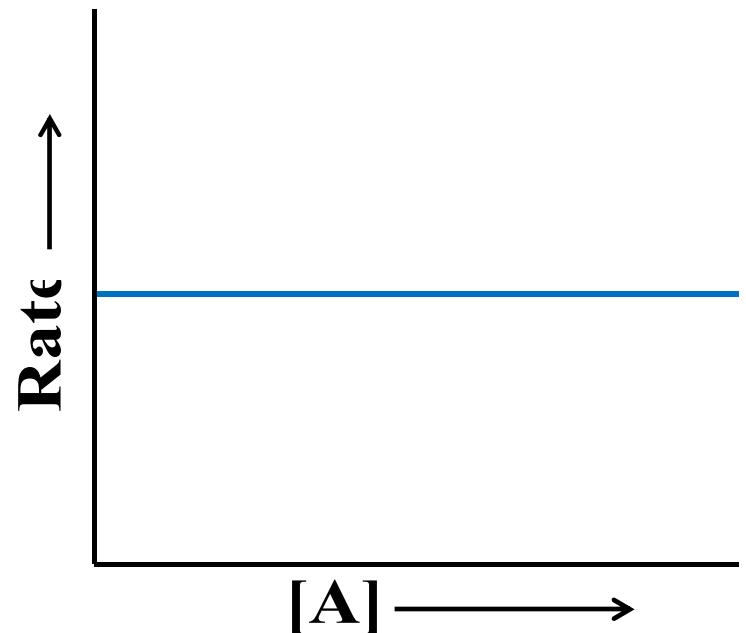
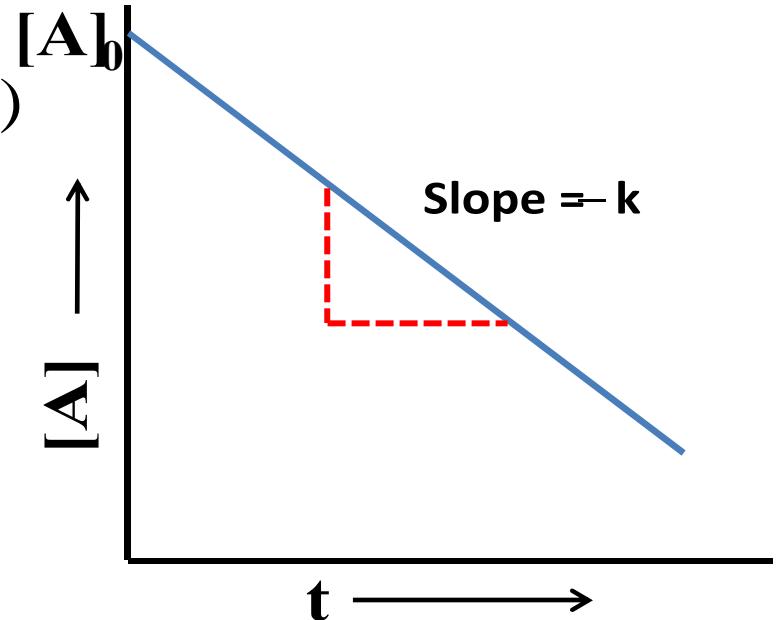
$$\text{Rate} = k[\text{A}]^p = k(\text{constant})$$

$$-\frac{d[\text{A}]}{dt} = k$$

$$-\int_{[\text{A}]_0}^{[\text{A}]} d[\text{A}] = k \int_0^t dt$$

$$kt = [\text{A}]_0 - [\text{A}]$$

Dr. U Subuddhi, NITRkl



4. nth-Order Reaction

Let's consider the reaction $A \rightarrow P$

$$\frac{dx}{dt} = k (a_0 - x)^n$$

$$\frac{dx}{(a_0 - x)^n} = k dt$$

$$\int_0^x \frac{dx}{(a_0 - x)^n} = k \int_0^t dt$$

$$\frac{1}{(n-1)t} \left[\frac{1}{(a_0 - x)^{n-1}} - \frac{1}{a_0^{n-1}} \right] = k$$

Dr. U. Subuddhi, NITRkl

Methods for Determination of Order of a Reaction

1. Differential Method

2. Method of Integration

3. Half-life Method

4. Isolation Method

3. Method of Half-Life

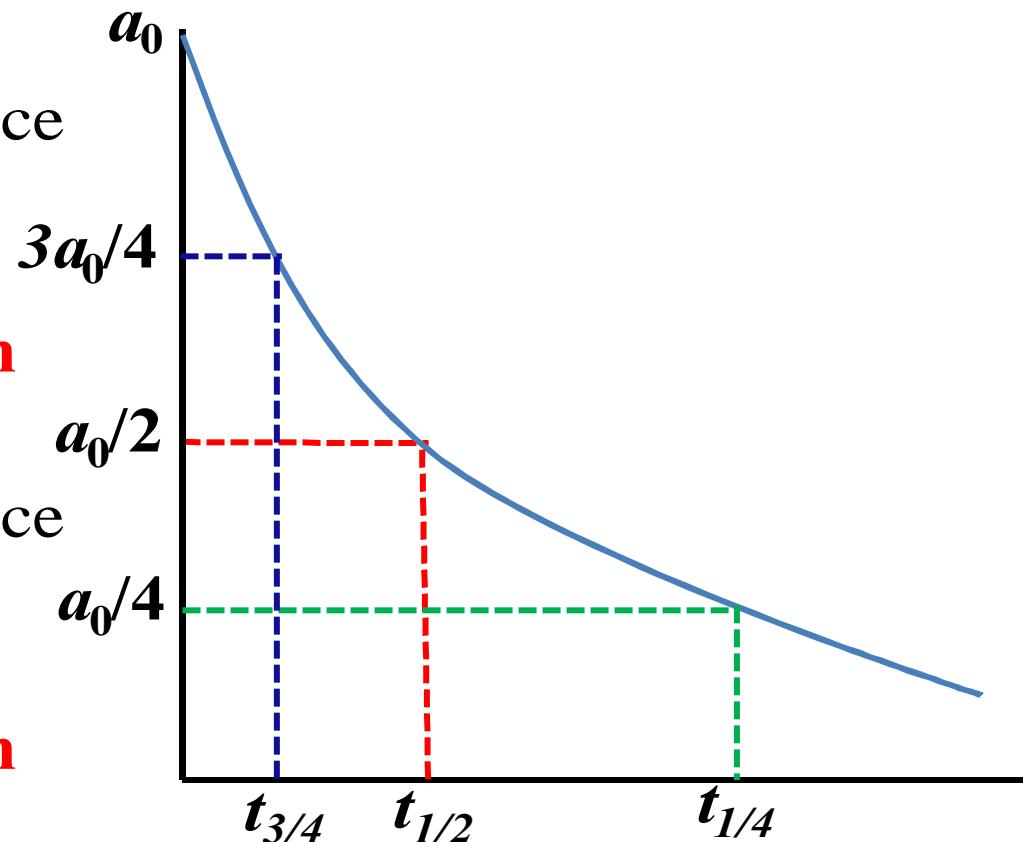
For a reaction the half-life $t_{1/2}$ of a particular reactant is defined as the time required **reduce the concentration to half of initial value**

$t_{1/4}$: the time required to reduce the concentration to one-fourth of the initial value

(75% completion of reaction)

$t_{3/4}$: the time required to reduce the concentration to three-fourth of the initial value

(25% completion of reaction)



For a 1st order reaction

$$\ln \frac{a_0}{(a_0 - x)} = kt$$

$$\text{At } t_{1/2} \quad (a_0 - x) = a_0/2 \Rightarrow x = a_0/2$$

$$\ln \frac{a_0}{\left(a_0 - \frac{a_0}{2}\right)} = kt_{1/2}$$

$$t_{1/2} = \frac{0.693}{k}$$

For 1st order reaction the **half-life is independent of the initial concentration of the reactant**

Dr. U. Subuddhi, NITRkl

Another indication of the rate of a first-order reaction is the **time constant, τ** , the **time required for the concentration of a reactant to fall to $(1/e)$ of its initial value**.

$$\ln \frac{a_0}{a_x} = kt$$

$t = \tau$ = relaxation time time constant

$(a_0 - a_x) / a_0$

$$k\tau = \ln \frac{a_0}{a_0 - a_x}$$

$$\tau = \frac{1}{k} \text{ relaxation time}$$

Dr. U. Subuddhi, NITRkl

For a 2^d order reaction

For a 2^d order reaction involving a single reactant or two reactants of equal initial concentrations and reacting acc to the stoichiometry



$$\frac{1}{(a_0 - x)} - \frac{1}{a_0} = kt$$

$$\text{At } t_{1/2} \quad (a_0 - x) = a_0/2 \Rightarrow x = a_0/2$$

$$t_{\frac{1}{2}} = \frac{1}{k a_0}$$

For 2nd order reaction the **half life is inversely proportional to the initial concentration of the reactant**

Dr. U. Subuddhi, NITRkl

When there is only one reactant the half-life of the reactant is also the half-life of the reaction

But this is not true particularly for reactions of higher order with more than one type of reactants and of unequal initial concentration and/or different stoichiometry



$$\text{At } t=0 \quad a_0 \quad b_0 \quad 0$$

$$\text{At } t=t \quad (a_0 - x) \quad (b_0 - x) \quad x$$

$$\text{Rate} = k(a_0 - x)(b_0 - x)$$



$$\text{At } t=0 \quad a_0 \quad b_0 \quad 0$$

$$\text{At } t=t \quad (a_0 - x) \quad (b_0 - 2x) \quad x$$

$$\text{Rate} = k(a_0 - x)(b_0 - 2x)$$

At $t_{1/2}$ of A, $(a_0 - x) = a_0/2$ but it is not necessary that at this time $(b_0 - x) = b_0/2$ and vice versa

Dr. U. Subuddhi, NITRkl

For a Zero order reaction

$$kt = [A]_0 - [A]$$

$$\text{At } t = t_{1/2} \quad [A] = [A_0]/2$$

$$kt_{1/2} = [A_0] - [A_0]/2$$

$$t_{1/2} = [A_0]/2k$$

$$t_{1/2} \propto [A_0]$$

For a zero order reaction the **halflife is directly proportional to the initial concentration of the reactant**

Dr. U. Subuddhi, NITRkl

For a n^{th} order reaction

$$\frac{1}{(n-1)} \left[\frac{1}{\left(a_0 - \frac{a_0}{2}\right)^{n-1}} - \frac{1}{a_0^{n-1}} \right] = kt_{1/2}$$

$$\frac{1}{(n-1)} \left[\frac{2^{n-1}}{a_0^{n-1}} - \frac{1}{a_0^{n-1}} \right] = kt_{1/2}$$

$$\frac{(2^{n-1} - 1)}{(n-1)} \left[\frac{1}{a_0^{n-1}} \right] = kt_{1/2}$$

$$t_{1/2} \propto \frac{1}{a_0^{n-1}}$$

Dr. U. Subuddhi, NITRKL

$$t_{1/2} \propto \frac{1}{a_0^{n-1}}$$

If $(t_{1/2})_1$ and $(t_{1/2})_2$ are the half lives at two initial concentrations $a_0)_1$ and $(a_0)_2$, respectively then

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{(a_0)_2}{(a_0)_1}\right)^{n-1}$$

$$\log \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n - 1) \log \left(\frac{(a_0)_2}{(a_0)_1}\right)$$

4. Isolation Method

If **all the reactants except one are present in excess**, the apparent order will be the order w.r.t. the one “isolated reactant”

If a reaction rate is expressed as: Rate = $k [A]^{\alpha} [B]^{\beta} [C]^{\gamma}$
B and C are taken in excess of A and the order w.r.t A is determined which will be ‘ α ’.

The order w.r.t. B and C can also be determined by similar procedure

This method is often used in conjunction with other methods.

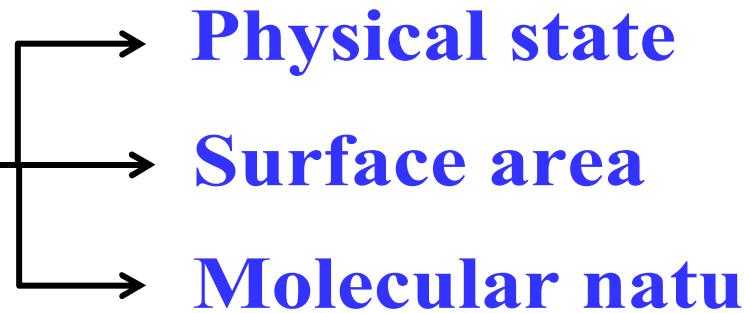
Sometimes taking a large excess of concentration of a particular reactant may change the mechanism of a composite reaction

Dr. U. Subuddhi, NITRkl

Factors Affecting the Rate of a Reaction

1. Concentration of the reactants

2. Nature of reactants



3. Effect of Temperature

4. Presence of a Catalyst

3. Effect of Temperature

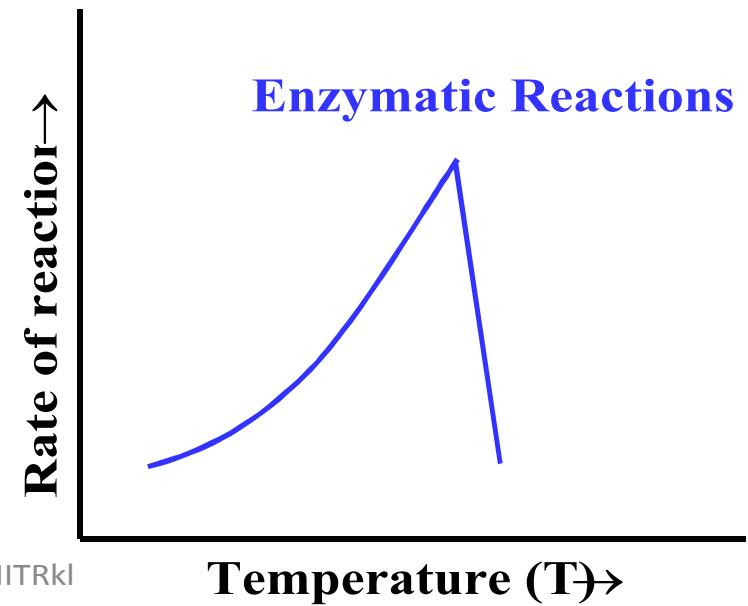
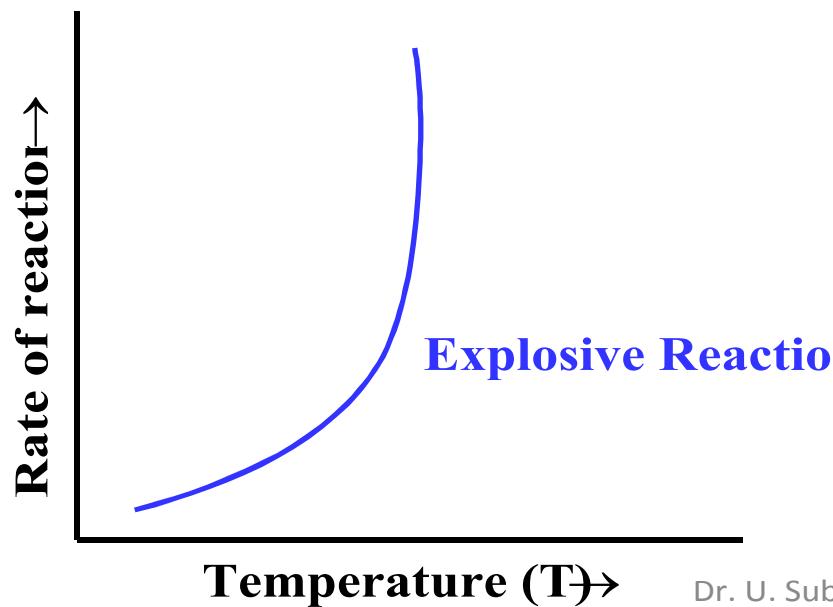
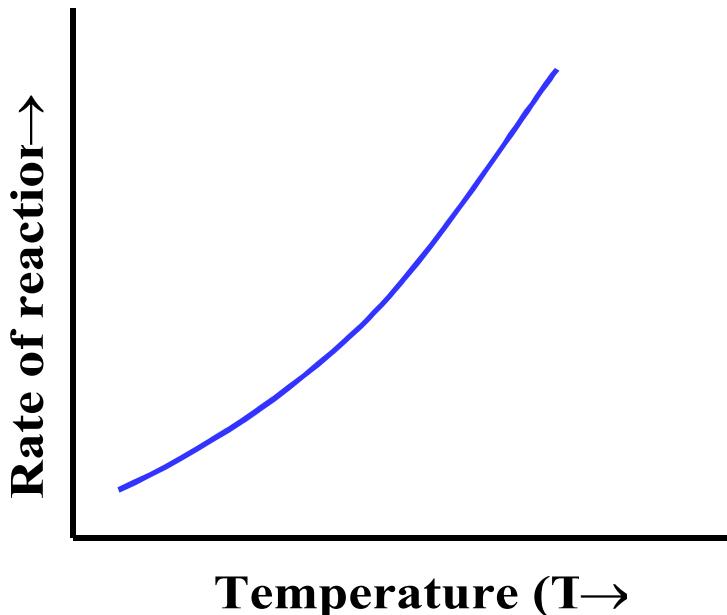
Temperature has a marked effect on the reaction.

- (i) Can initiate a reaction
- (ii) Increases the rate of the reaction

For a reaction the thermodynamic requirement is $\Delta G^0 = -ve$
$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

If temperature (T) is increased,
the term $T\Delta S^0$ increases relatively by a larger extent as
compared to that of ΔH^0 hence ΔG^0 can become $-ve$ and the
reaction can be initiated

Rate of reaction increases with increase in temperature



For most of the reactions the rate of the reaction doubles or triples by raising the temperature by 10 K

$$\text{Temperature Coefficient} = \frac{\text{Rate constant at } (T+10)}{\text{Rate constant at } T \text{ K}}$$

Why does temperature speed up a reaction ?

A chemical reaction takes place due to intermolecular collisions. On increasing temperature the kinetic energy of reacting molecules increases and hence collision frequency increases.

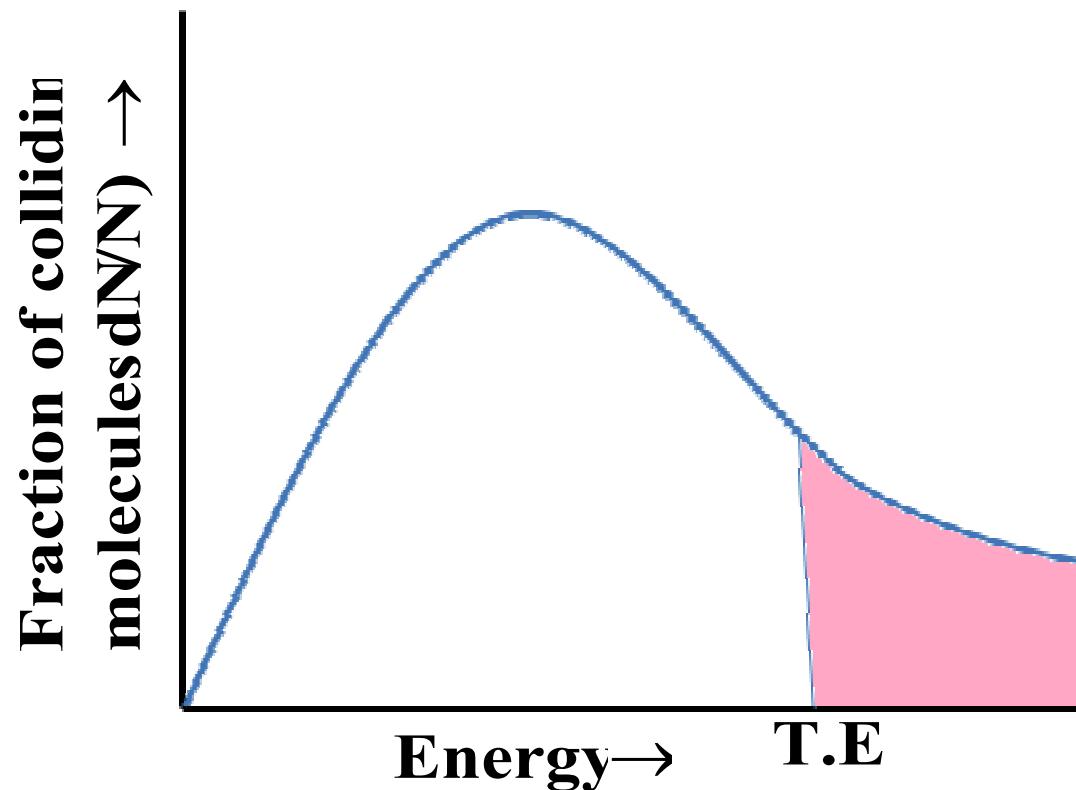
$$Z \propto \sqrt{T}$$

$$\frac{Z_{300}}{Z_{298}} = \sqrt{\frac{308}{298}} \approx 1.02 \quad \text{Only 2% increase!!}$$

Increase in collision frequency alone can't explain the large increase in rates with temperature

Dr. U. Subudhi, NTRKI

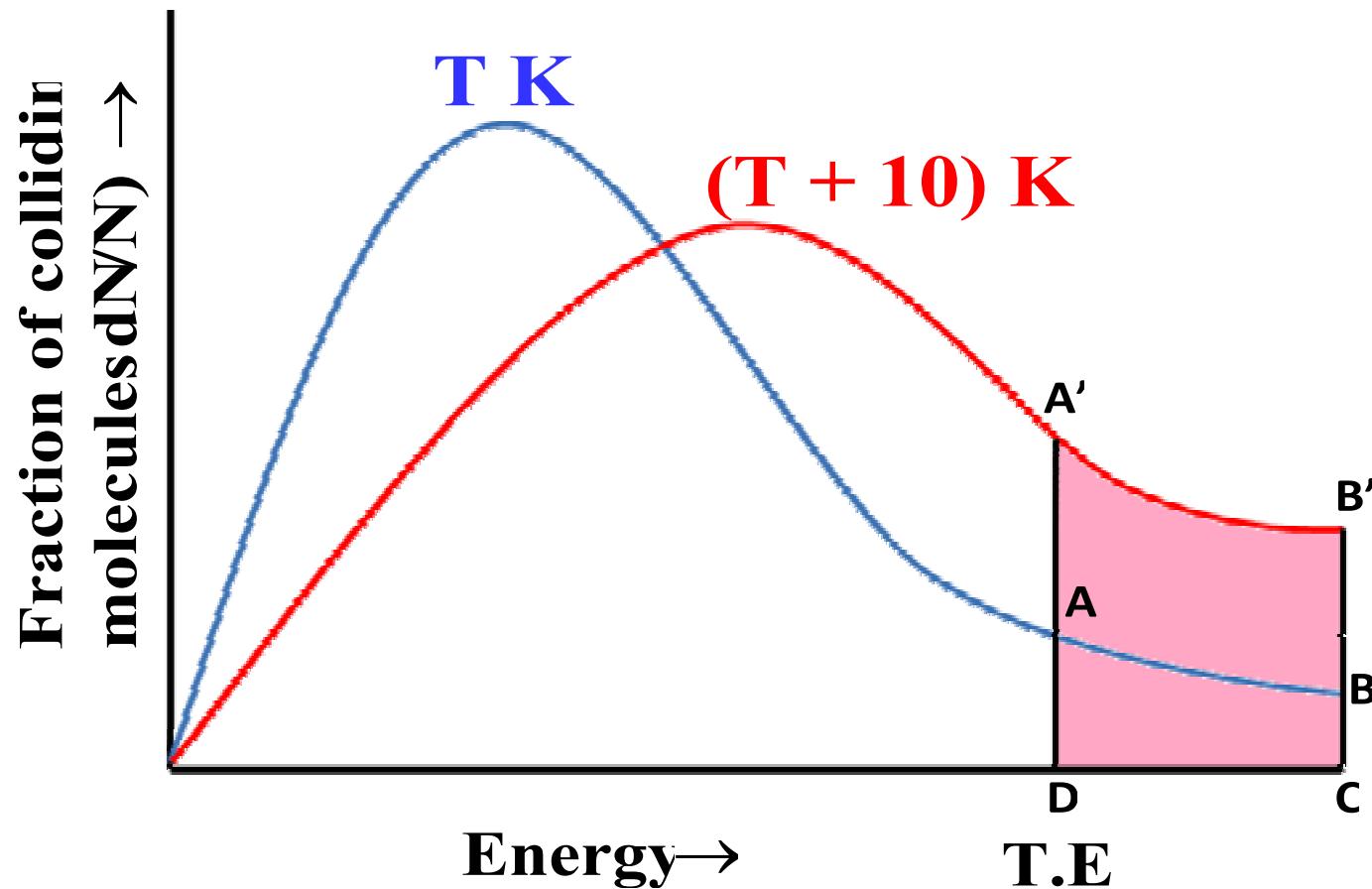
Collision theory along with Maxwell's distribution of energies is necessary to explain the effect of temperature on the rate of a chemical reaction



Collision between molecules possessing energy equal to or greater than the threshold energy is called effective collision

Dr. U. Subuddhi, NITRkl

Number of molecules possessing lower energies decreases, whereas the number of molecules possessing higher energies increases with increase in temperature



Number of effective collisions become double or more, which results in the observed increase in the rate



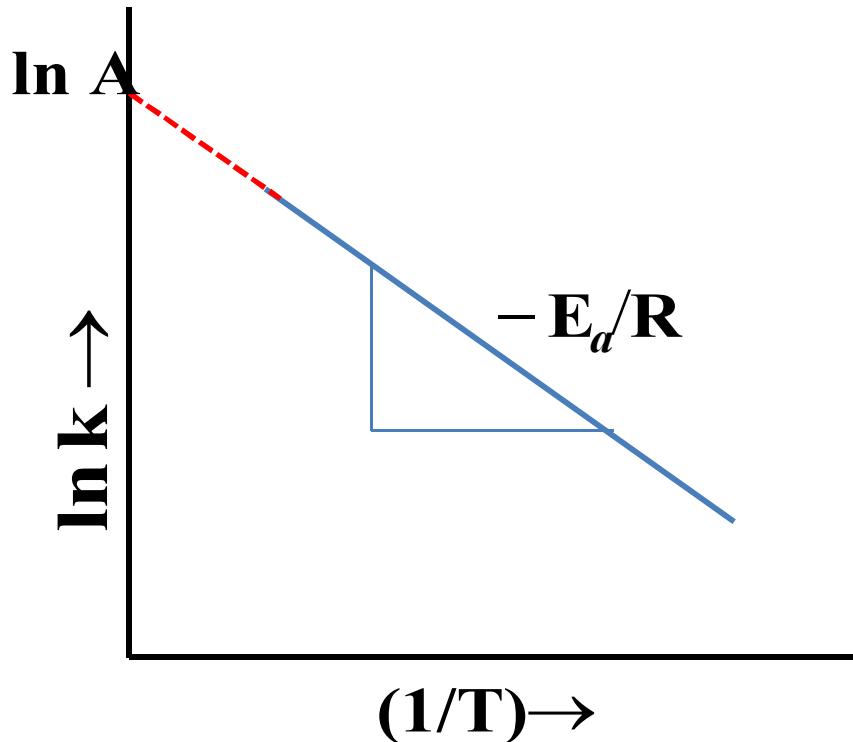
Svante August Arrhenius
(1859–1927)

Nobel Prize for Chemistry (1903): conductivities of electrolytes

In 1889 Arrhenius explained the fact that most reactions require added heat energy to proceed by formulating the concept of activation energy, an energy barrier that must be overcome before two molecules will react. The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds.

Dr. U. Subuddhi, NITRkl

Arrhenius Equation



$$\ln k = \ln A - \frac{E_a}{RT}$$

$$k = A e^{-E_a/RT}$$

'A' and ' E_a ' are called Arrhenius parameters

A : Preexponential factor or Frequency factor or
Limiting rate constant

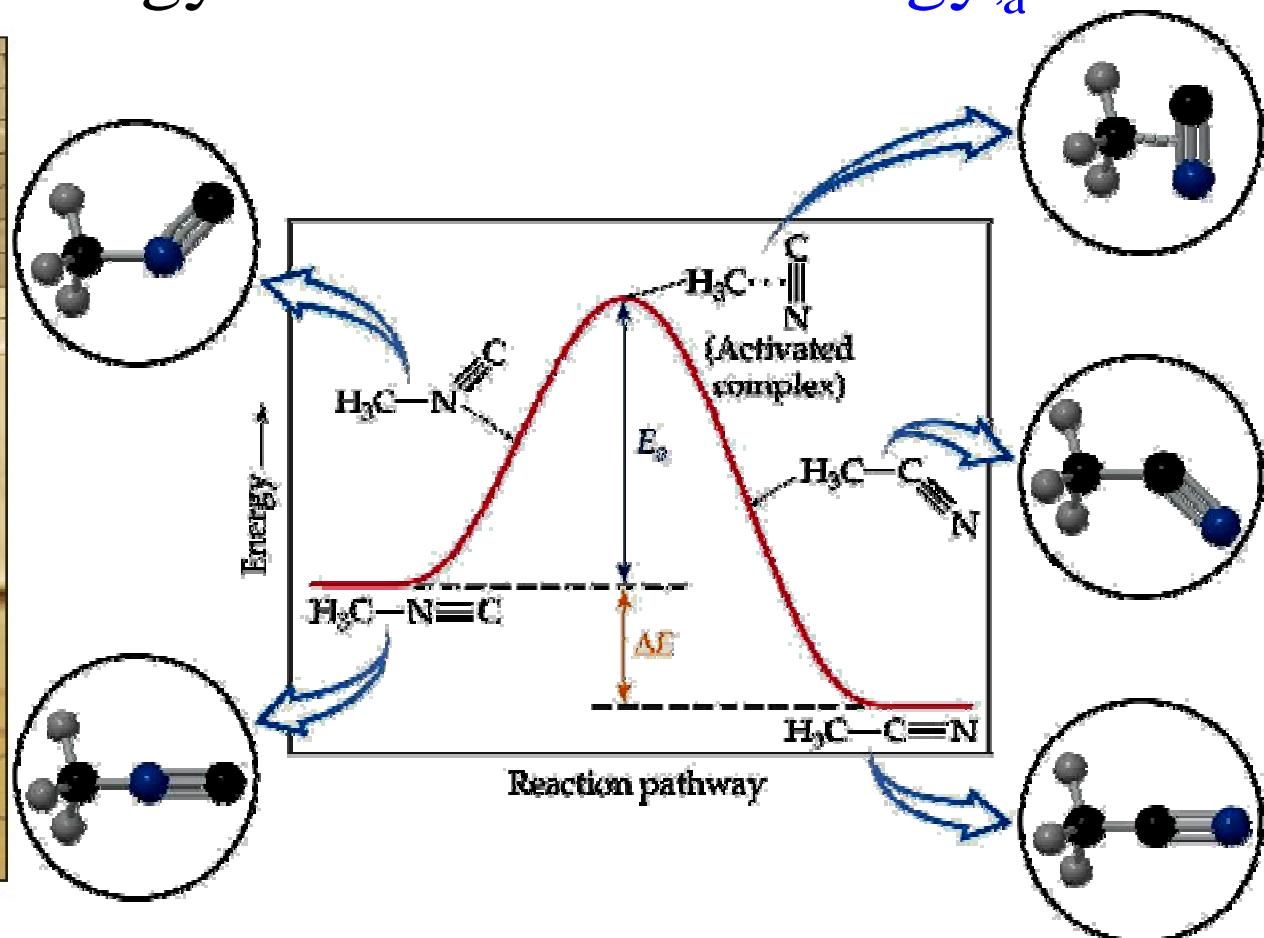
E_a : Activation energy

A higher activation energy signifies that the rate constant depends strongly on temp.

Activation Energy

Molecules need a minimum amount of energy to react.

Visualized as an energy barrier- activation energy,_a



Even though reaction is exothermic, the reaction still needs an activation en-

The lower the Activation barrier, the faster is the reaction

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

If the activation energy (E_a) and pre-exponential factor (A) are independent of temperature

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Dr. U. Subuddhi, NITRkl

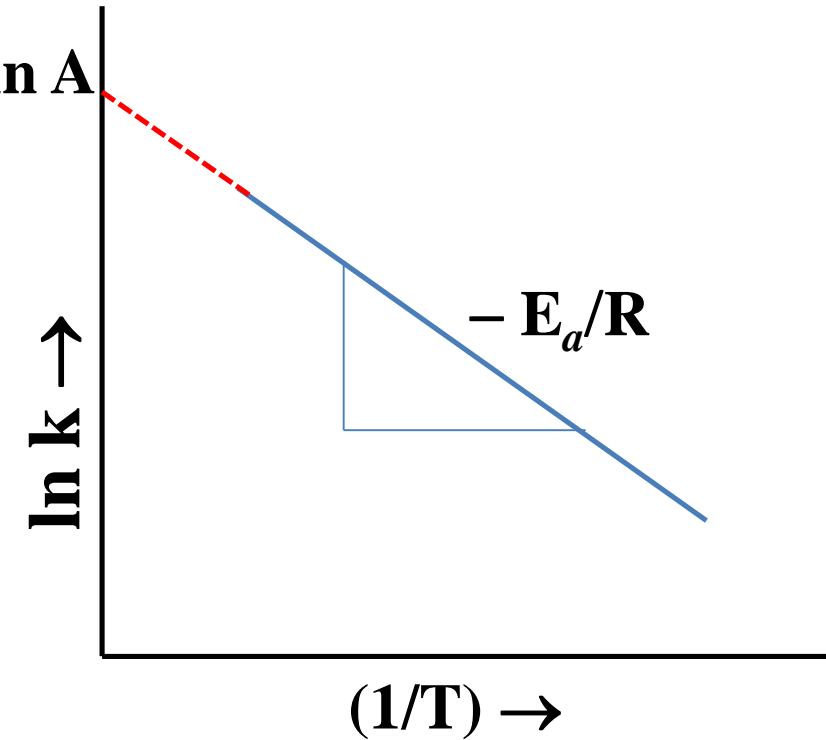


Svante August Arrhenius
(1859 –1927)

Nobel Prize for Chemistry (1903): conductivities of electrolytes

In 1889 Arrhenius explained the fact that most reactions require added heat energy to proceed by formulating the concept of activation energy, an energy barrier that must be overcome before two molecules will react. The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds.

Arrhenius Equation



$$\ln k = \ln A - \frac{E_a}{RT}$$

$$k = A e^{-E_a/RT}$$

‘A’ and ‘ E_a ’ are called Arrhenius parameters

A: Pre-exponential factor or Frequency factor or
Limiting rate constant

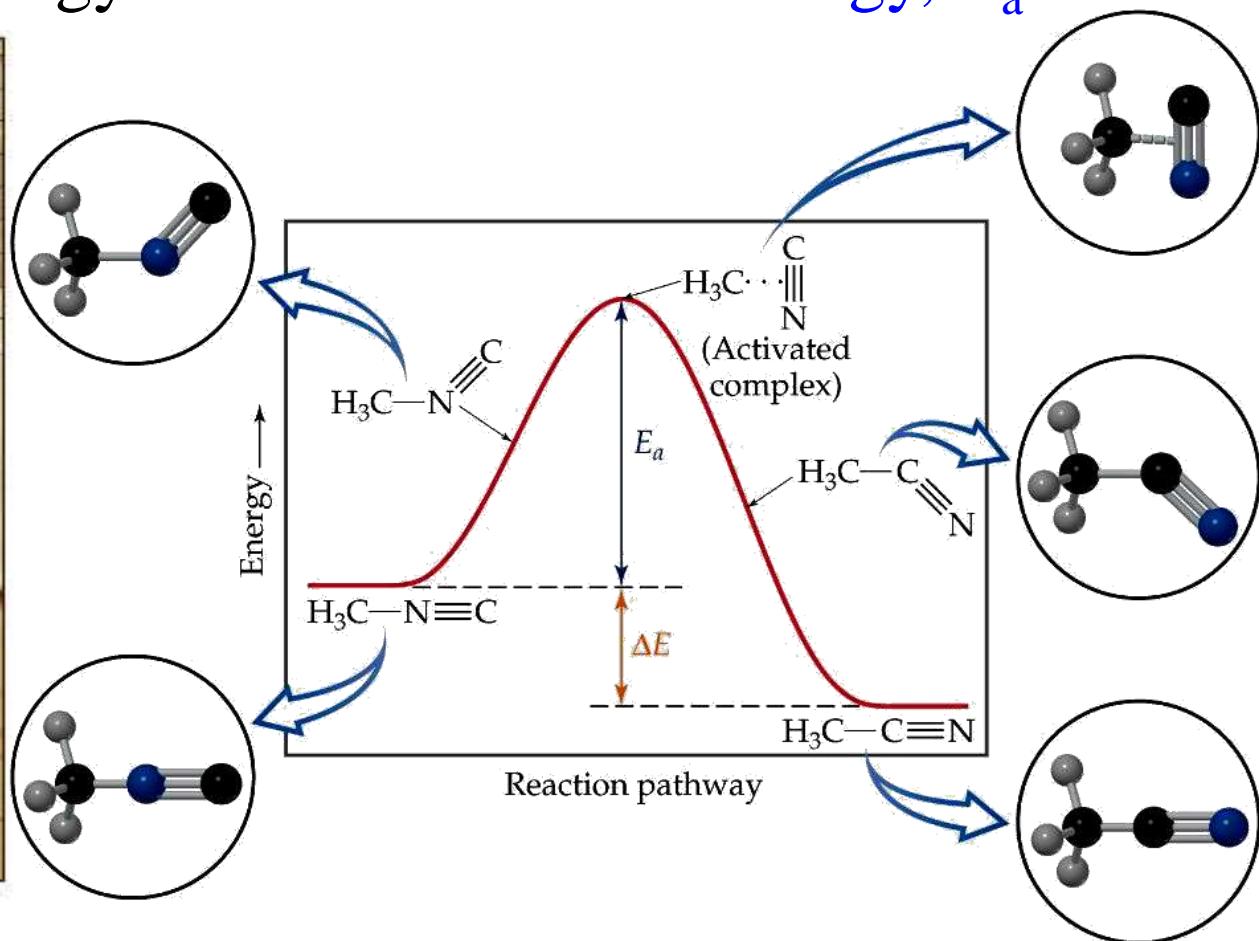
E_a : Activation energy

A higher activation energy signifies that the rate constant depends strongly on temp.

Activation Energy

Molecules need a minimum amount of energy to react.

Visualized as an energy barrier - activation energy, E_a



Even though reaction is exothermic, the reaction still needs an activation energy.

The lower the Activation barrier, the faster is the reaction

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

If the activation energy (E_a) and pre-exponential factor (A) are independent of temperature

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

COMPLEX REACTIONS

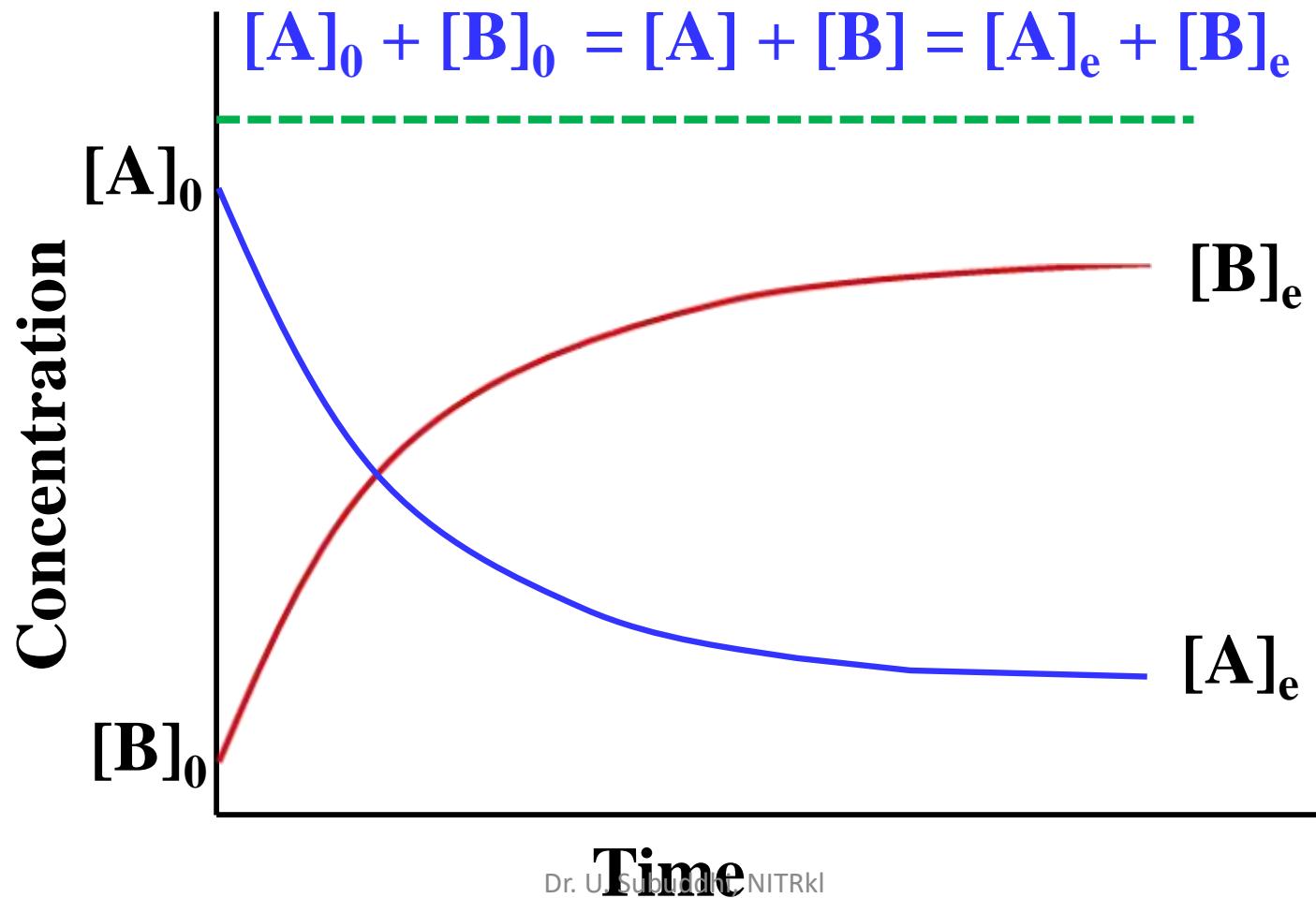
1. Reversible Reactions or Opposing Reactions

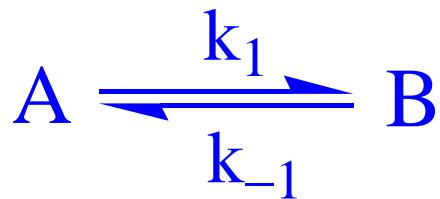
2. Parallel Reactions

3. Consecutive Reactions

4. Chain Reactions

1. Reversible Reactions or Opposing Reactions

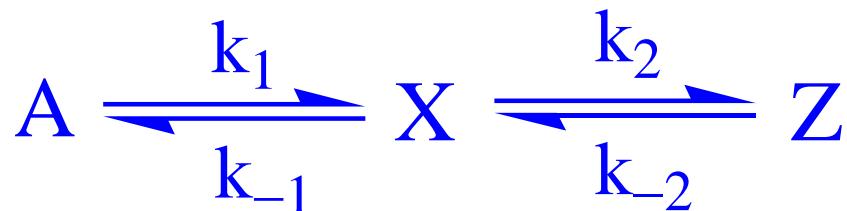




$$\frac{-d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$$

At equilibrium $k_1[A]_e = k_{-1}[B]_e$

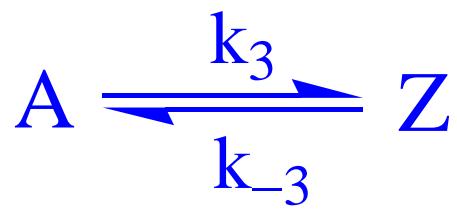
$$K_c = \frac{k_1}{k_{-1}} = \frac{[B]_e}{[A]_e}$$



$$\frac{k_1}{k_{-1}} = \frac{[X]_e}{[A]_e} = K_1$$

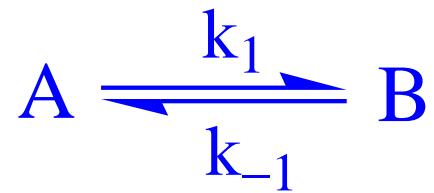
$$\frac{k_2}{k_{-2}} = \frac{[Z]_e}{[X]_e} = K_2$$

$$\frac{[Z]_e}{[A]_e} = \frac{k_1 k_2}{k_{-1} k_{-2}} = K_1 K_2$$



$$K_c = \frac{k_3}{k_{-3}} = \frac{[Z]_e}{[A]_e} = \frac{k_1 k_2}{k_{-1} k_{-2}} = K_1 K_2$$

Principle of Microscopic Reversibility



$$t = 0 \quad a_0 \quad 0$$

$$t = t \quad (a_0 - x) \quad x$$

$$t = t_e \quad (a_0 - x_e) \quad x_e$$

Rate of forward reaction = $k_1(a_o - x)$

Rate of backward reaction = $k_{-1}x$

The net rate of change of concentration of B

$$\frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x$$

At equilibrium the rate of forward reaction

= rate of backward reaction
Dr. U. Subuddhi, NITRkl

$$k_1(a_0 - x_e) = k_{-1}x_e \Rightarrow k_{-1} = \frac{k_1(a_0 - x_e)}{x_e}$$

$$\frac{dx}{dt} = k_1(a_0 - x) - \frac{k_1(a_0 - x_e)}{x_e} x$$

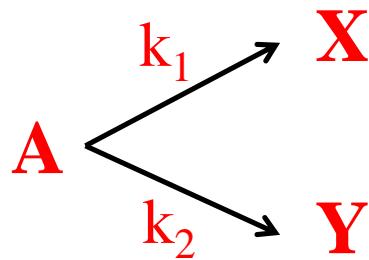
$$\frac{dx}{dt} = \frac{k_1 a_0}{x_e} (x_e - x) \quad \int_0^x \frac{dx}{(x_e - x)} = \frac{k_1 a_0}{x_e} \int_0^t dt$$

$$k_1 t = \frac{x_e}{a_0} \ln \frac{x_e}{(x_e - x)}$$

$$\frac{x_e}{a_0} = \frac{k_1}{k_1 + k_{-1}}$$

$$(k_1 + k_{-1}) = \frac{1}{t} \ln \frac{x_e}{(x_e - x)}$$

$$(k_1 + k_{-1}) = \frac{1}{t} \ln \frac{[A]_0 - [A]_{eq}}{[A] - [A]_{eq}}$$



Let's consider both are first order reactions

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A] = k[A]$$

$$[A] = [A]_0 e^{-kt}$$

$$\frac{d[X]}{dt} = k_1[A] = k_1[A]_0 e^{-kt}$$

$$\int_0^{[X]} d[X] = k_1[A]_0 \int_0^t e^{-kt} dt$$

$$[Y] = \frac{k_2[A]_0}{k} \left(1 - e^{-kt}\right)$$

$$[X] = \frac{k_1[A]_0}{k} \left(1 - e^{-kt}\right)$$

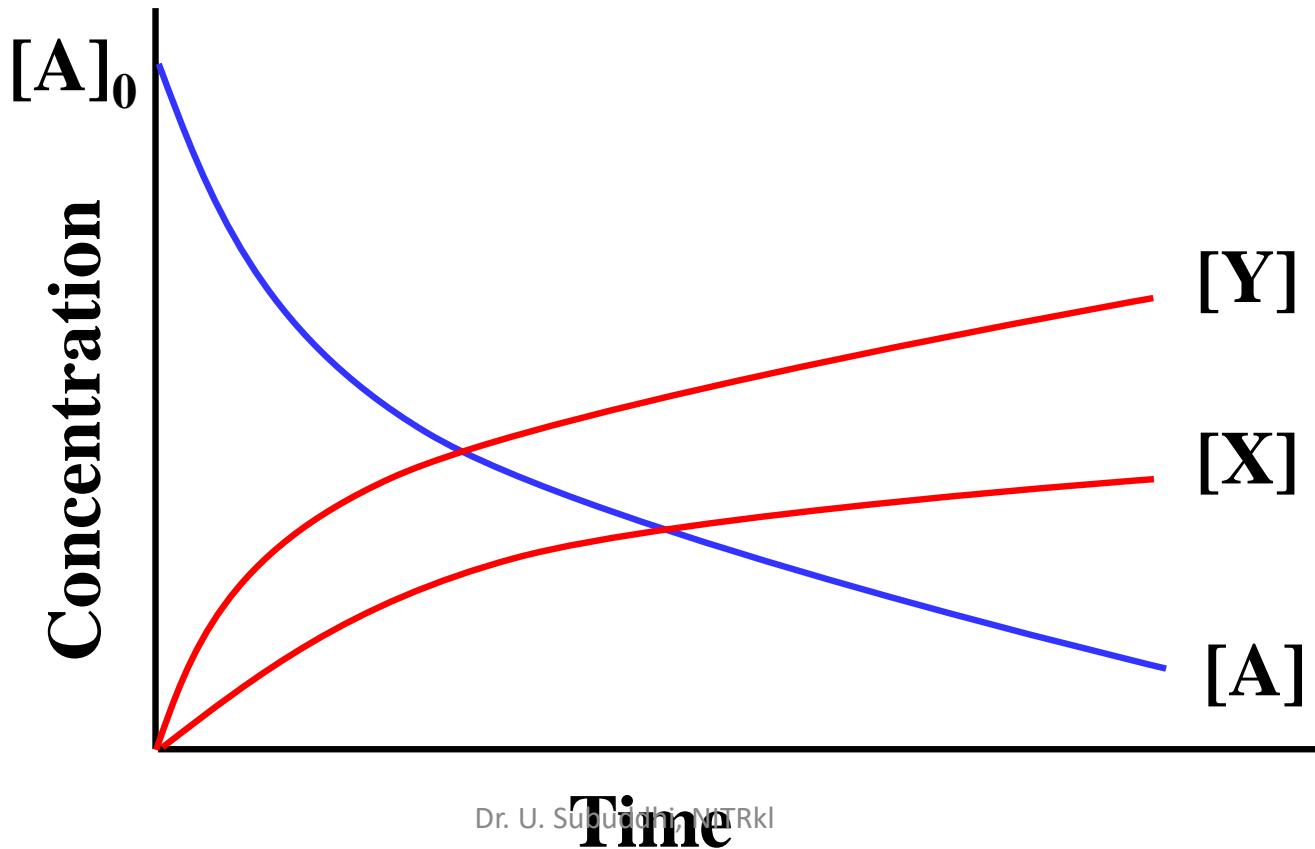
$$\frac{[X]}{[Y]} = \frac{k_1}{k_2}$$

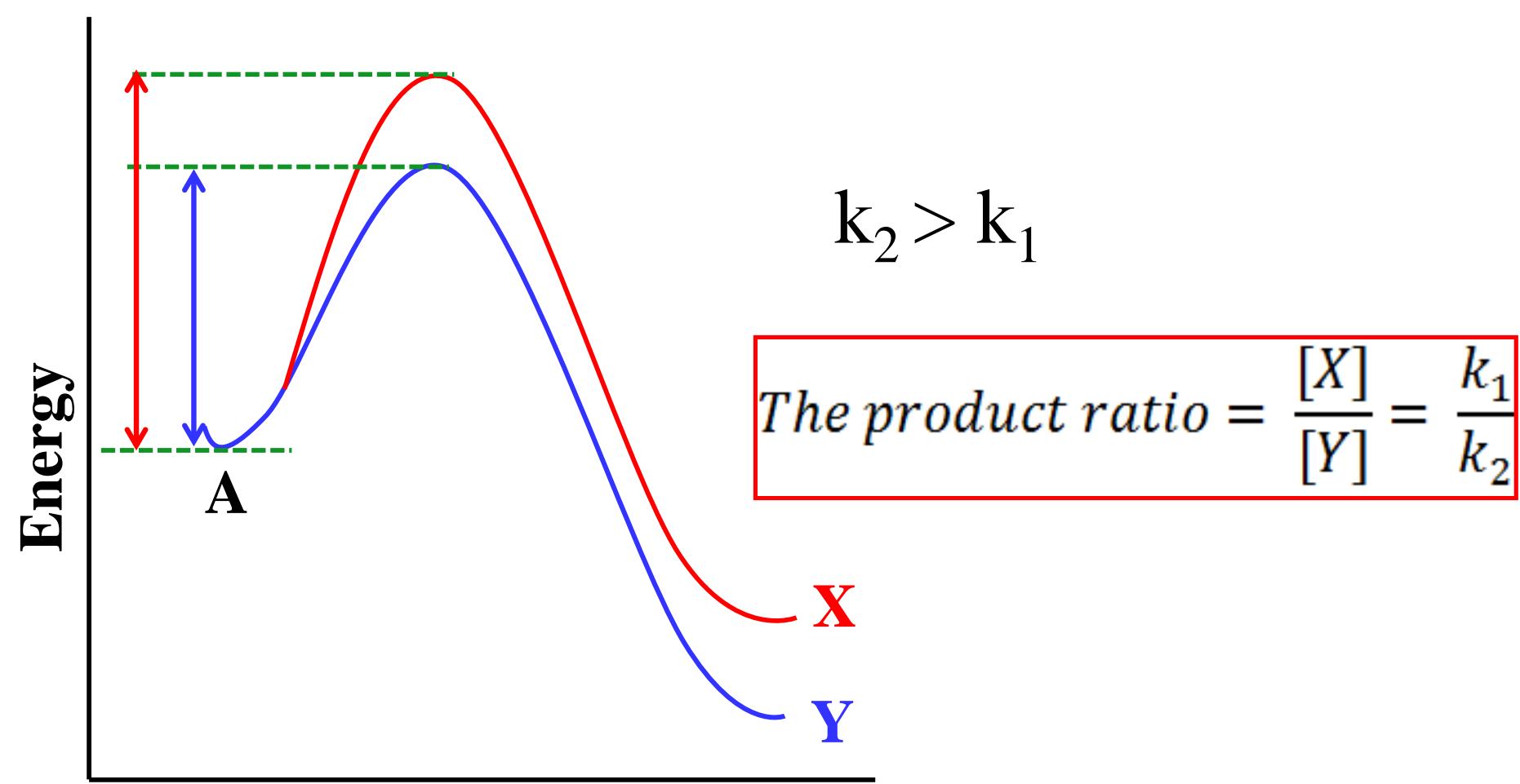
The product ratio is equal to the ratio of the corresponding rate constants

Parallel or Competitive Reaction



$$\frac{-d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A] = k[A]$$



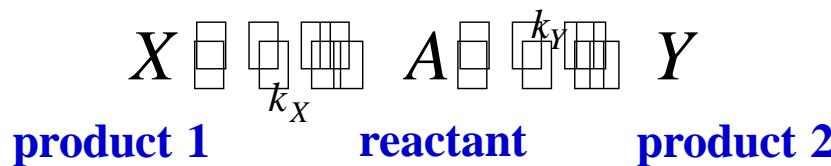


Wegscheider's test for side reactions

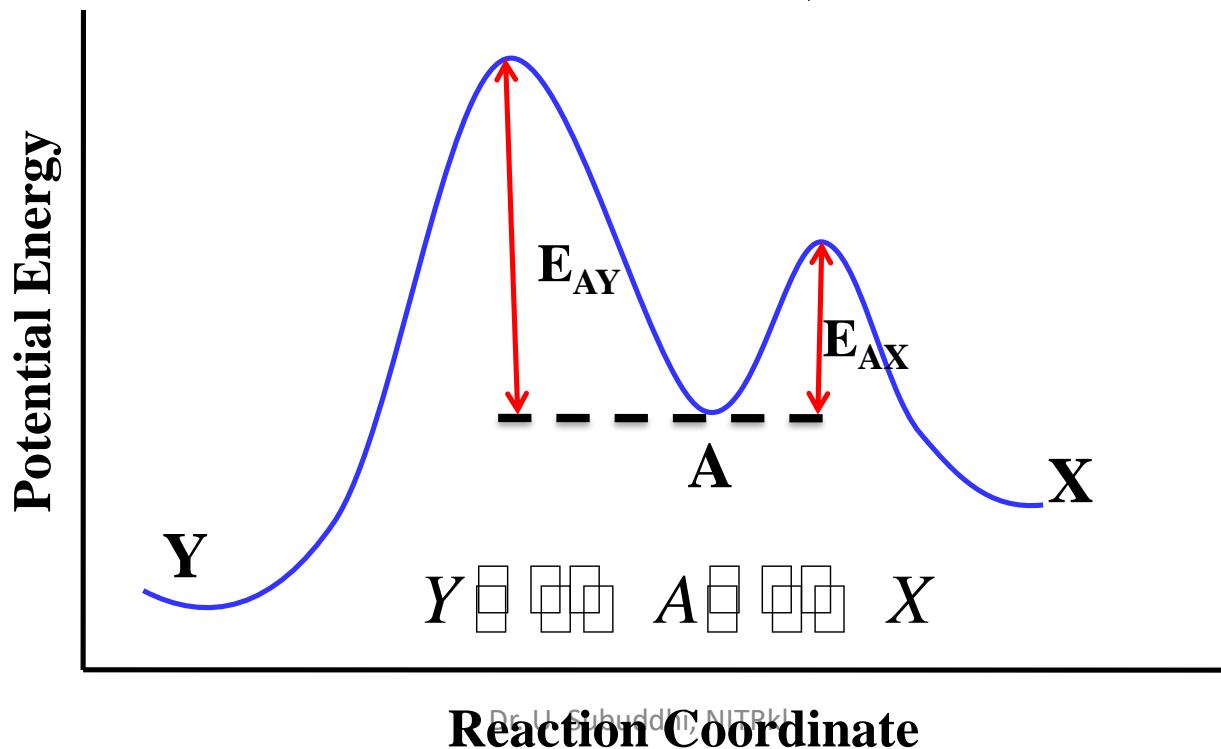
Ratio of the amounts of the substances formed in two side reactions is independent of time provided the order of the two side reactions is same

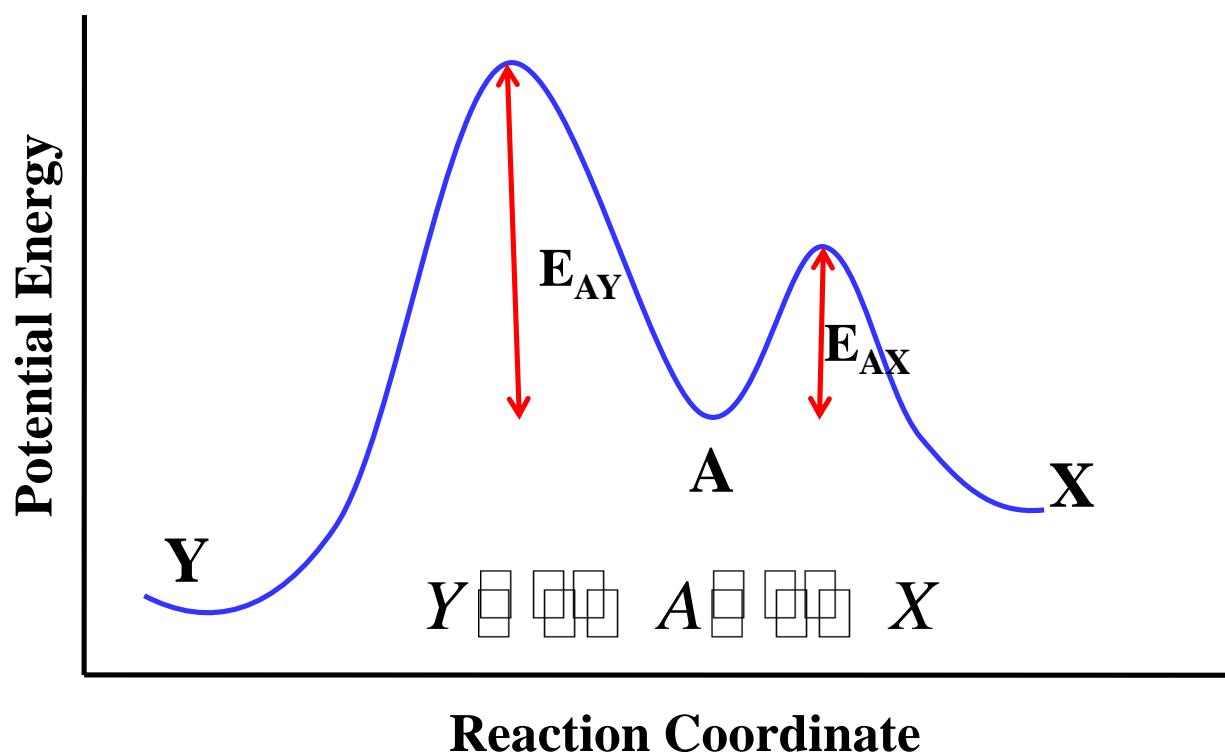
Kinetic and Thermodynamic Control

Parallel competing reactions leading to the formation of two different products from same reactants represent an interesting problem particularly if both reactions can reach equilibrium



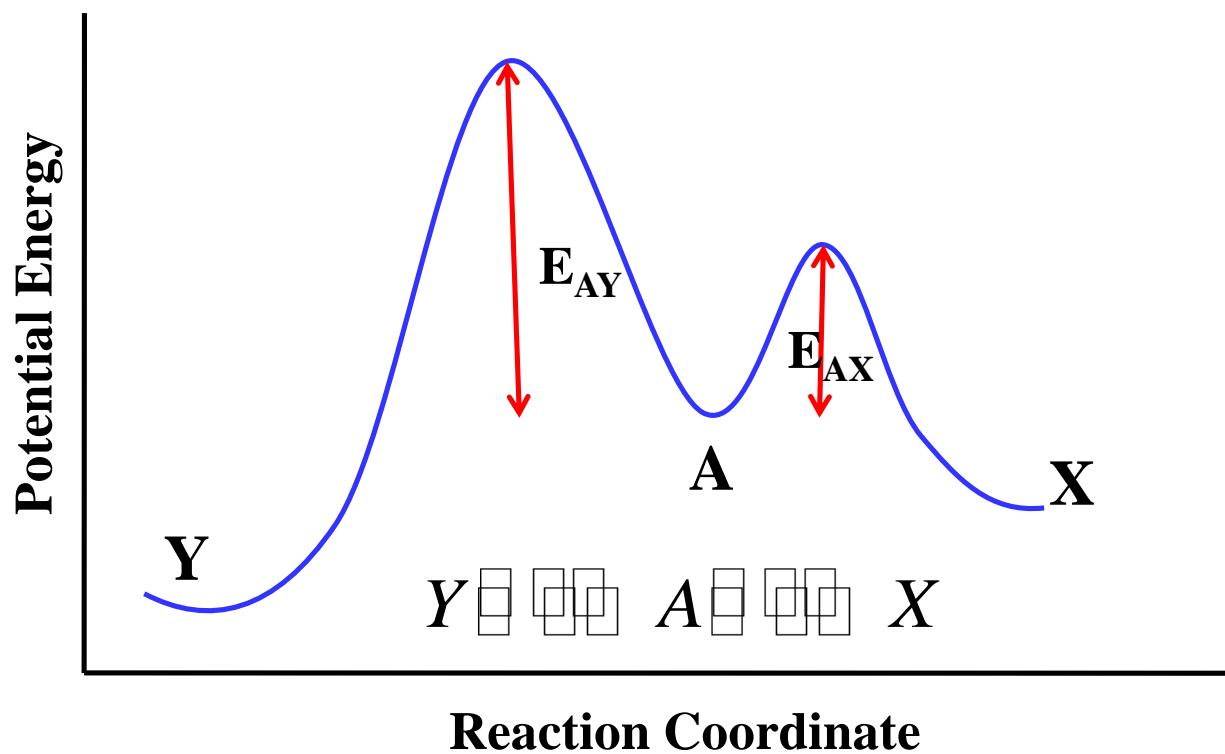
Let's assume that Y is more stable than X, but X forms faster than Y





Under milder conditions or for shorter reaction times, X will be formed in abundance. In such a case the reaction is known to be **kinetic controlled**

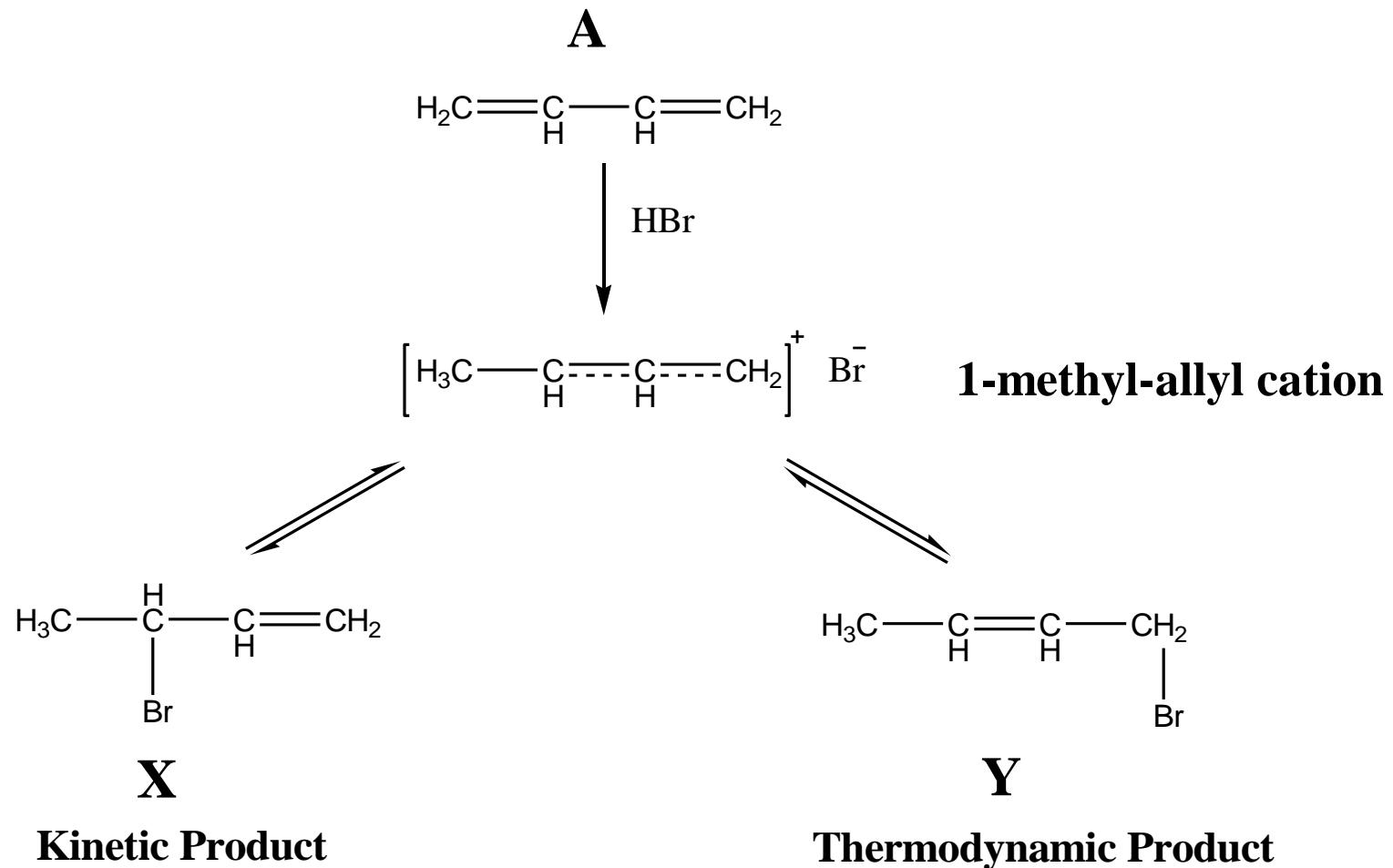
If the reaction time is longer or the reaction temperature is higher then the more stable product Y is formed in abundance. In such a case the reaction is known to be under **thermodynamic control**



Under milder conditions or for shorter reaction times, X will be formed in abundance. In such a case the reaction is known to be **kinetic controlled**

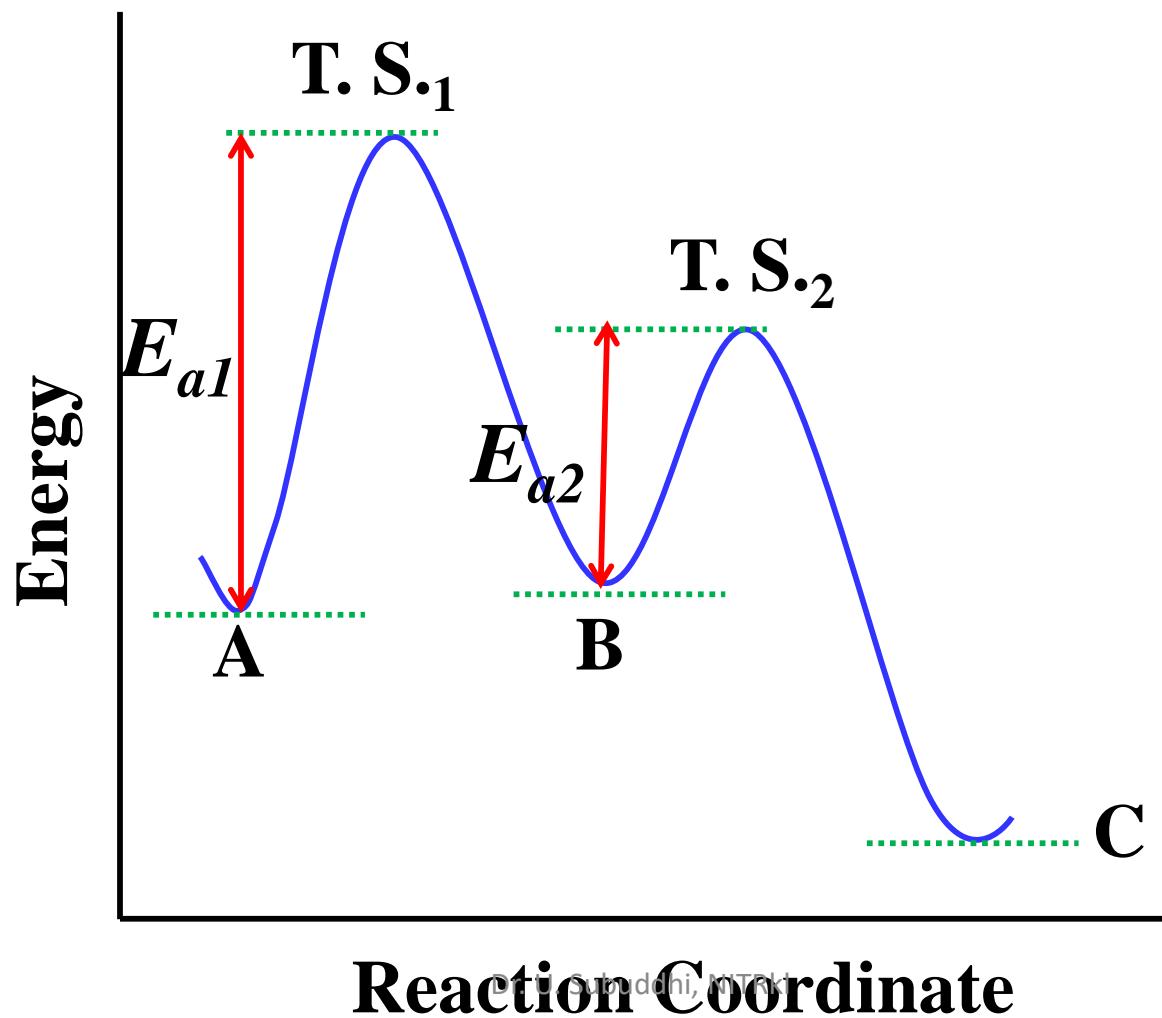
If the reaction time is longer or the reaction temperature is higher then the more stable product Y is formed in abundance. In such a case the reaction is known to be under **thermodynamic control**

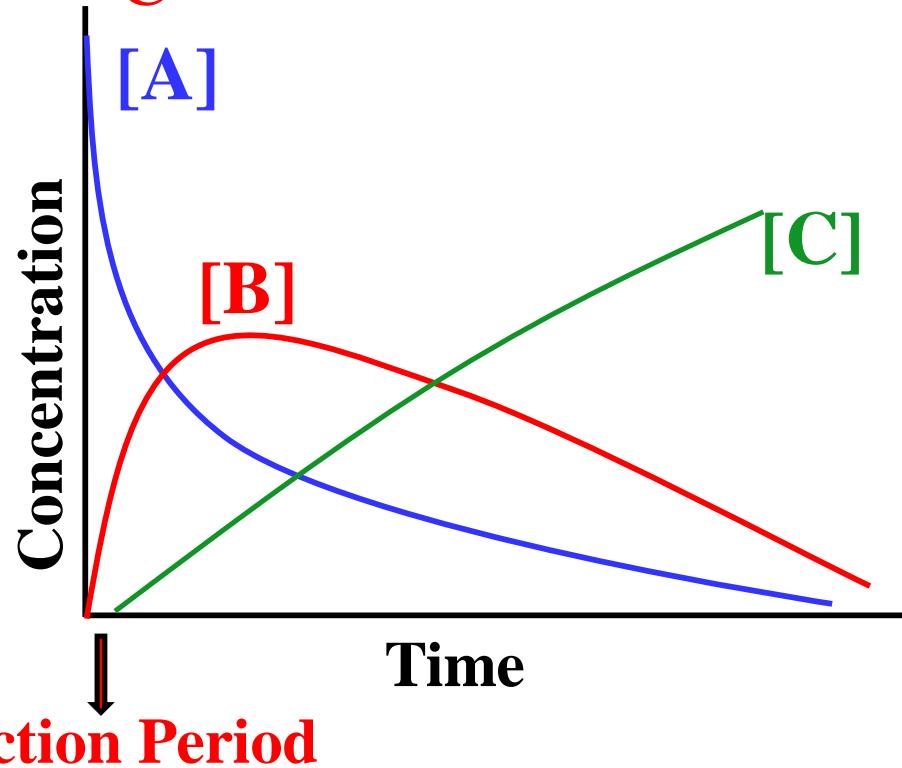
Addition of HBr to 1,3-butadiene



Temperature (°C)	% yield of X	% yield of Y
0	90	10
40	15	85
At equil.	15	85

3. Consecutive Reactions





$$\frac{-d[A]}{dt} = k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

$$\frac{-d[A]}{dt} = k_1[A]$$

$$[A] = [A]_0 e^{-k_1 t}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

The conc. of B depends on both its rate of formation (k_1) and its rate of decomposition (k_2), the solution for the equation will be of the form

$$[B] = Z_1 e^{-k_1 t} + Z_2 e^{-k_2 t}$$

$$\frac{d[B]}{dt} = -Z_1 k_1 e^{-k_1 t} - Z_2 k_2 e^{-k_2 t}$$

$$-Z_1 k_1 e^{-k_1 t} - Z_2 k_2 e^{-k_2 t} = k_1 [A]_0 e^{-k_1 t} - k_2 (Z_1 e^{-k_1 t} + Z_2 e^{-k_2 t})$$

$$Z_1 = \frac{k_1}{k_2 - k_1} [A]_0$$

$$[B] = \frac{k_1}{k_2 - k_1} [A]_0 e^{-k_1 t} + Z_2 e^{-k_2 t}$$

$$\text{At } t=0, [B]_0 = 0 \quad \frac{k_1}{k_2 - k_1} [A]_0 e^{-k_1 0} + Z_2 e^{-k_2 0} = 0$$

$$Z_2 = -\frac{k_1}{k_2 - k_1} [A]_0$$

$$[B] = \frac{k_1}{k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_2 t})$$

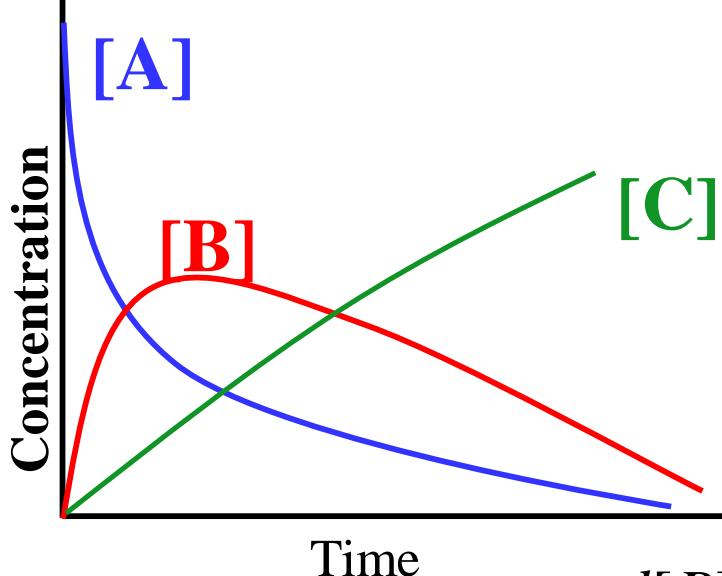
$$[C] = [A]_0 - [A] - [B]$$

$$[C] = [A]_0 - [A]_0 e^{-k_1 t} - \frac{k_1}{k_2 - k_1} [A]_0 \left(e^{-k_1 t} - e^{-k_2 t} \right)$$

$$[C] = \frac{[A]_0}{k_2 - k_1} \left[k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right]$$

$$[B] = \frac{k_1}{k_2 - k_1} [A]_0 \left(e^{-k_1 t} - e^{-k_2 t} \right)$$

$$[A] = [A]_0 e^{-k_1 t}$$



The $[B]_{\max}$ can be calculated by setting $\frac{d[B]}{dt} = 0$ at $[B]_{\max}$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

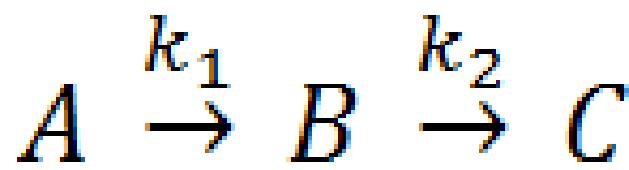
$$[B] = \frac{k_1}{k_2 - k_1} [A]_0 \left(e^{-k_1 t} - e^{-k_2 t} \right)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]_{\max} = 0$$

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

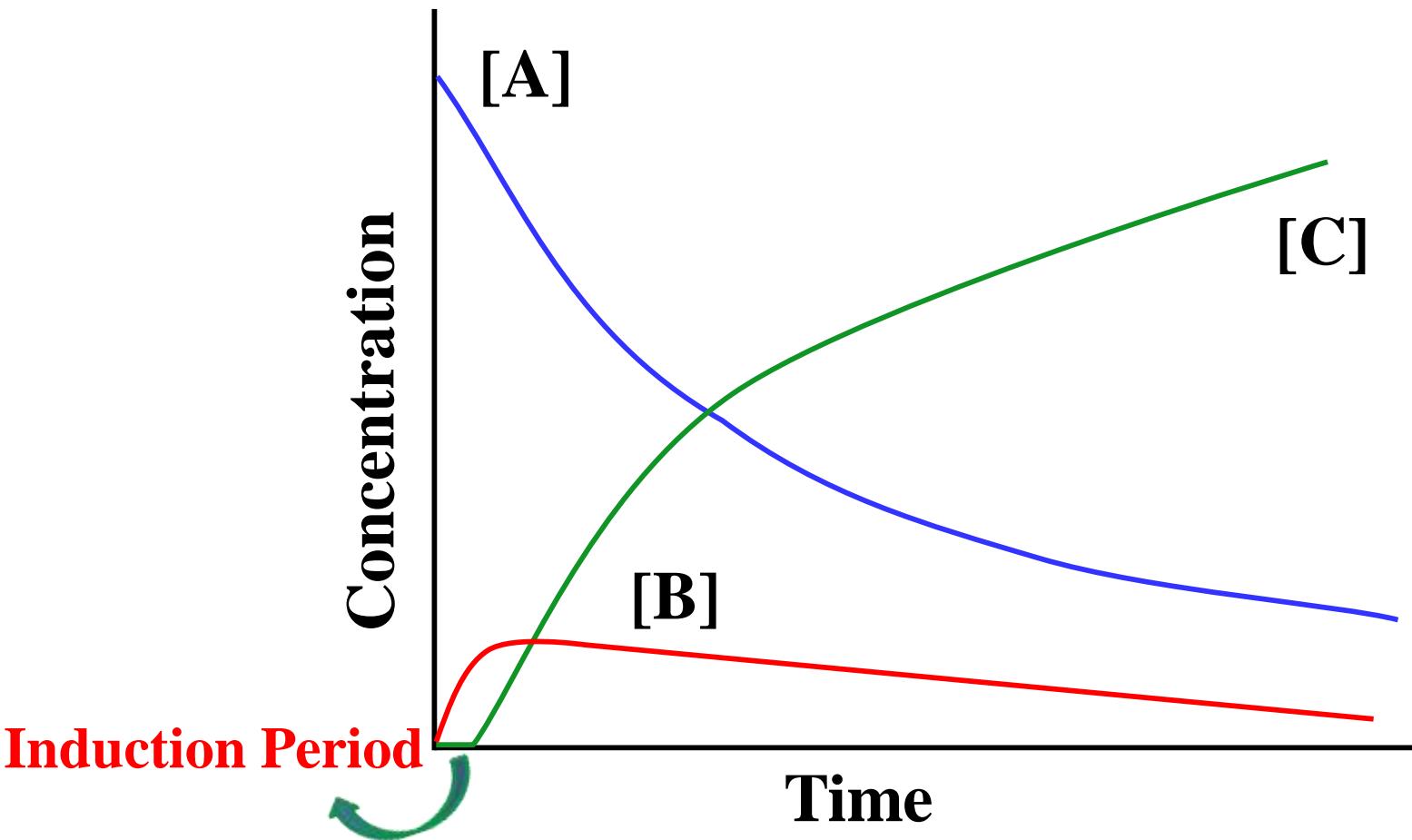
$$\frac{k_1}{k_2} = \frac{[B]_{\max}}{[A]}$$

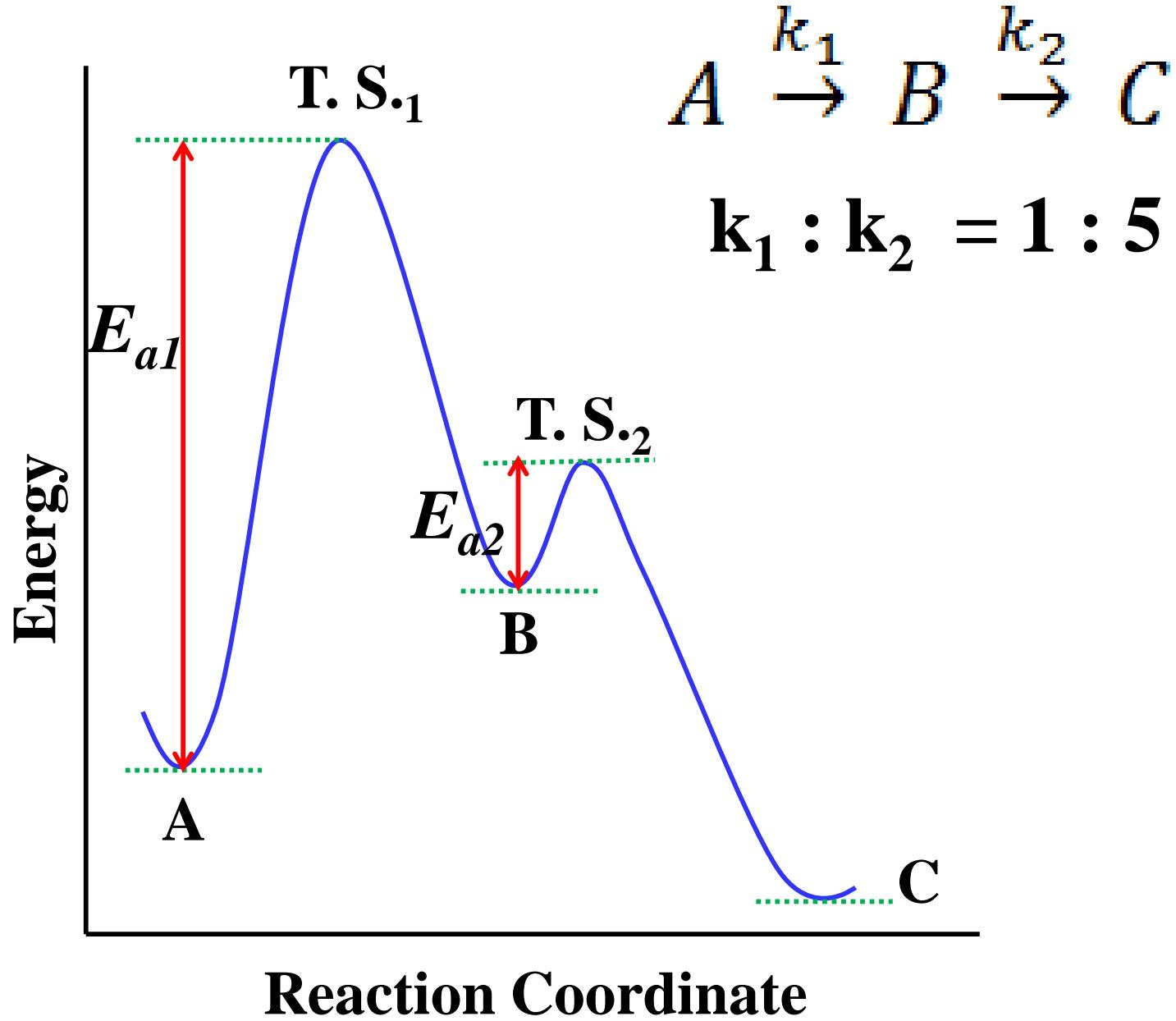
$$[B]_{\max} = [A]_0 \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_1 - k_2}}$$

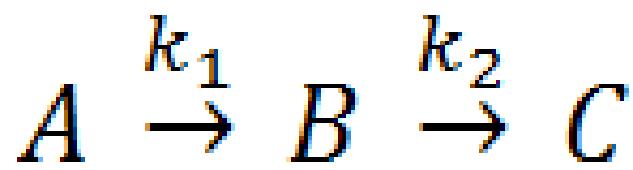


$$k_1 : k_2 = 1 : 5$$

$$k_2 > k_1$$

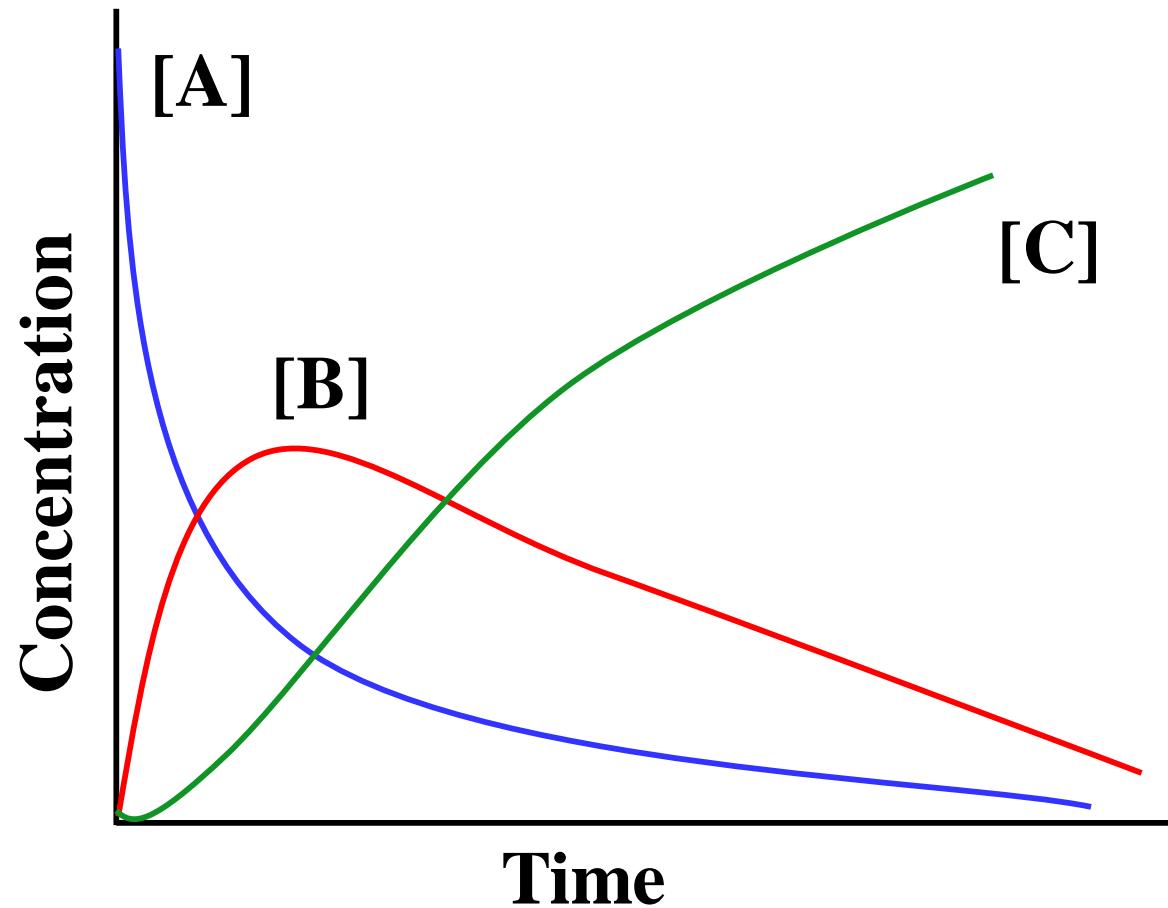


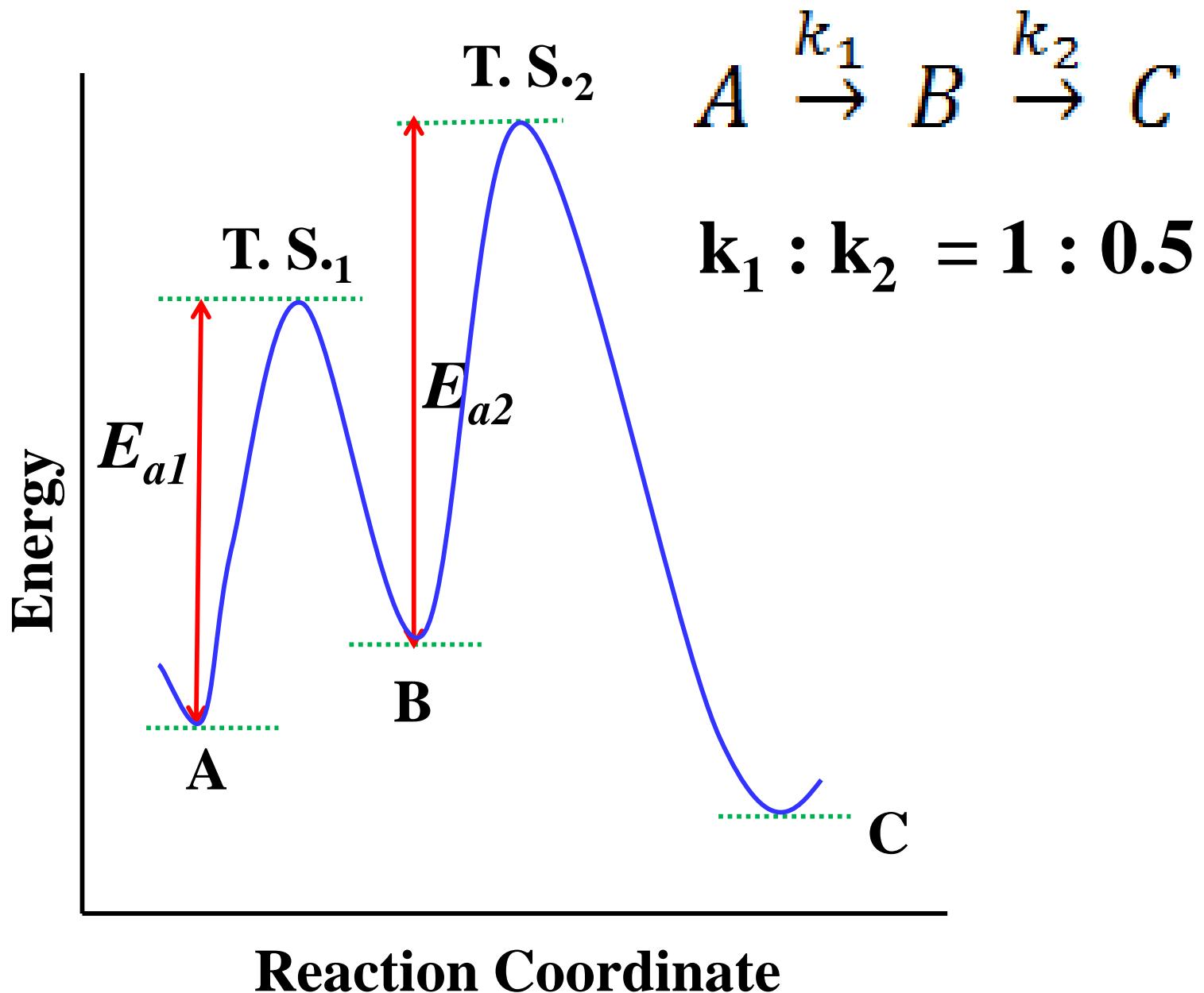




$$k_1 : k_2 = 1 : 0.5$$

$$k_1 > k_2$$







$$[C] = \frac{[A]_0}{k_2 - k_1} [k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})]$$

$$e^{-k_1 t} \lll e^{-k_2 t}$$

$$k_2 - k_1 \approx -k_1$$

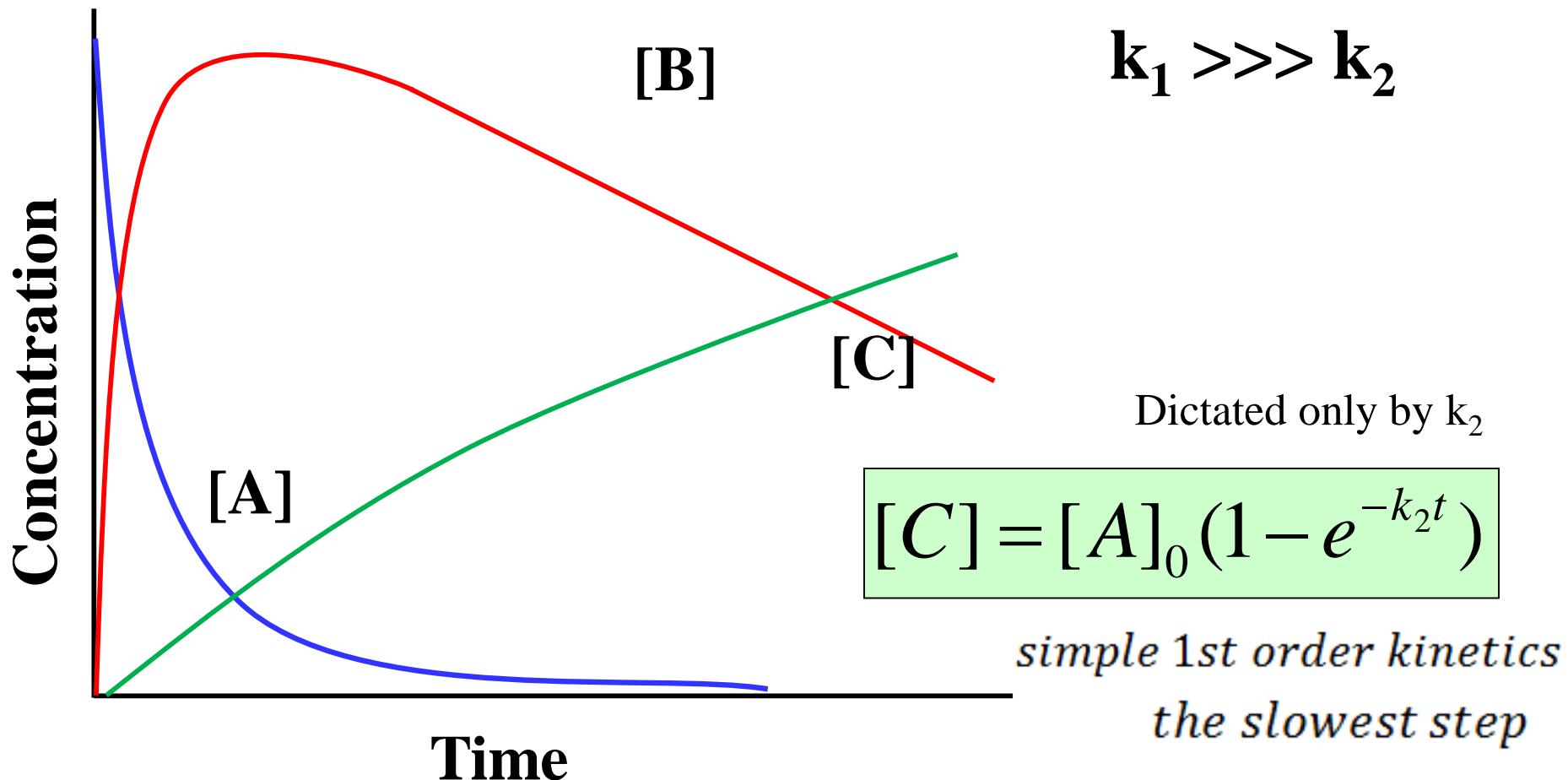
$$[C] = \frac{[A]_0}{-k_1} [-k_1(1 - e^{-k_2 t})]$$

$$[C] = [A]_0 (1 - e^{-k_2 t})$$

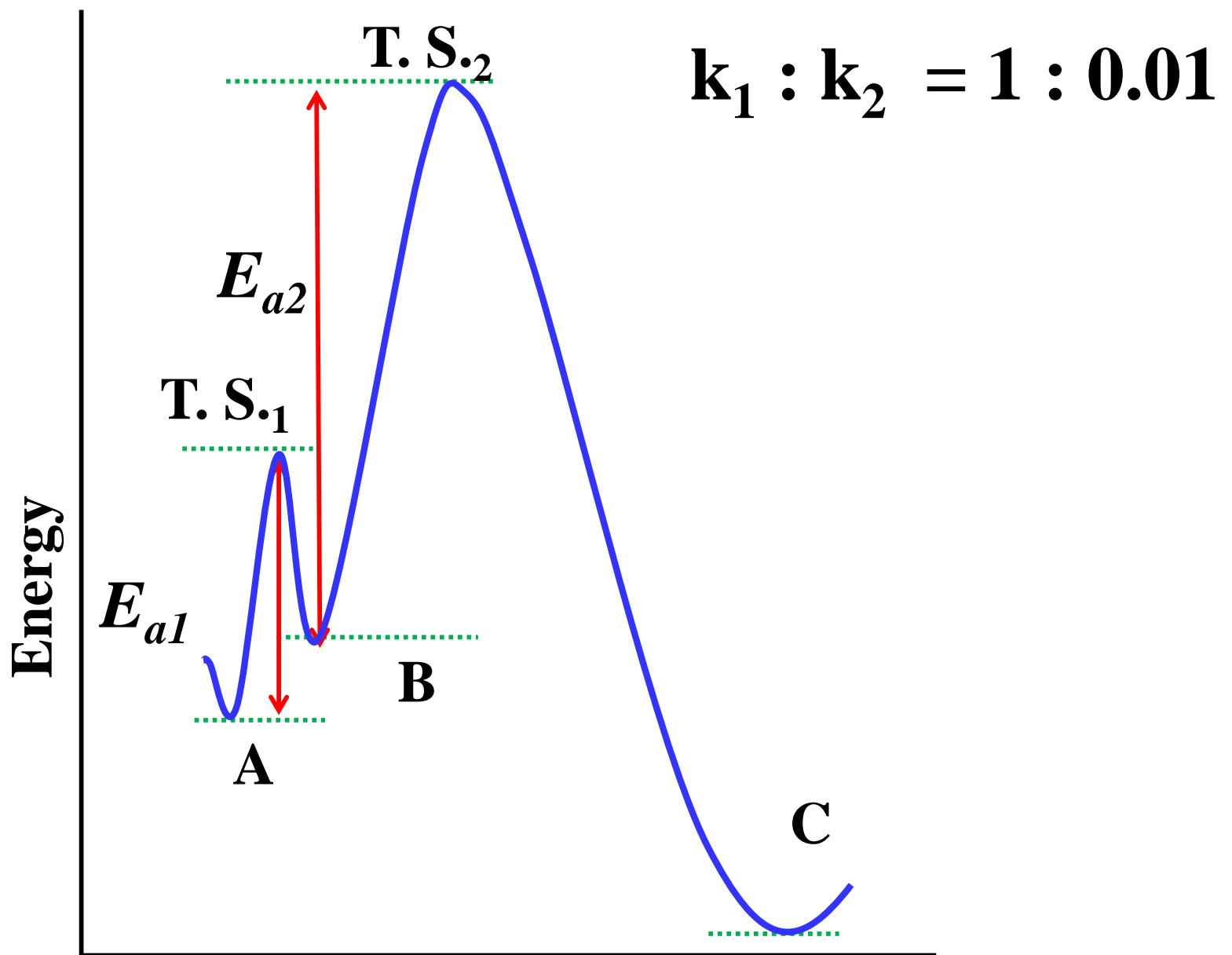
Rate of the reaction depends on k_2
i.e. the rate of decomposition of B
(RDS)



$$k_1 : k_2 = 1 : 0.01$$



$$[C] = \frac{[A]_0}{k_2 - k_1} \left[k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t}) \right]$$



Reaction Coordinate
Dr. U. Subuddhi, NITRkl



$$[C] = \frac{[A]_0}{k_2 - k_1} [k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})]$$

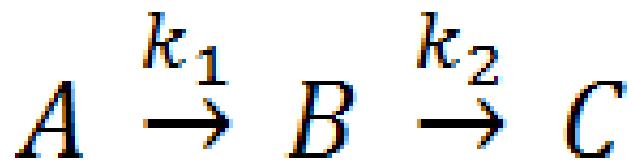
$$e^{-k_2 t} <<< e^{-k_1 t}$$

$$k_2 - k_1 \approx k_2$$

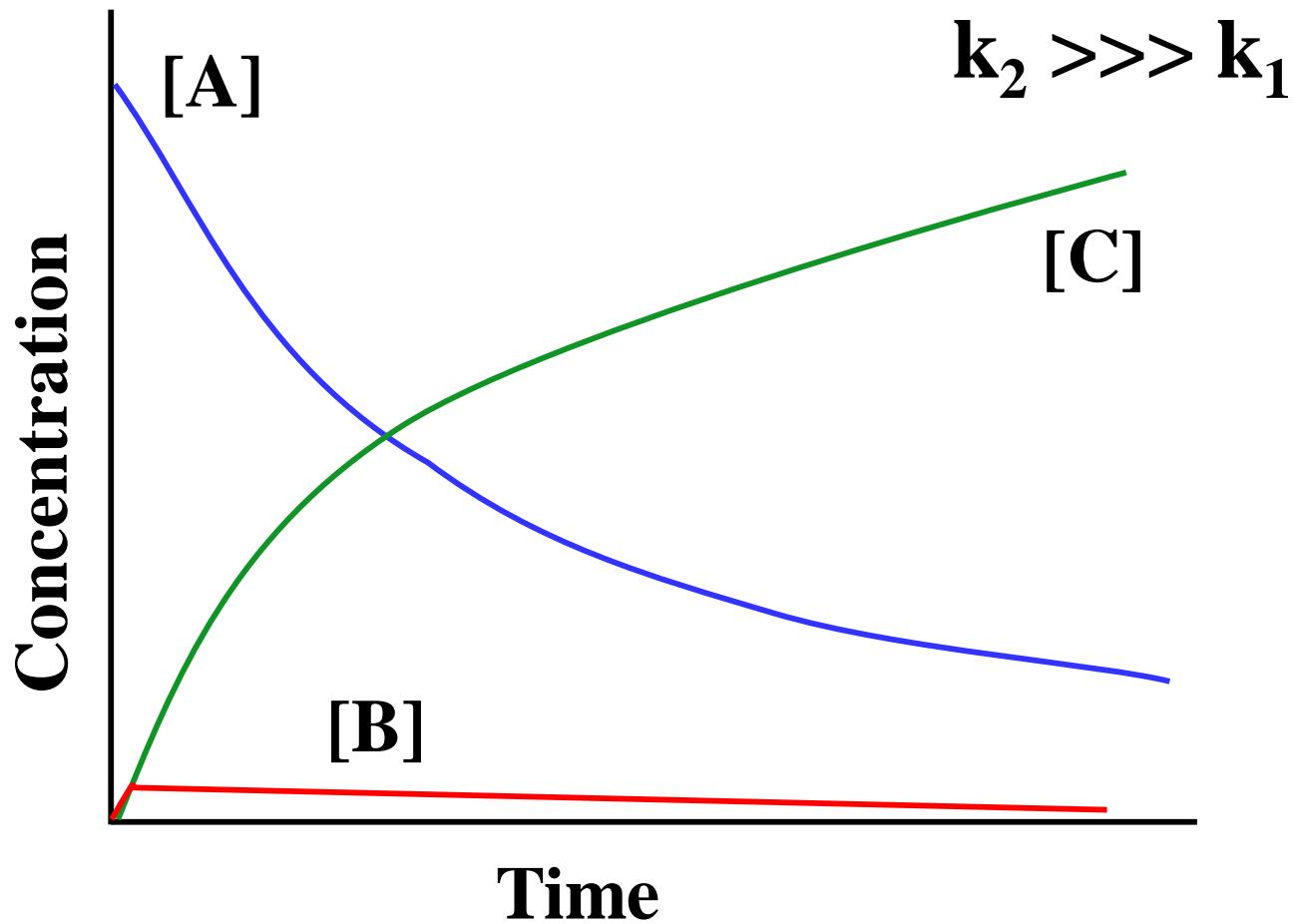
$$[C] = \frac{[A]_0}{k_2} [k_2(1 - e^{-k_1 t})]$$

$$[C] = [A]_0 (1 - e^{-k_1 t})$$

Rate of the reaction depends on k_1
i.e. the rate of formation of B (RDS)

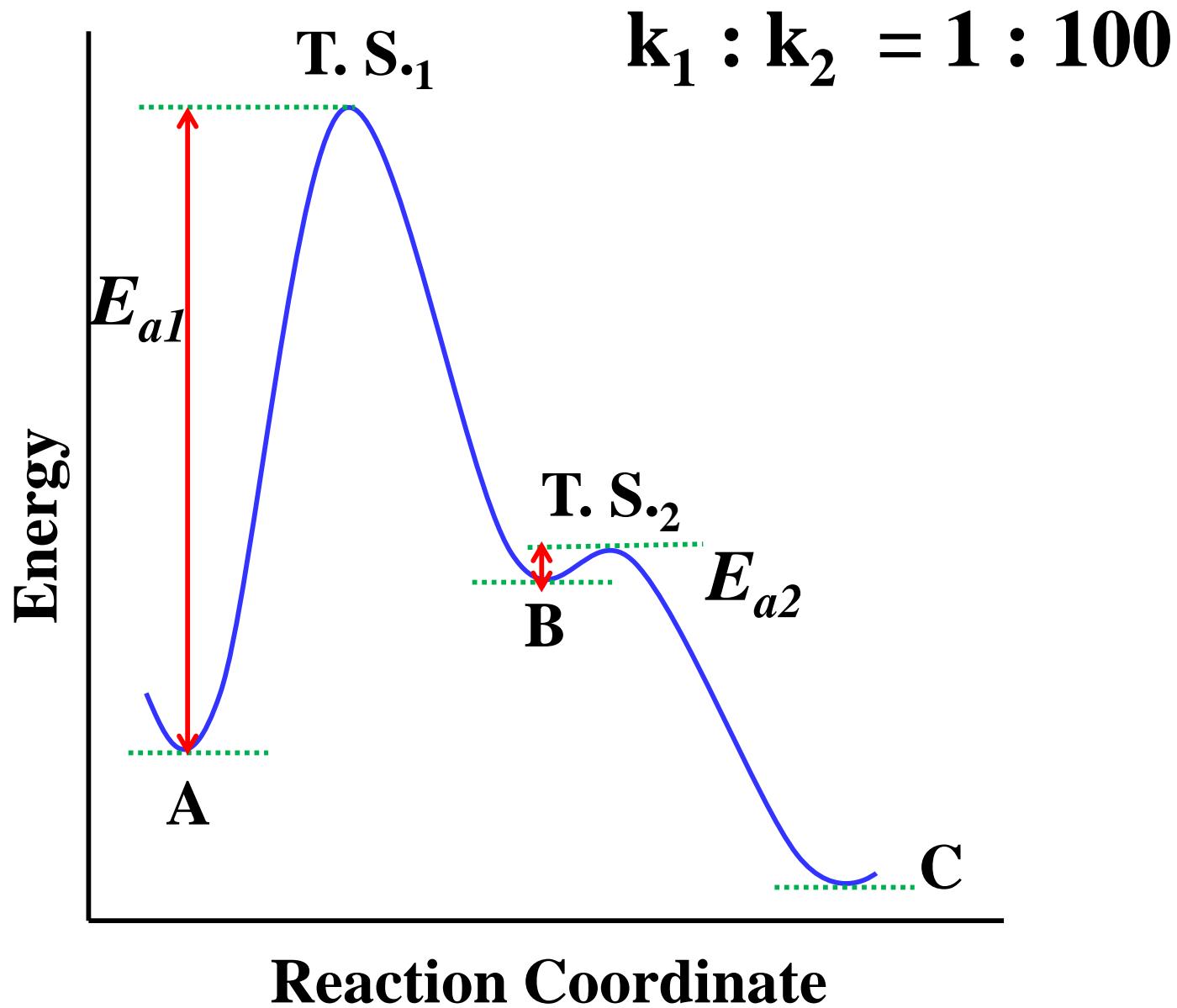


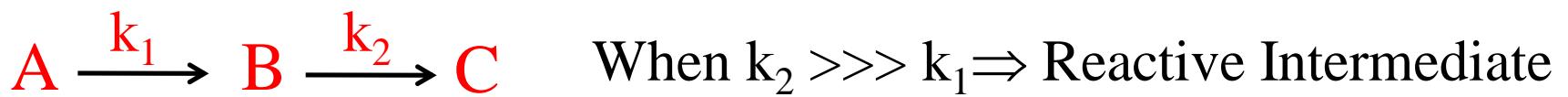
$$k_1 : k_2 = 1 : 100$$



Steady State Approximation

$$\frac{d[B]}{dt} = 0$$





The value of $[B]$ reaches a value that remains practically constant during the course of reaction (**Steady State Approximation**)

$$\frac{d[B]}{dt} = 0$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] = 0 \quad [B] = \frac{k_1}{k_2}[A]$$

$$\frac{d[C]}{dt} = k_2[B] = k_2 \frac{k_1}{k_2}[A] \quad \frac{d[C]}{dt} = k_1[A]_0 e^{-k_1 t}$$

$$\int_0^t d[C] = k_1[A]_0 \int_0^t e^{-k_1 t} dt$$

$$[C] = [A]_0 (1 - e^{-k_1 t})$$

Thus the rate of formation of C depends on the rate at which B is formed and not on the rate at which B is converted to C

Concept of pre-equilibrium and Pre-equilibrium approximation



If $k_1, k_{-1} \gg k_2$ then an equilibrium is set in the 1st step quickly in comparison to the second step. Under such condition the second step becomes the rate determining step and the pre-equilibrium is not perturbing the 2nd step as [C] is predetermined by the equilibrium in the 1st step

$$K = \frac{[C]_e}{[A]_e[B]_e} \cong \frac{[C]}{[A][B]}$$

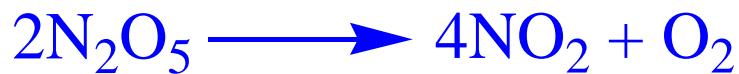
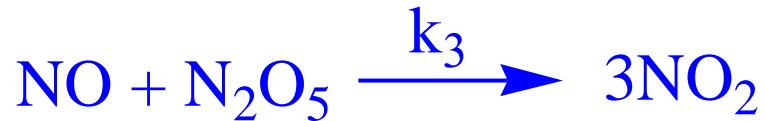
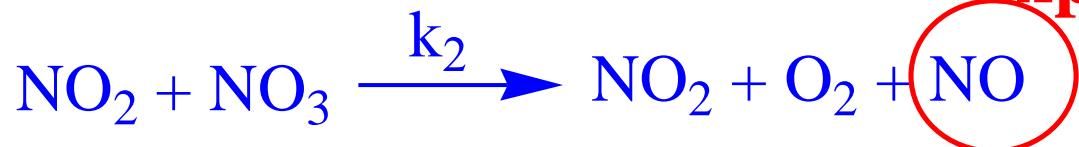
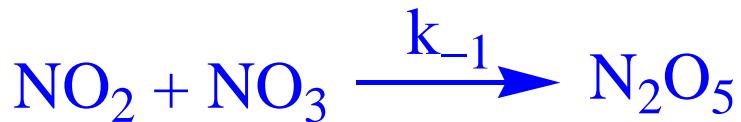
$$\frac{d[D]}{dt} = k_2[C] = k_2 K[A][B] = k_{obs}[A][B]$$

$$k_{obs} = k_2 K = \frac{k_2 k_1}{k_{-1}}$$

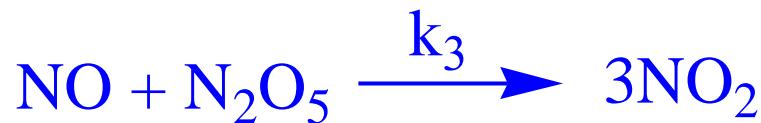
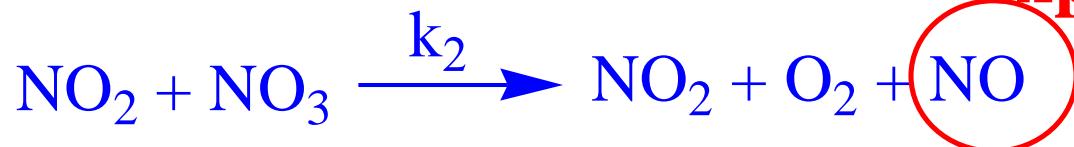
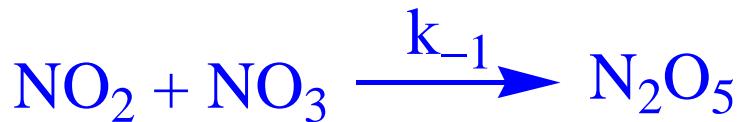
If the condition is not considered and SSA is applied then

$$\frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C] - k_2[C] = 0$$

$$\frac{d[D]}{dt} = k_2[C] = \frac{k_1 k_2 [A][B]}{k_{-1} + k_2}$$



- Identify the intermediates
- Apply SSA
- Substitute in the final rate expression



- Identify the intermediates
- Apply SSA
- Substitute in the final rate expression



$$-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] + k_3[NO][N_2O_5]$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] = 0$$

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][N_2O_5] = 0$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] = 0$$

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][N_2O_5] = 0$$

$$[NO] = \frac{k_2[NO_2][NO_3]}{k_3[N_2O_5]} \quad [NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2]}$$

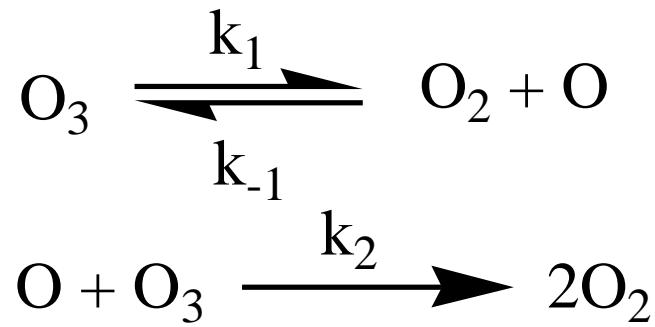
Substituting $[NO_3]$ in $[NO]$

$$[NO] = \frac{k_1 k_2}{k_3(k_{-1} + k_2)}$$

$$\frac{-d[N_2O_5]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] + k_3[NO][N_2O_5]$$

$$\boxed{\frac{-d[N_2O_5]}{dt} = \frac{2k_1 k_2}{(k_{-1} + k_2)} [N_2O_5]}$$

Derive the rate law for the decomposition of O_3 in the reaction $2O_3(g) \rightarrow 3O_2(g)$ on the basis of the following mechanism



Under (i) Steady state and (ii) Pre-equilibrium conditions

$$\frac{-d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} \quad \text{Applying SSA}$$

$$\frac{-d[O_3]}{dt} = \frac{k_1k_2[O_3]^2}{k_{-1}[O_2]} \quad \text{Applying PEA}$$

Chain Reaction

One of the most studied stationary reaction is the reaction between hydrogen and bromine to form hydrogen bromide. The thermal reaction was first studied by Bodenstein and Lind.

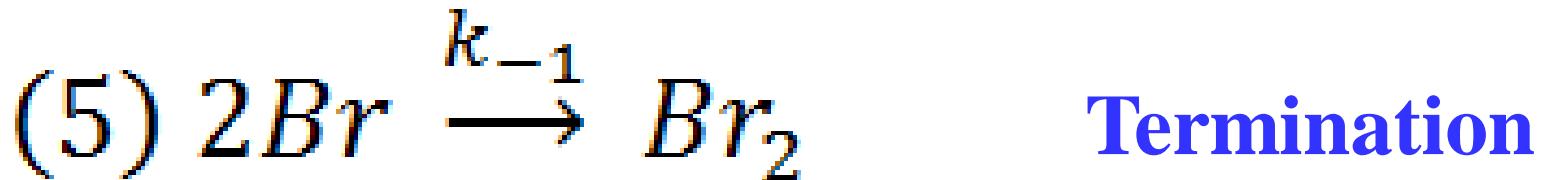
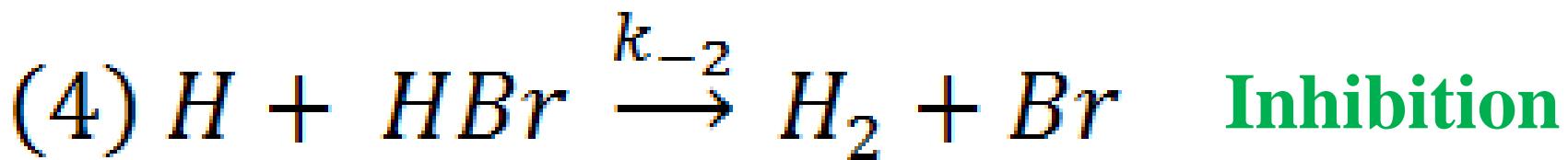
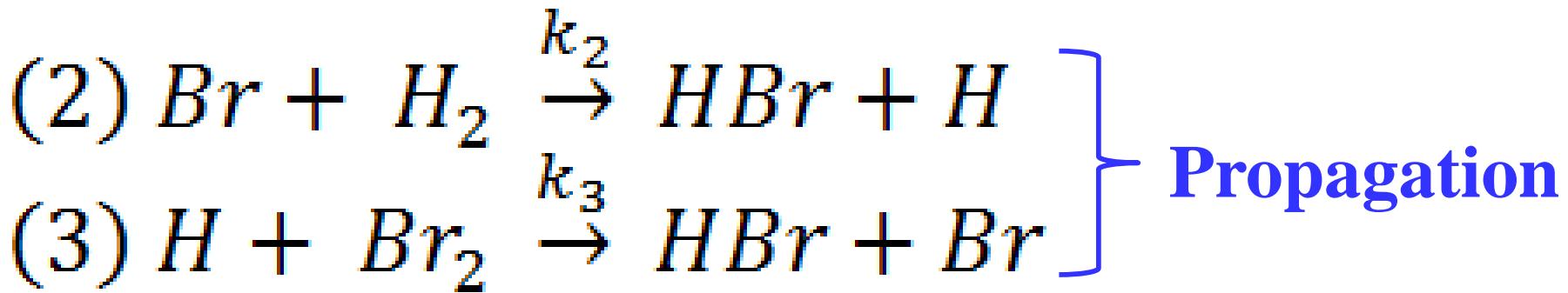
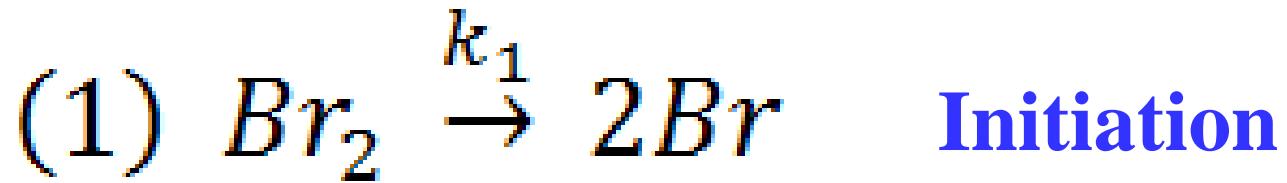
The kinetics satisfied the following rate expression

$$\frac{-d[H_2]}{dt} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} = \frac{k[H_2][Br_2]^{1/2}}{1 + k' \frac{[HBr]}{[Br_2]}}$$

This complex rate expression provides some valuable clues to the mechanism

1. The reaction must be a multistep reaction
2. The fractional power suggests that bromine molecules dissociate during the reaction *i.e.* either radicals or atomic species are involved
3. Appearance of HBr in the denominator indicates that it inhibits the reaction *i.e.* the reaction slows down as the product is formed
4. The inhibition by HBr is reduced by addition of Br₂.

Chain Reaction



$$-\frac{d[H_2]}{dt} = k_2[Br][H_2] - k_{-2}[H][HBr]$$

- Identify the intermediates
- Apply SSA
- Substitute in the rate expression

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_{-2}[H][HBr] = 0$$

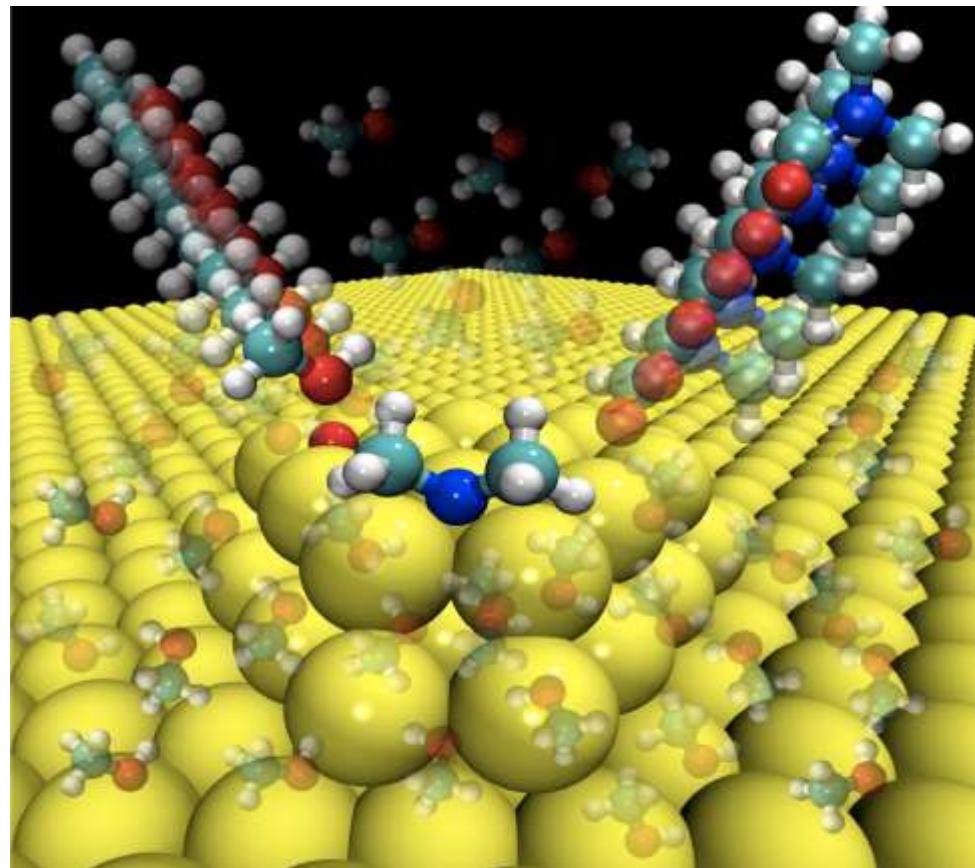
$$\frac{d[Br]}{dt} = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_{-2}[H][HBr] - 2k_{-1}[Br]^2 = 0$$

$$[Br] = \sqrt{\frac{k_1}{k_{-1}}} [Br_2]^{1/2}$$

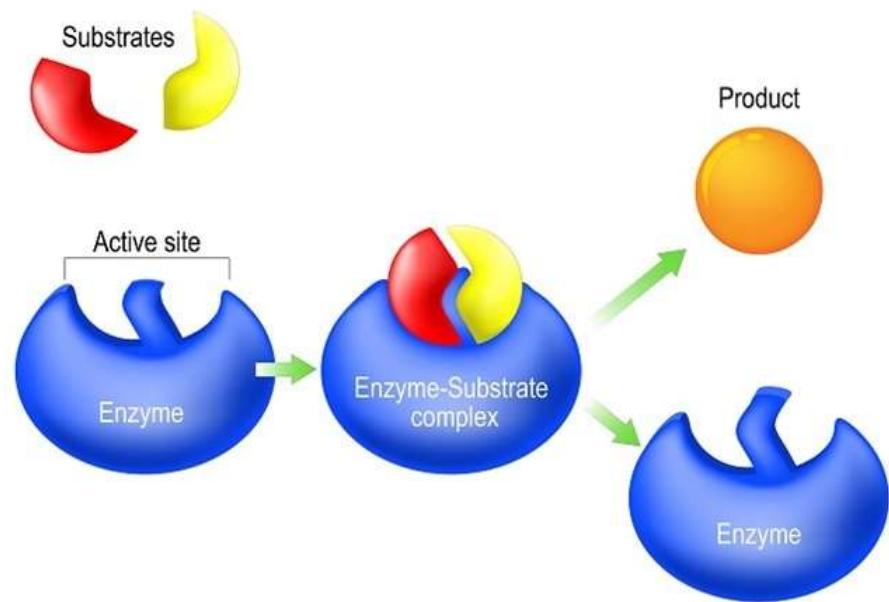
$$[H] = \frac{k_2 \left(\frac{k_1}{k_{-1}} \right)^{1/2} [H_2][Br_2]^{1/2}}{k_3[Br_2] + k_{-2}[HBr]}$$

$$\begin{aligned} \frac{-d[H_2]}{dt} &= \frac{k_2 k_3 \left(\frac{k_1}{k_{-1}} \right)^{1/2} [H_2][Br_2]^{3/2}}{k_3[Br_2] + k_{-2}[HBr]} \\ &= \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \end{aligned}$$

CATALYSIS



"LOCK and KEY" model
SYNTHESIS



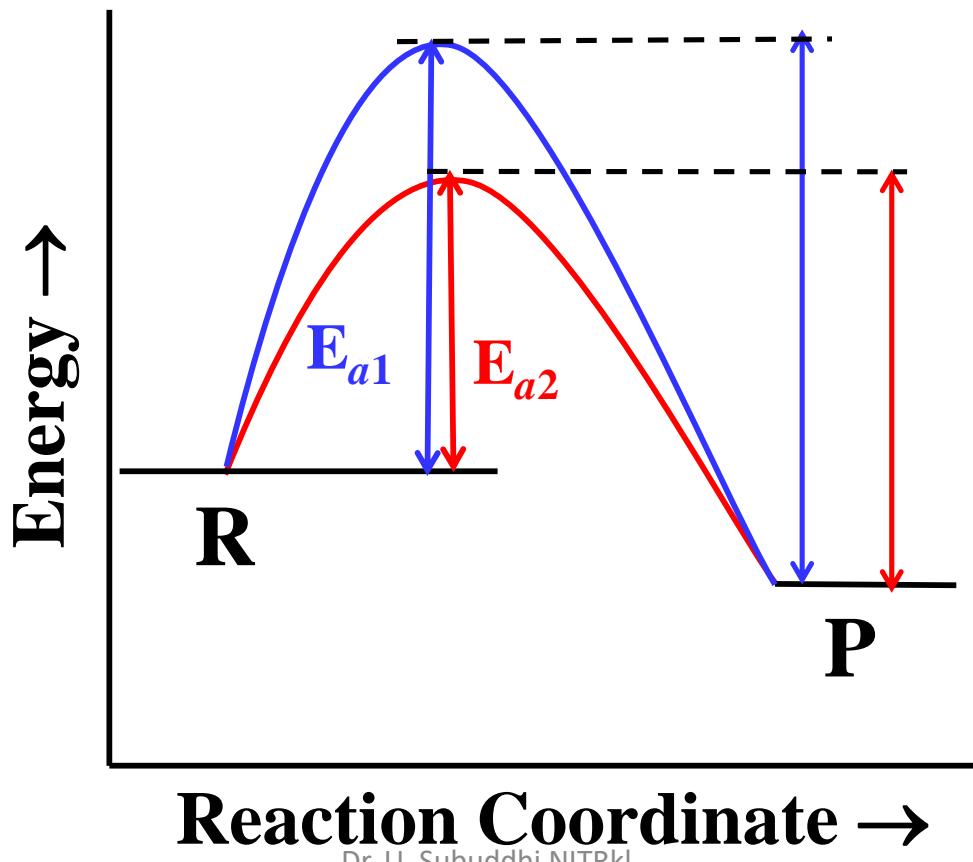
©Designua/ Shutterstock.com

- Heterogeneous
- Homogeneous

Presence of a Catalyst

A catalyst is a substance that may increase or decrease the rate of a reaction

Increase in rate \Rightarrow +ve catalyst or promoter
Decrease in rate \Rightarrow -ve catalyst or inhibitor



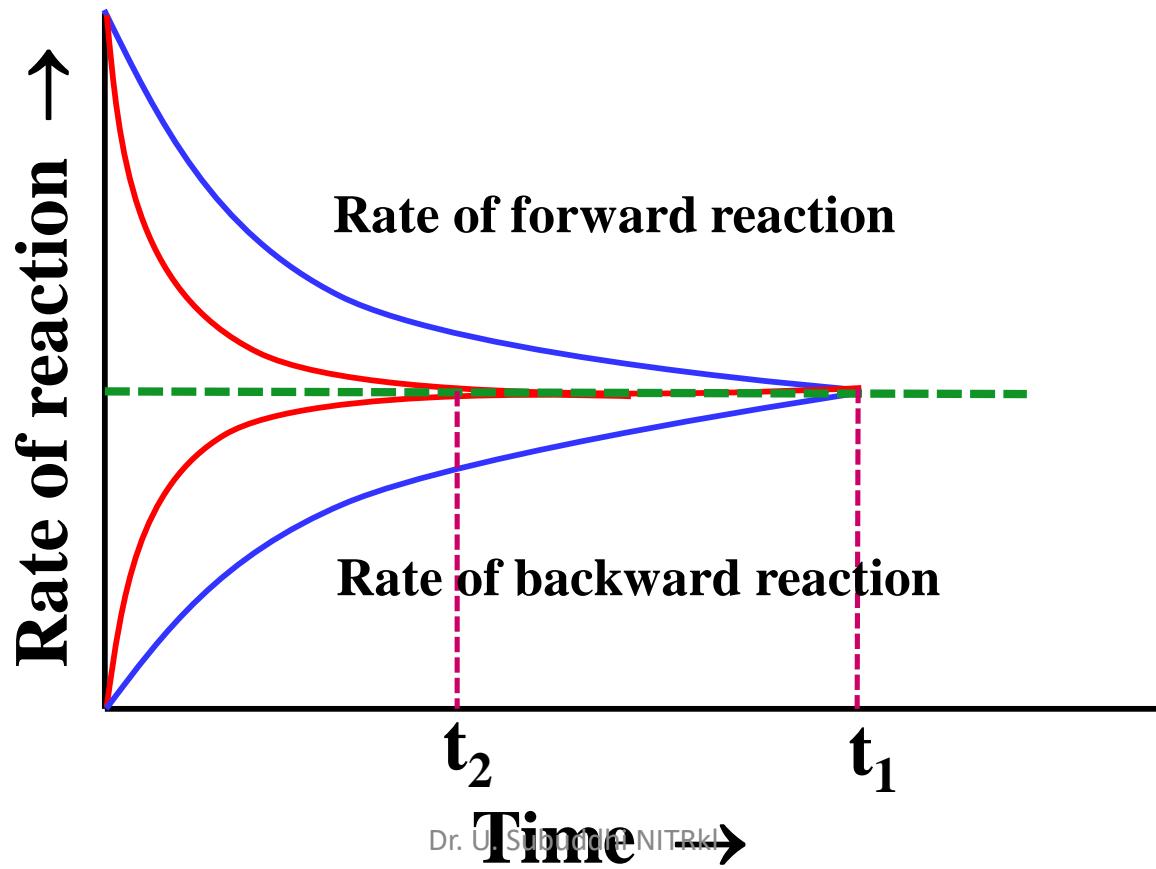
Catalyst provides an alternative pathway



By providing an alternative pathway (or mechanism) with lower activation energy.

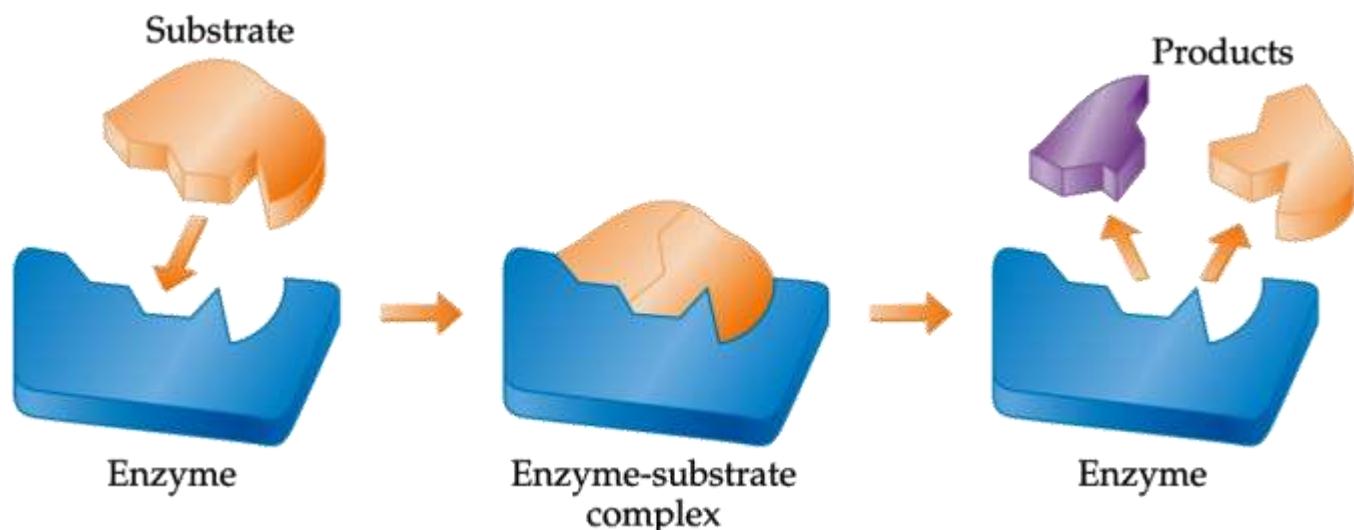
A catalyst affects both the forward and backward reaction equally.

Thus it doesn't change the state of equilibrium, it only hastens the approach of equilibrium.

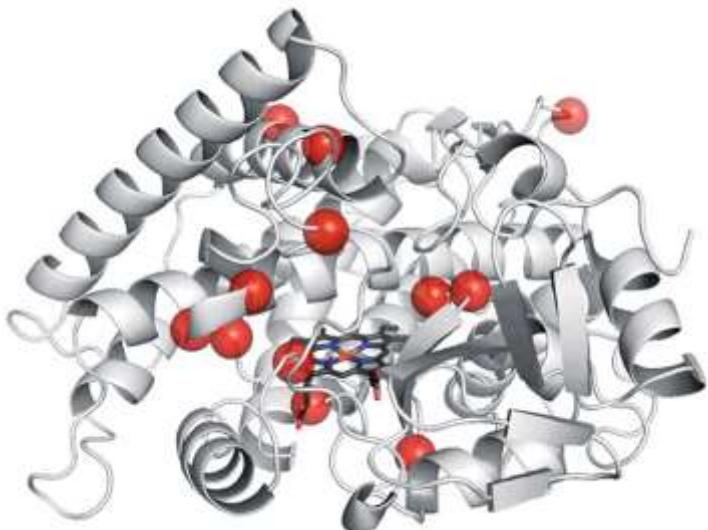


Heterogeneous Catalyst- In a different phase, for example a solid catalyst for a gas phase reaction.

Homogeneous Catalyst- In the same phase as the reactants.
Acid-base catalysis, *Enzymatic catalysis*



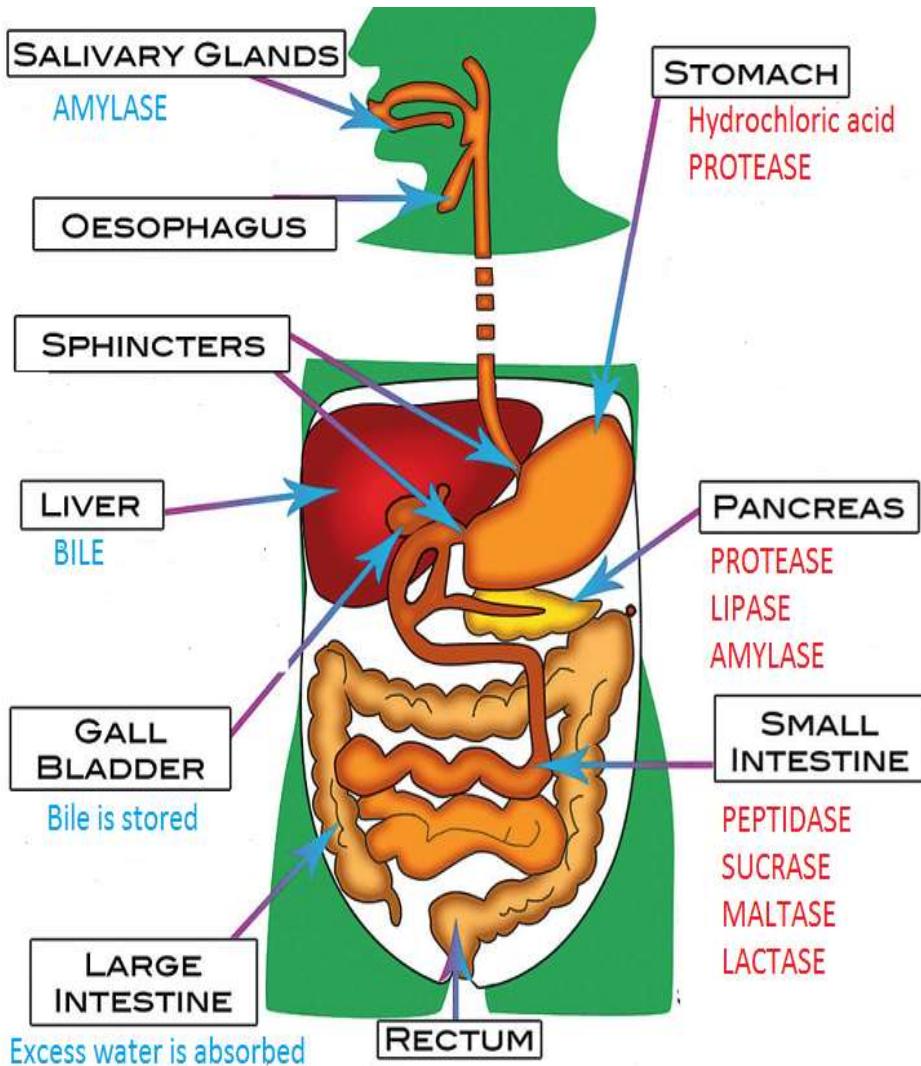
Enzyme catalysis: homogeneous aqueous phase reaction



Enzymes are biomolecules: proteins

They have a particular region/groove where it binds with reactants (substrate) and called as active site

Source: cen.acs.org



Some important digestive enzymes

Dr. U. Subuddhi, NITRkl

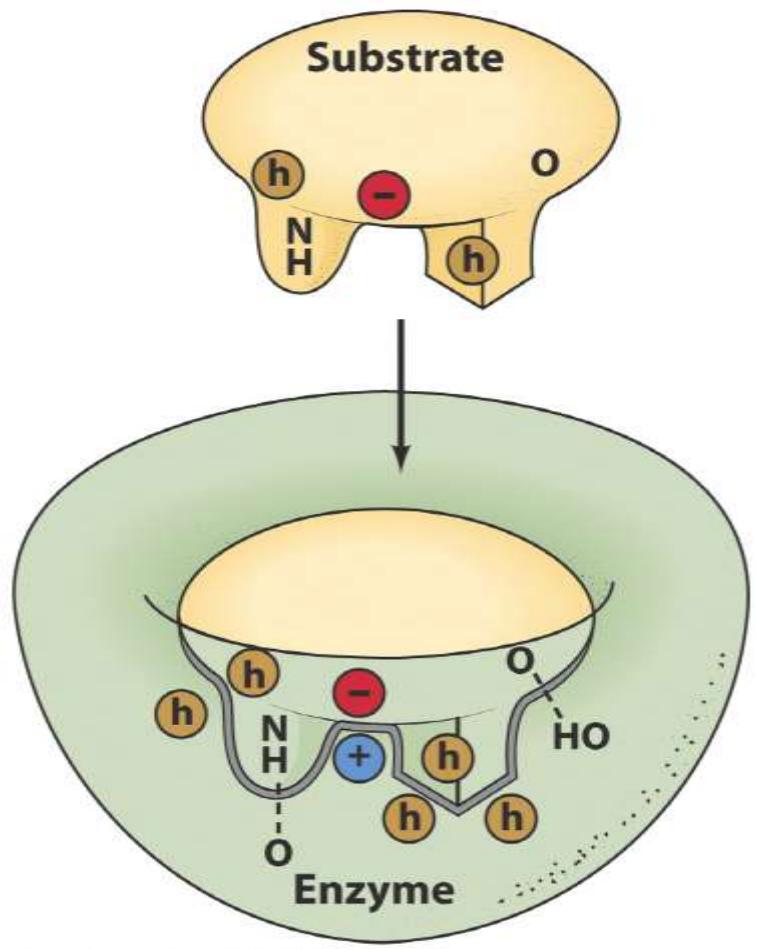


Figure 11-1 Fundamentals of Biochemistry, 2/e
© 2006 John Wiley & Sons

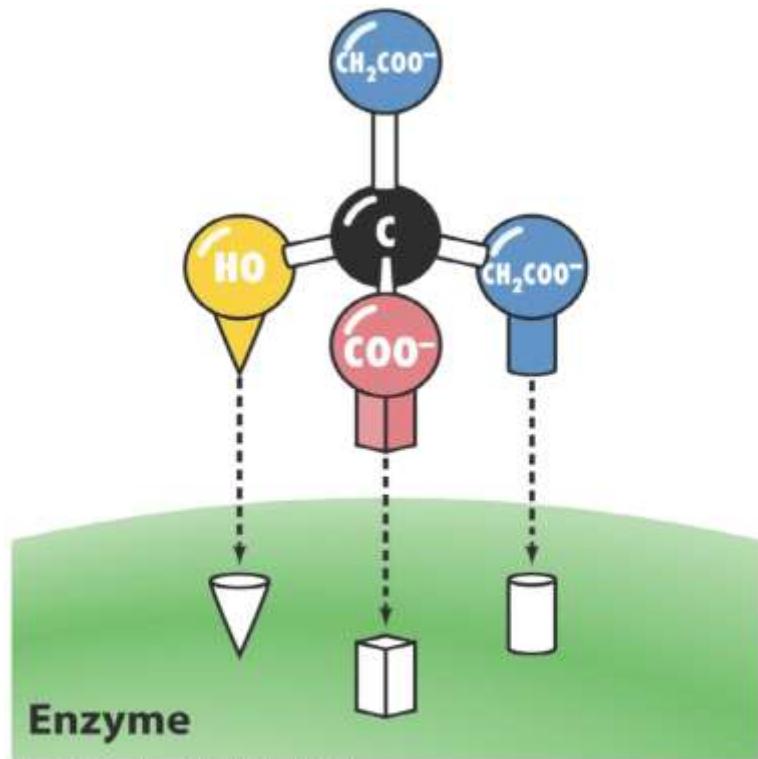
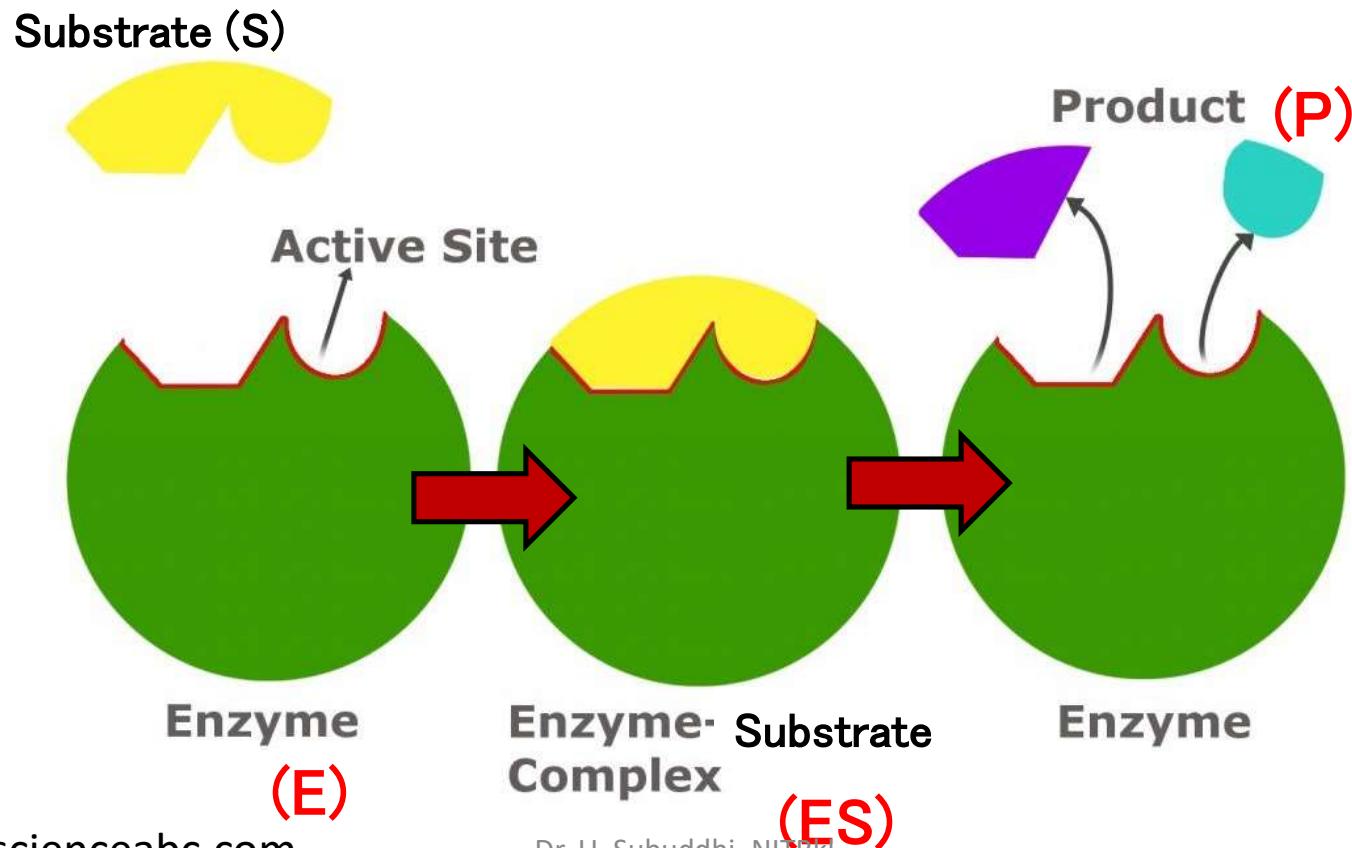


Figure 11-2 Fundamentals of Biochemistry, 2/e
© 2006 John Wiley & Sons.

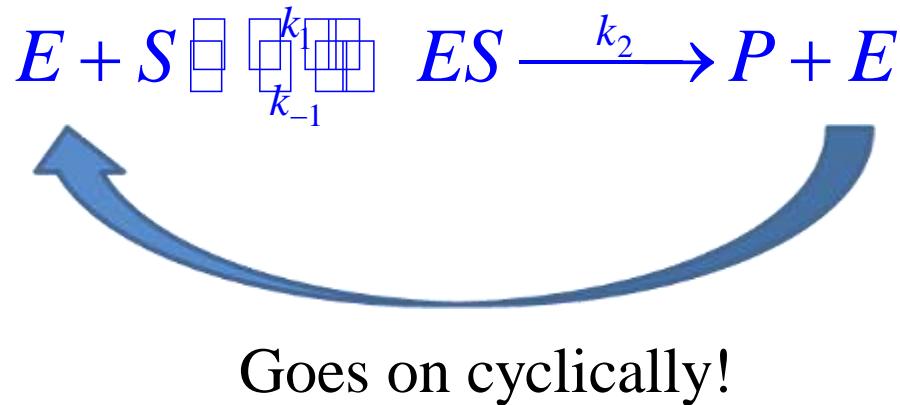
Mechanism: Lock & key

Binding (first) step is proposed to be reversible, while the next step is irreversible

Each active site of an enzyme is specific to a particular substrate!



Proposed mechanistic pathway:



Question is which approach should we adopt?

Option A: **Pre-equilibrium?**

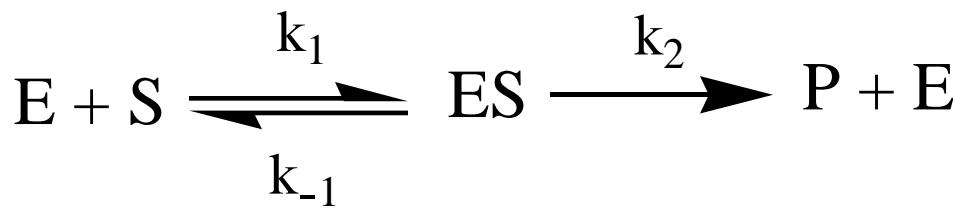
Option B: **Steady-state?**

Michaelis-Menten Kinetics



Leonor Michaelis
(German; 1875-1949)

Maud Menten
(Canadian; 1879-1960)



$$Rate = \frac{d[P]}{dt} = velocity (v) = k_2[\text{ES}]$$

Applying SSA for ES

$$\frac{d[\text{ES}]}{dt} = k_1[\text{E}][\text{S}] - k_{-1}[\text{ES}] - k_2[\text{ES}] = 0$$

$$[\text{E}]_0 = [\text{E}] + [\text{ES}] \Rightarrow [\text{E}] = [\text{E}]_0 - [\text{ES}]$$

$$k_1([\text{E}]_0 - [\text{ES}])[\text{S}] - k_{-1}[\text{ES}] - k_2[\text{ES}] = 0$$

$$v = k_2[\text{ES}] = \frac{k_1 k_2 [\text{E}]_0 [\text{S}]}{(k_{-1} + k_2) + k_1 [\text{S}]} \quad [\text{ES}] = \frac{k_1 [\text{E}]_0 [\text{S}]}{(k_{-1} + k_2) + k_1 [\text{S}]}$$

$$v = \frac{k_2 [\text{E}]_0 [\text{S}]}{K_M + [\text{S}]}$$

Michaelis-Menten Equation

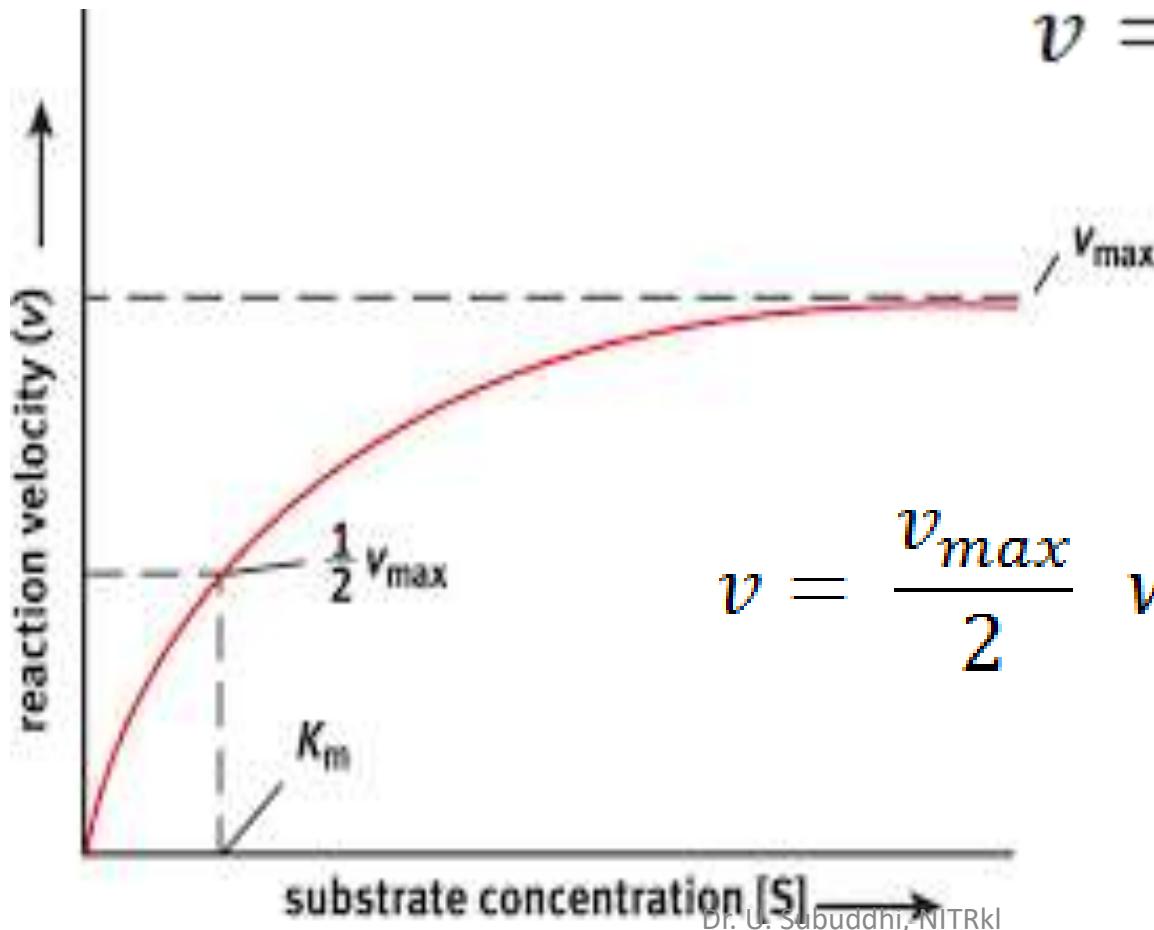
$$K_M = \frac{k_{-1} + k_2}{k_1} = \text{Michaelis Constant}$$

Michaelis-Menten equation for enzyme kinetics:

$$v = \frac{k_2 [E]_0 [S]}{K_M + [S]}$$

Michaelis-Menten Equation

$$v = \frac{v_{max} [S]}{[S] + K_M}$$



$$v = \frac{v_{max}}{2} \text{ when } [S] = K_M$$

Physical significance of Michaelis constant:

- ✓ K_M is a constant, specific to a particular enzyme catalysis
- ✓ It is the measure of the enzyme's affinity towards the substrate
- ✓ It is also known as half-saturation constant
- ✓ It is also a function of temperature and pH

Can you tell which enzyme performs better catalysis, the one with a Lower K_M or higher K_M value?

Small value of $K_M \Rightarrow$ high affinity of the enzyme towards the substrate

If an enzyme has a small value of K_M it achieves maximal catalytic efficiency at low substrate concentrations.

Caution:

K_M is the measure of enzyme's affinity to the substrate but it is not the direct measure of enzyme's efficiency !

Also, K_M and v_{max} are independent of each other!

The catalytic constant (k_{cat}) of an enzyme is defined as $k_{cat} = \frac{v_{max}}{E_0}$

$$v_{max} = k_2 E_0 \quad \Rightarrow k_{cat} = k_2$$

This quantity is also known as the **turn over number** of an enzyme because it is the number of reaction processes (turnovers) that each active site catalyzes per unit time.

k_{cat}/K_M is a Measure of Catalytic Efficiency

So, higher the turn over number, better is the enzyme.

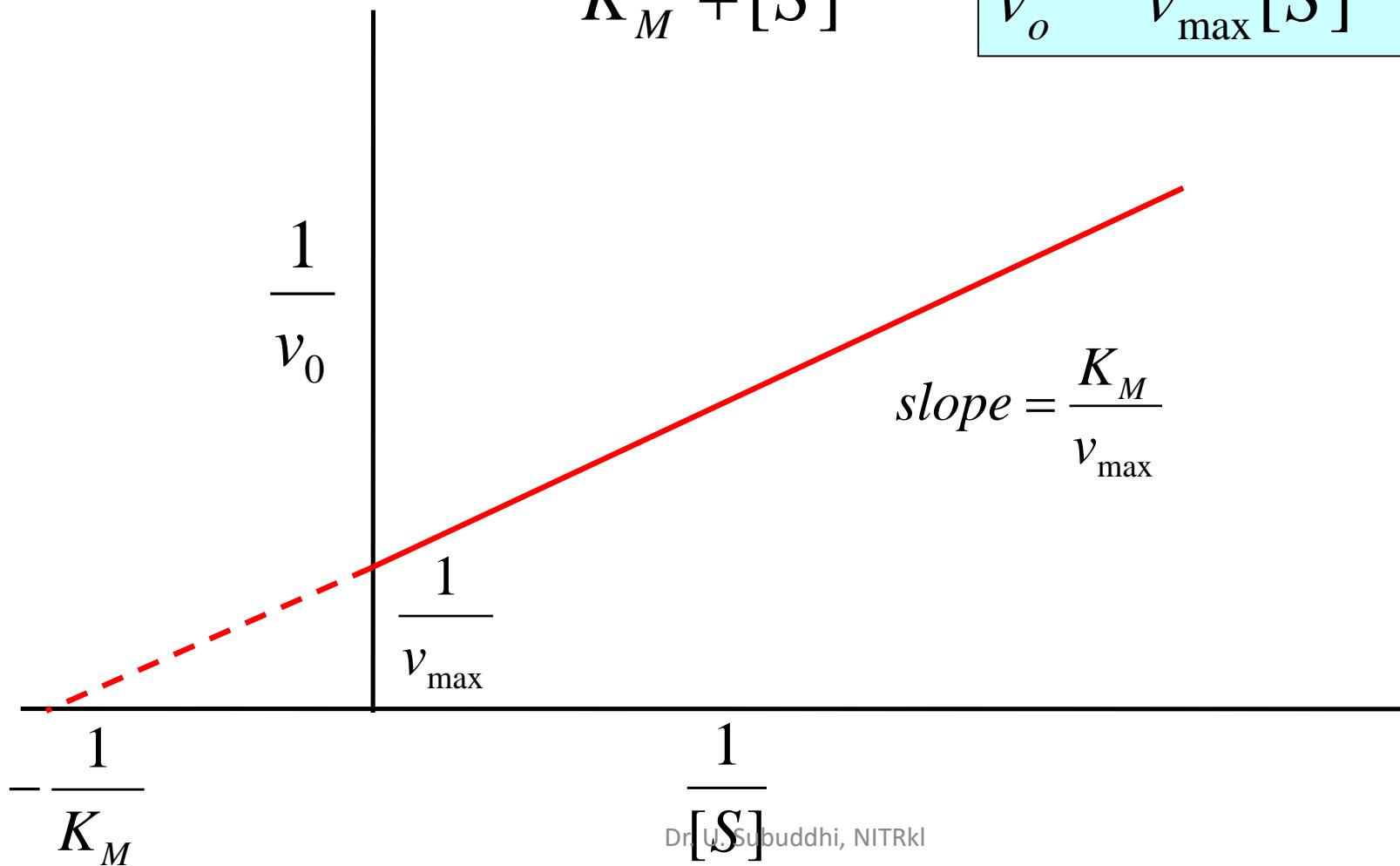
The enzyme carbonic anhydrase has turn over number $\sim 10^5$

Graphical Analysis of Kinetic Data

Lineweaver–Burk or double reciprocal plot

$$v_o = \frac{v_{\max}[S]}{K_M + [S]}$$

$$\frac{1}{v_o} = \frac{K_M}{v_{\max}[S]} + \frac{1}{v_{\max}}$$



ENZYME INHIBITION

Substances that reduce an enzyme's activity are known as **inhibitors**.

Enzyme inhibitors are molecules that interfere with catalysis, slowing or halting enzymatic reactions.

Many inhibitors are substances that structurally resemble their enzyme's substrate but either do not react or react very slowly compared to substrate.

Enzyme inhibitors are among the most important pharmaceutical agents known.

Aspirin (drug) inhibits an enzyme that catalyzes the 1st step of forming **Prostaglandin** (cause of pain in some cases)

Q: What's the importance kinetics of enzyme inhibition?

A: It helps us to understand various metabolic pathways in organisms

Types of enzyme inhibition

Reversible

enzyme is not destroyed
product is formed but slowly

Irreversible

technically destroys
the enzyme

Competitive

Uncompetitive

Mixed / Noncompetitive

Types of enzyme inhibition

Reversible

enzyme is not destroyed
product is formed but slowly

Irreversible

technically destroys
the enzyme

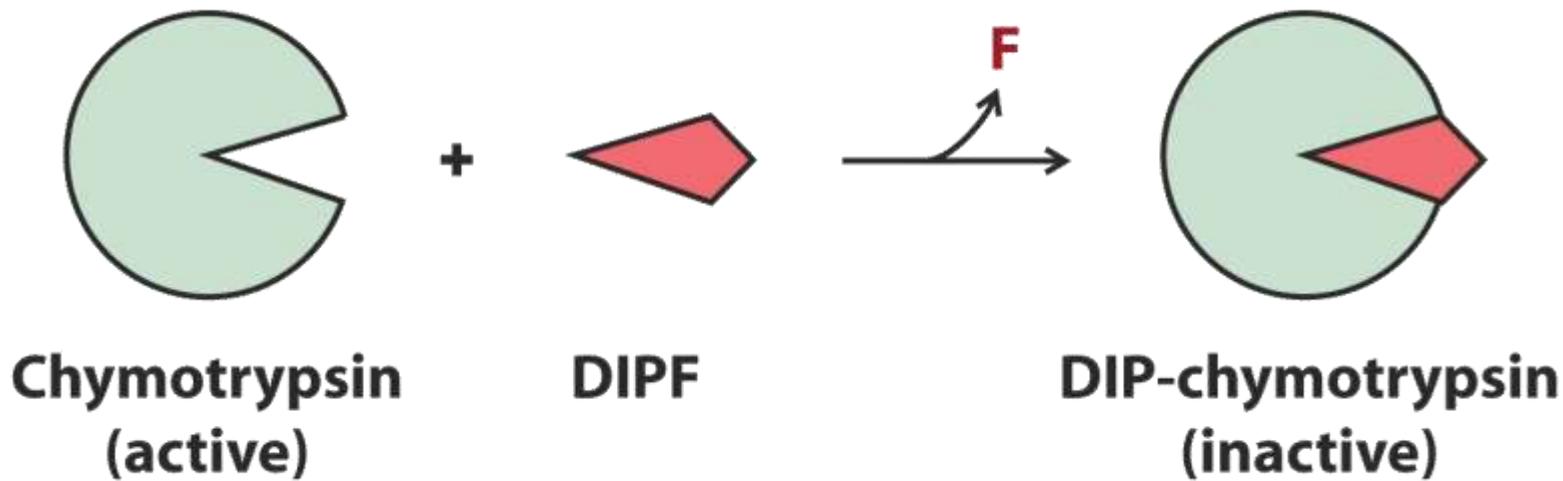
Competitive

Uncompetitive

Mixed / Noncompetitive

Irreversible Inhibition

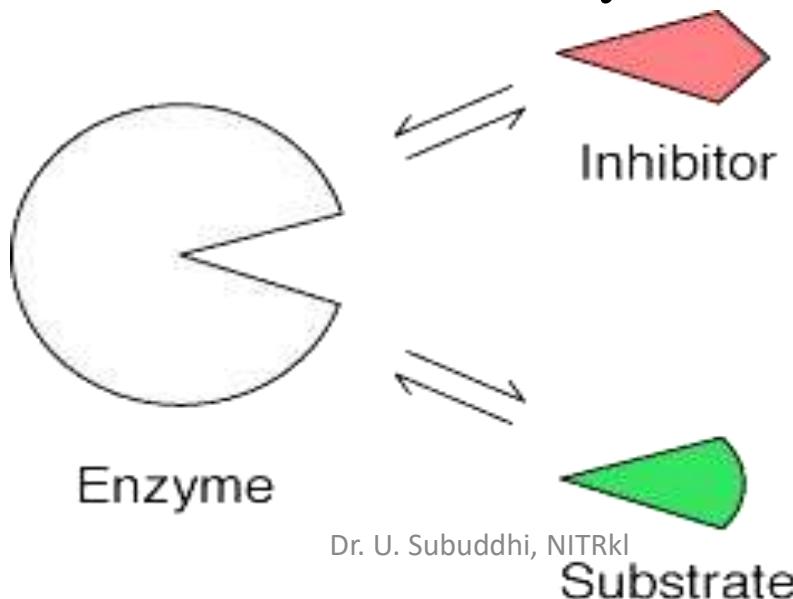
- Certain compounds interact with enzyme so tightly that their effect is irreversible.
 - Any agent that covalently modifies the amino acid side chain in a protein or destroys a functional group on an enzyme that is essential for the enzyme's activity
 - In such cases the inhibitor can't be removed by dilution or dialysis

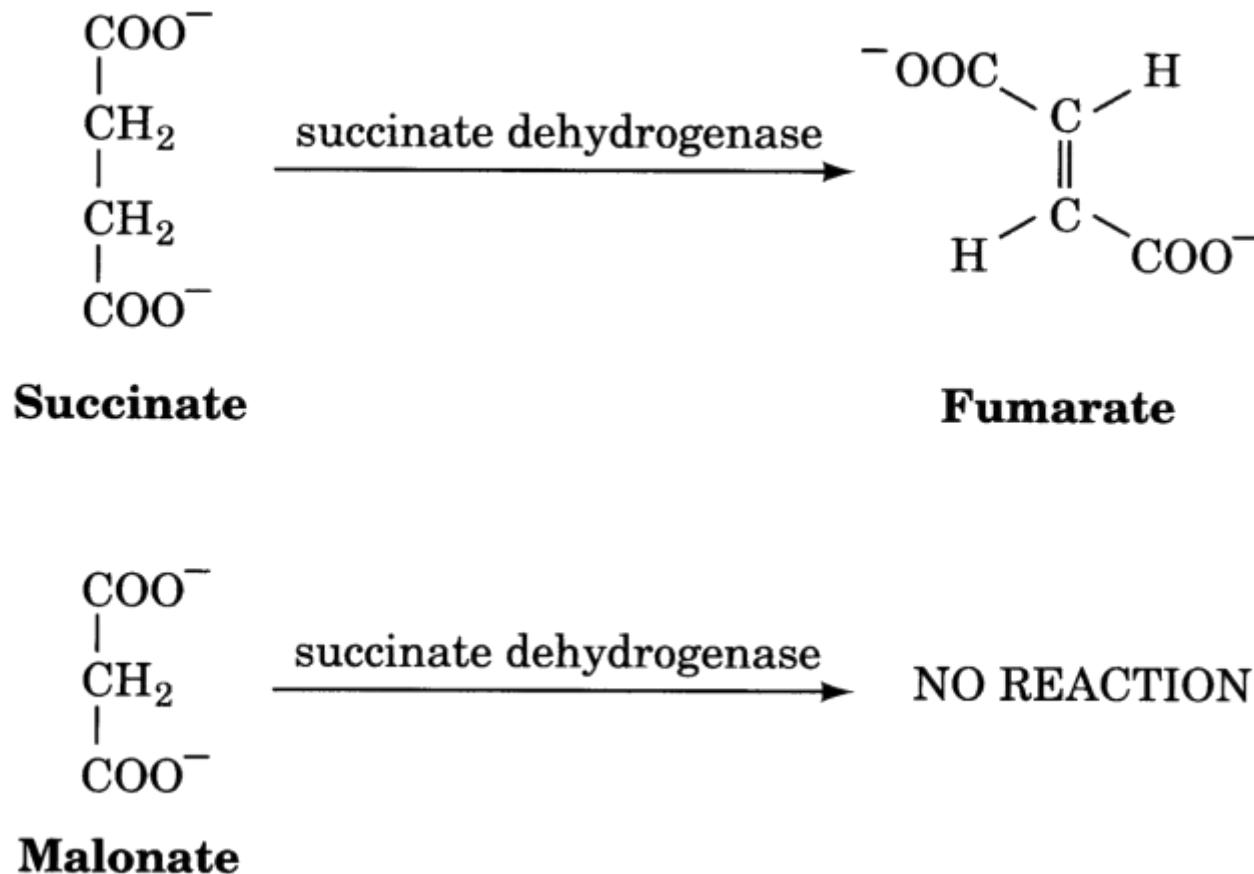


Diisopropylphosphofluoridate (DIPF) is an irreversible inhibitor of the enzyme chymotrypsin

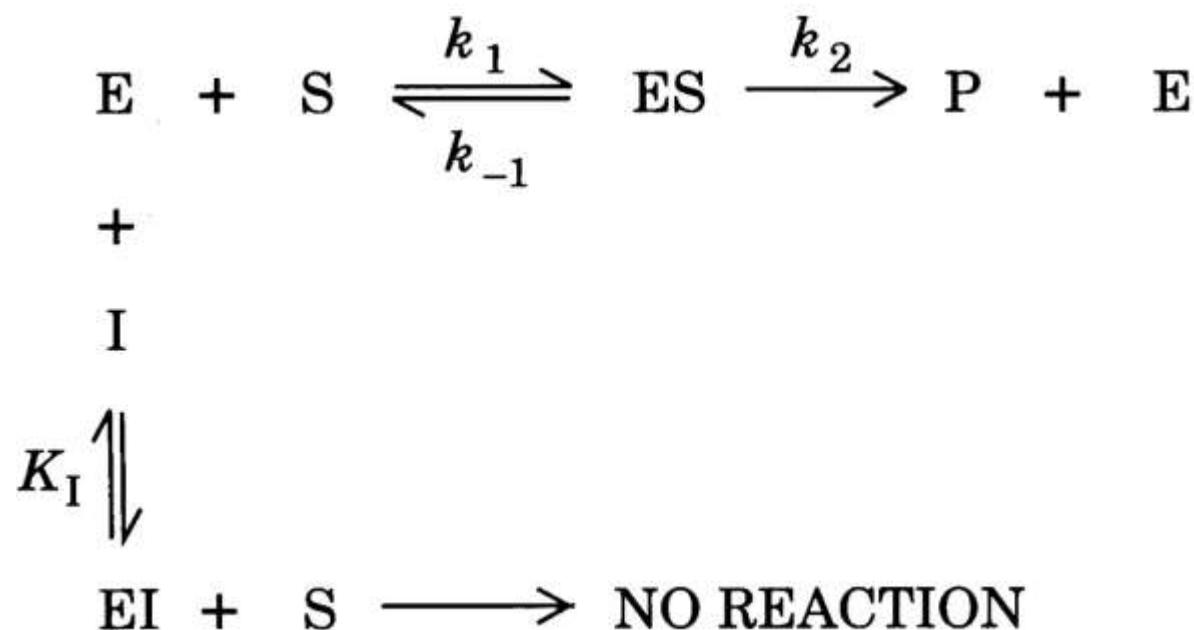
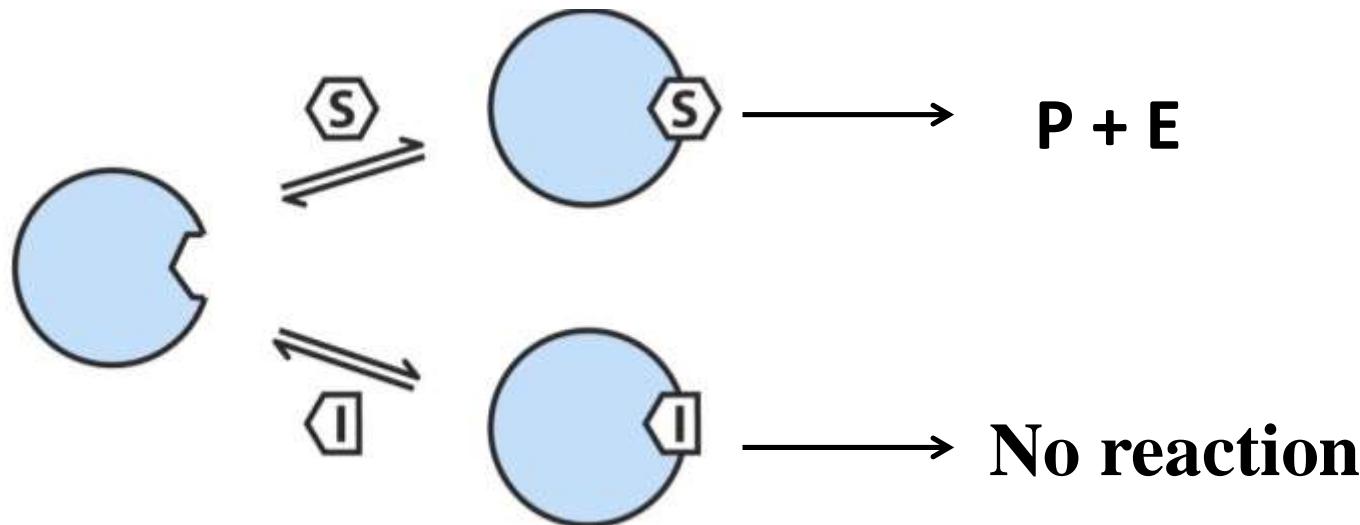
Competitive inhibition

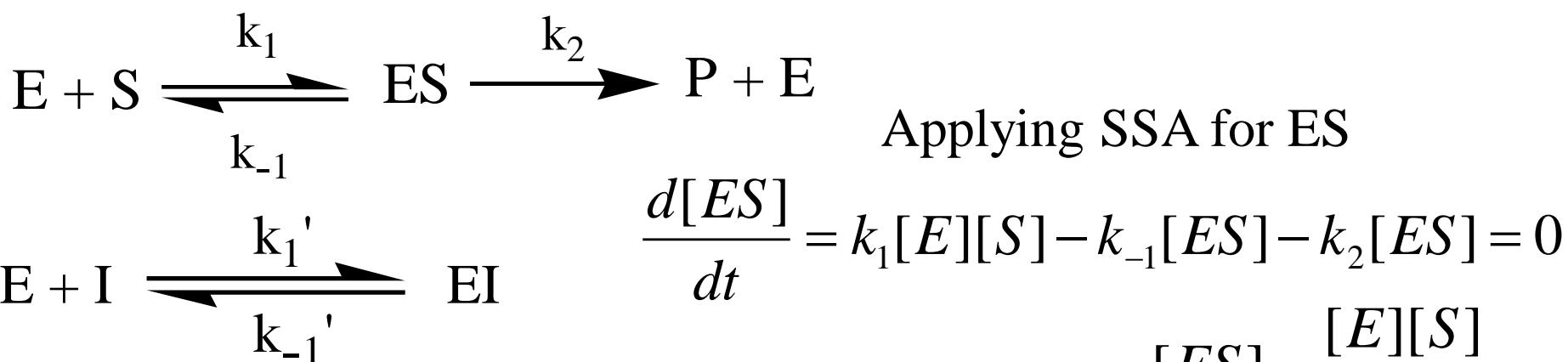
- In competitive inhibition, the inhibitor is a substance that directly competes with a substrate for binding to the enzyme's active site.
 - Competitive inhibitors are molecules which are similar in shape and chemical properties to substrates and capable of binding to enzyme active sites. They lack the exact electronic charge that allows it to react
 - While the inhibitor occupies the active site, it prevents the binding of the substrate to the enzyme and blocks the reaction.





Succinate dehydrogenase, a citric acid cycle enzyme that functions to convert **succinate to fumarate** is competitively inhibited by **malonate**, which structurally resembles succinate but cannot be dehydrogenated





Applying SSA for ES

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0$$

$$[ES] = \frac{[E][S]}{K_M}$$

$$[E]_0 = [E] + [ES] + [EI]$$

$$K_I \text{ is the dissociation constant of EI complex} \quad K_I = \frac{[E][I]}{[EI]}$$

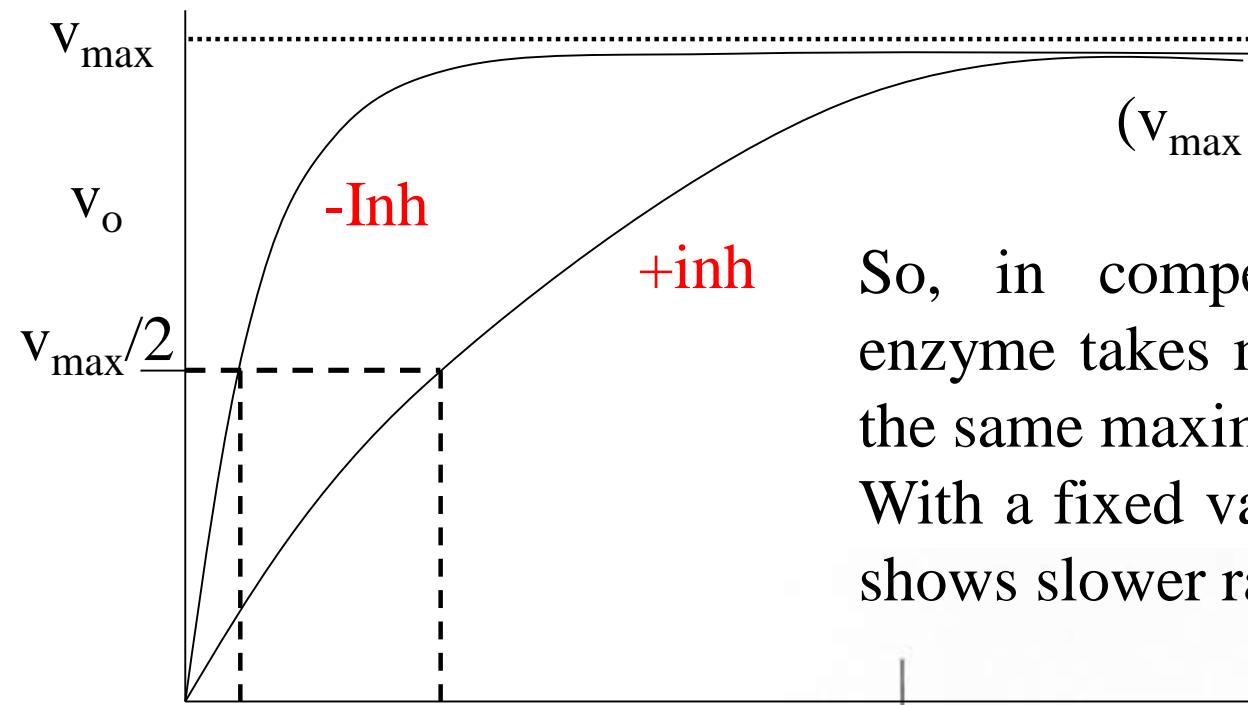
$$[E]_0 = [E] + \frac{[E][S]}{K_M} + \frac{[E][I]}{K_I}$$

$$[ES] = \frac{[E]_0[S]}{[S] + K_M \left(1 + \frac{[I]}{K_I} \right)}$$

$$\text{Rate} = k_2[ES]$$

$$v_o = \frac{V_{\max} [S]}{\alpha K_M + [S]}$$

$$\alpha = \left(1 + \frac{[I]}{K_I} \right)$$

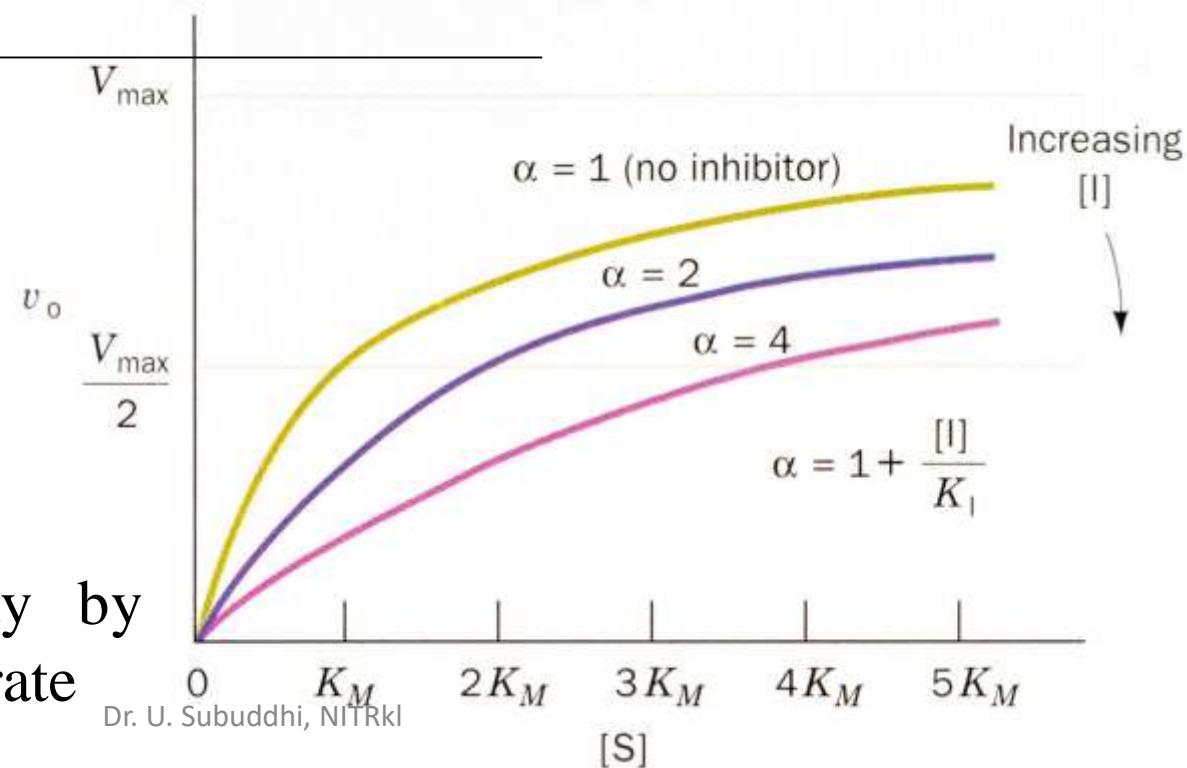


$(v_{max}$ is not affected by $[I]$)

So, in competitive inhibition, the enzyme takes more substrate to reach the same maximum velocity!
With a fixed value of $[S]$, the enzyme shows slower rate!

$$v_o = \frac{v_{max} [S]}{\alpha K_M + [S]}$$

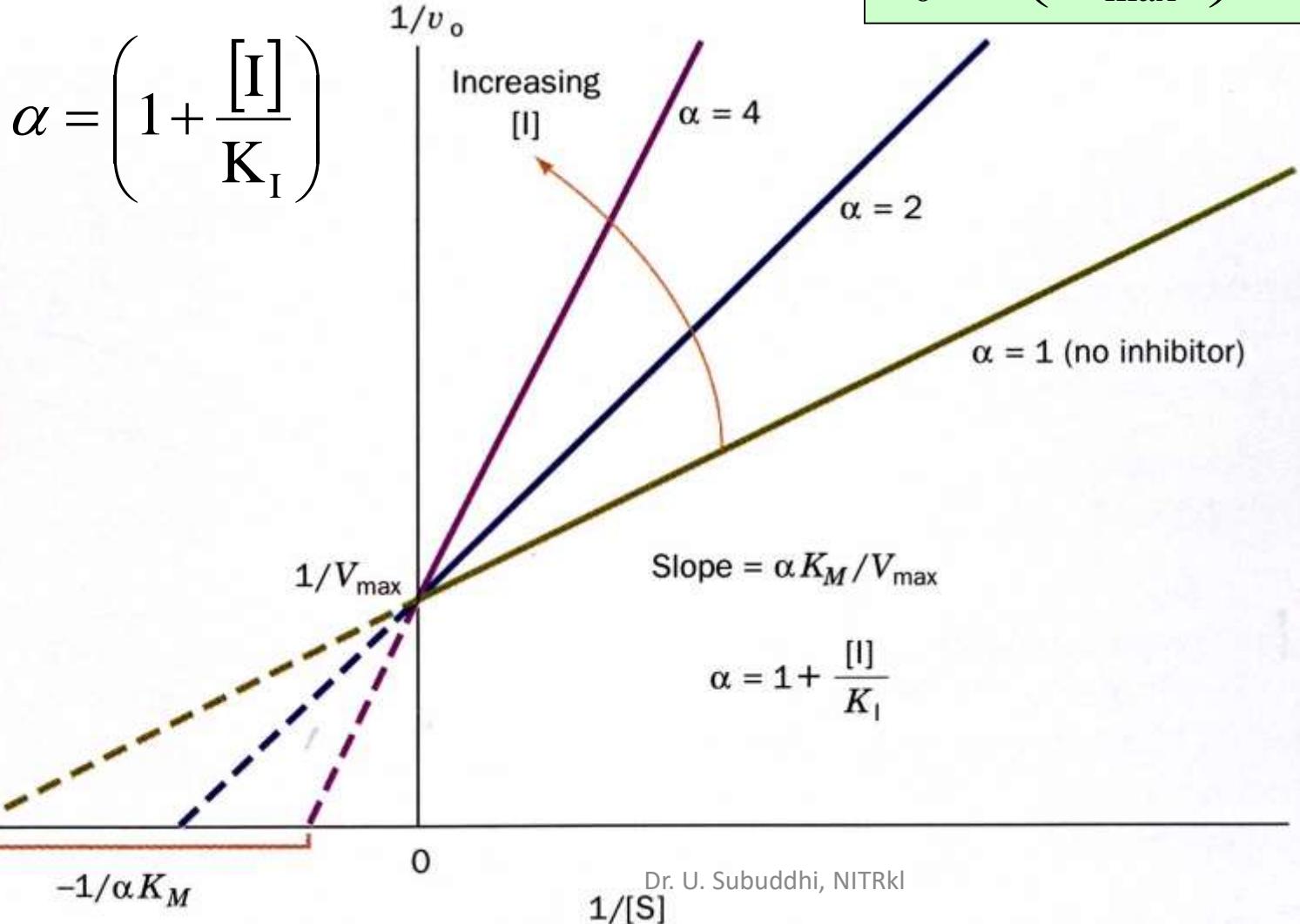
Can be competed away by increasing conc. of substrate



Competitive Inhibition: Lineweaver-Burke Plot

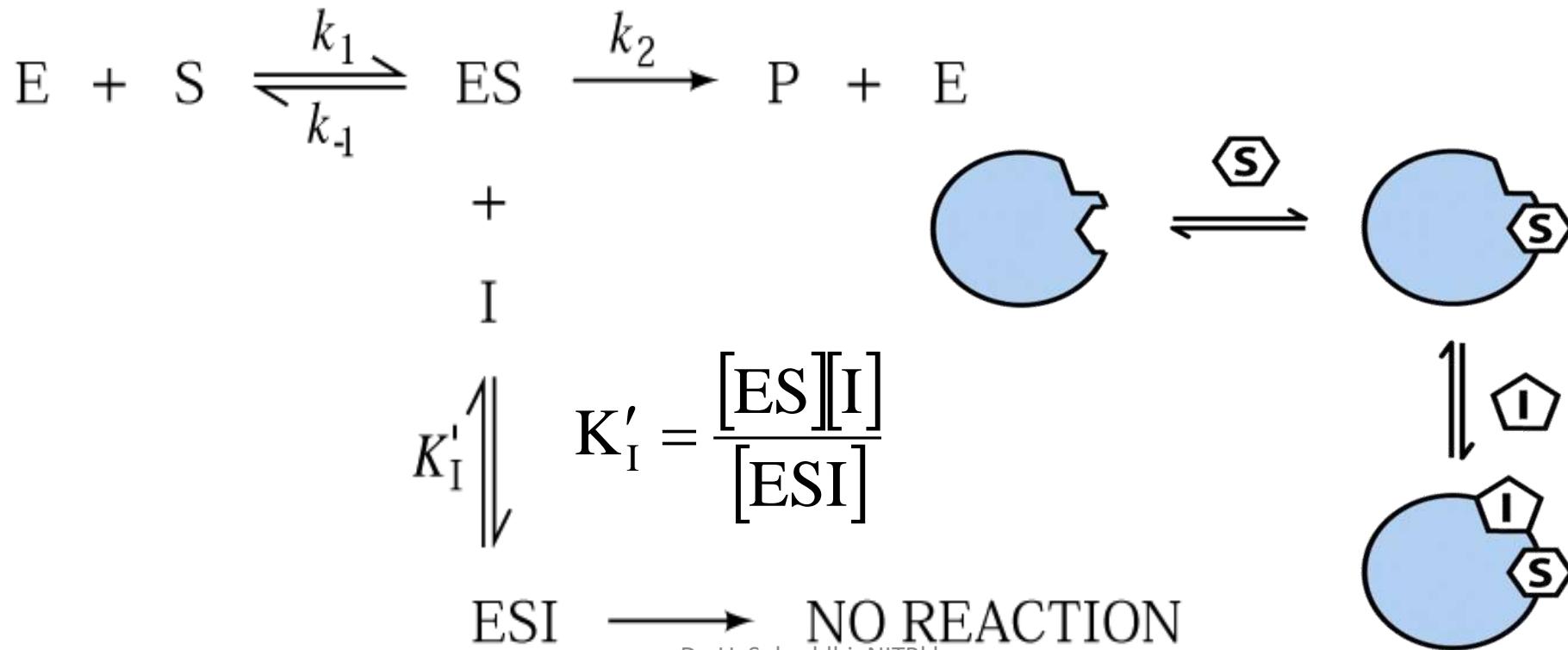
$$v_o = \frac{V_{\max} [S]}{\alpha K_M + [S]}$$

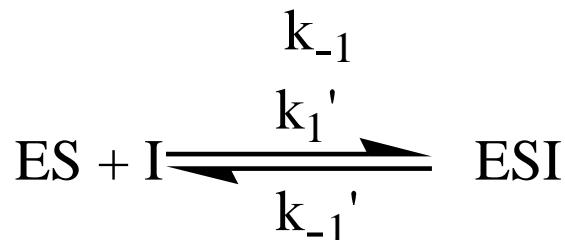
$$\frac{1}{v_0} = \left(\frac{\alpha K_M}{V_{\max}} \right) \frac{1}{[S]} + \frac{1}{V_{\max}}$$



Uncompetitive Inhibition

- Binds only to ES complex but not free enzyme
- Binds at a location other than active site
- Binding of inhibitor alters active site property thus affecting catalysis
- Cannot be competed away by increasing conc. of substrate





$$K_M = \frac{[E][S]}{[ES]}$$

$$[E]_0 = [E] + [ES] + [ESI]$$

K'_I is the dissociation constant of ESI complex $K'_I = \frac{[ES][I]}{[ESI]}$

$$[E]_0 = \frac{K_M[ES]}{[S]} + [ES] + \frac{[I][ES]}{K'_I} = \frac{[ES]}{[S]} \left\{ K_M + \left(1 + \frac{[I]}{K'_I} \right) [S] \right\}$$

$$[ES] = \frac{[E]_0[S]}{K_M + \left(1 + \frac{[I]}{K'_I} \right) [S]}$$

$$\text{Rate} = k_2[ES]$$

$$v = \frac{v_{\max}[S]}{K_M + \alpha'[S]}$$

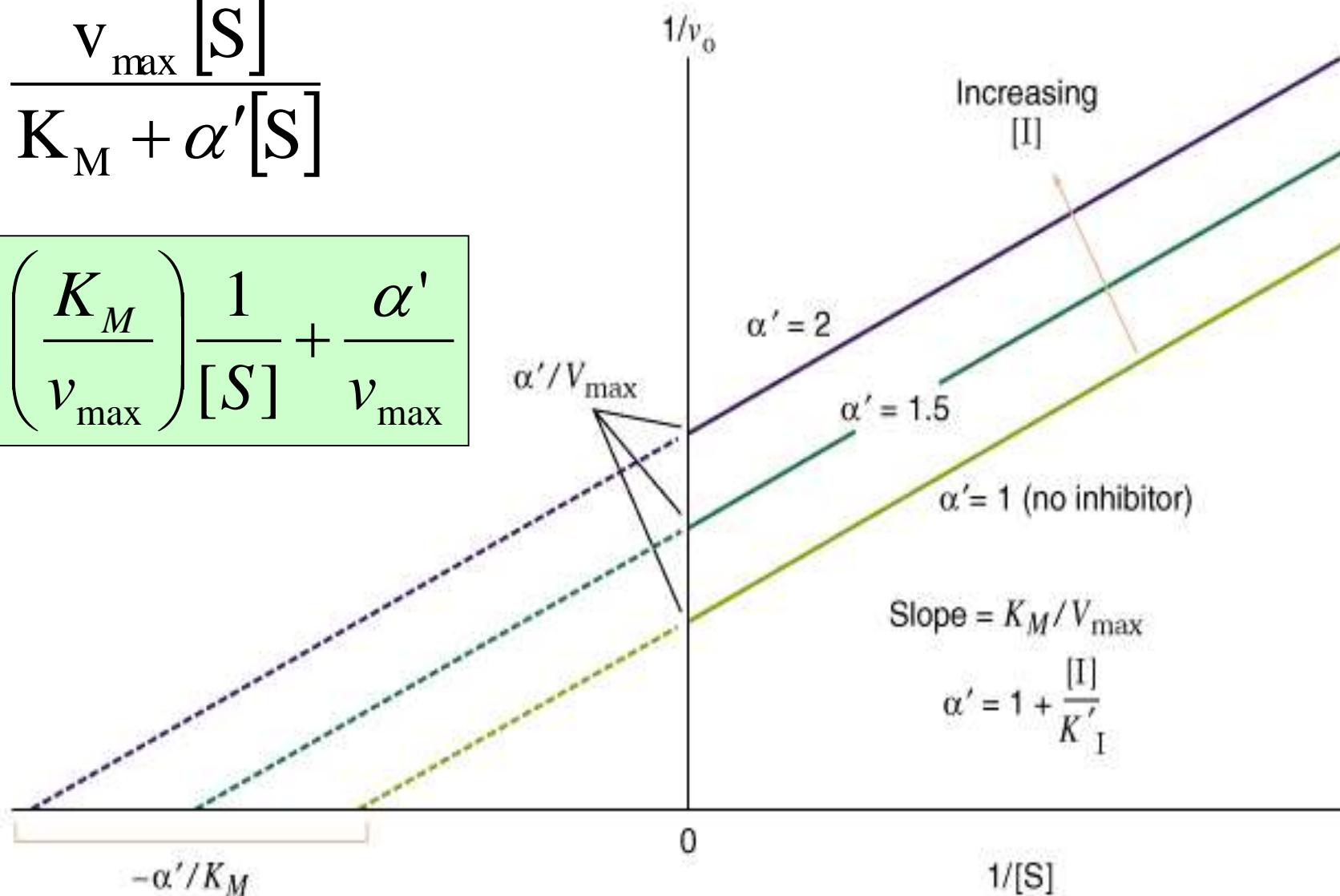
v_{max} is affected by [I]

$$\alpha' = \left(1 + \frac{[I]}{K'_I} \right)$$

Uncompetitive Inhibition: Lineweaver-Burke Plot

$$v = \frac{V_{\max} [S]}{K_M + \alpha' [S]}$$

$$\frac{1}{v_0} = \left(\frac{K_M}{V_{\max}} \right) \frac{1}{[S]} + \frac{\alpha'}{V_{\max}}$$

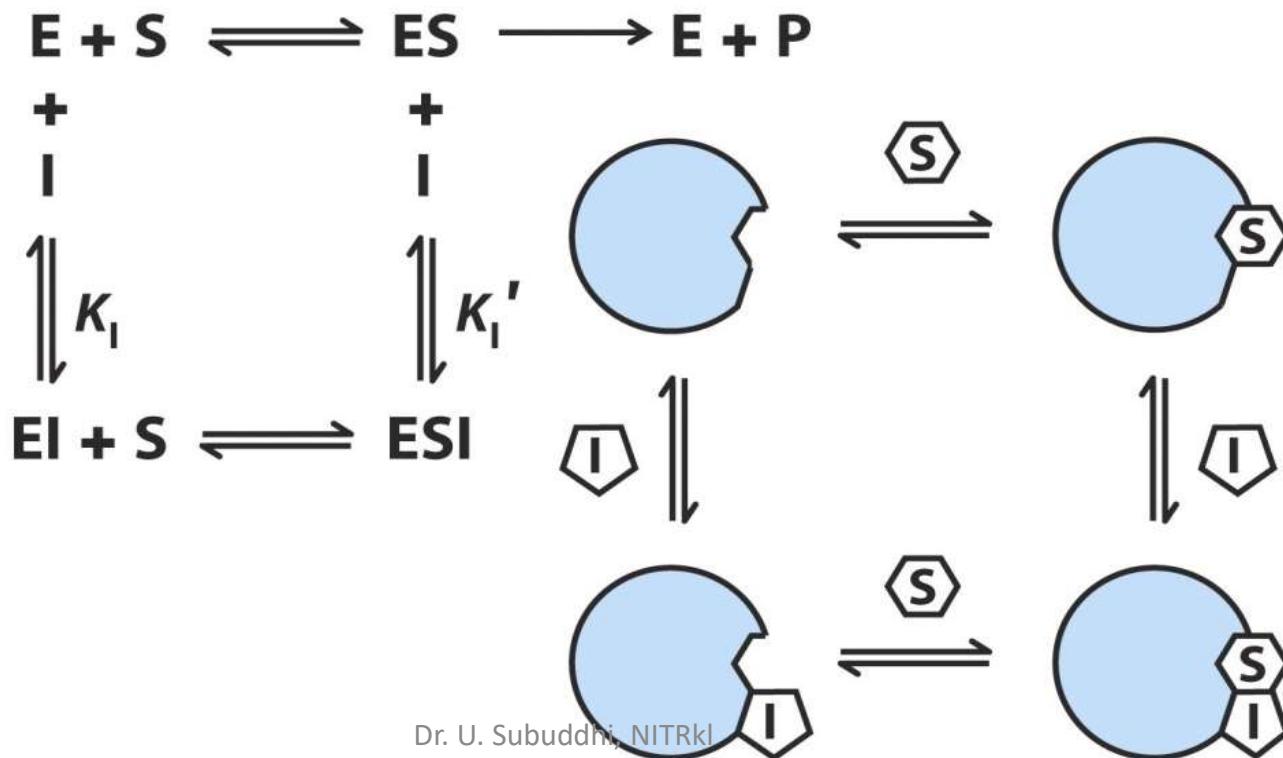


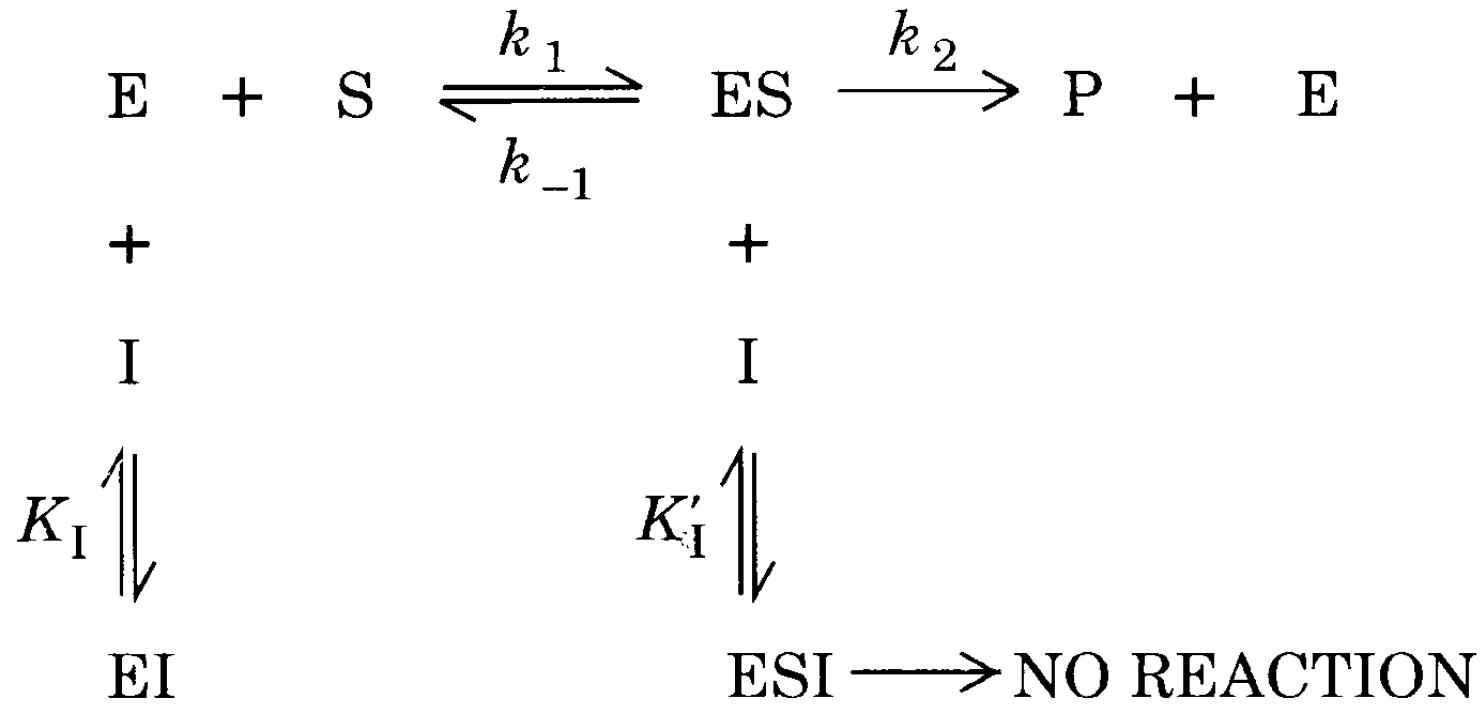
Mixed Inhibition

If the inhibitor binds to both the enzyme and the enzyme–substrate complex

The inhibitor binds to the enzyme at a location distinct from the substrate binding site.

The binding of the inhibitor will either alter the K_M or v_{max} or both.





$$K_I = \frac{[E][I]}{[EI]}$$

$$K'_I = \frac{[ES][I]}{[ESI]}$$

$$[E]_0 = [E] + [EI] + [ES] + [ESI]$$

$$= [E] + \frac{[E][I]}{K_I} + [ES] + \frac{[ES][I]}{K'_I}$$

$$= [E] \left(1 + \frac{[I]}{K_I} \right) + [ES] \left(1 + \frac{[I]}{K'_I} \right) = [E]\alpha + [ES]\alpha'$$

$$[E]_0 = \left(\frac{[ES]K_M}{[S]} \right) \alpha + [ES]\alpha' \quad \text{Rate} = k_2[ES]$$

$$\alpha = \left(1 + \frac{[I]}{K_I} \right) \quad \alpha' = \left(1 + \frac{[I]}{K'_I} \right)$$

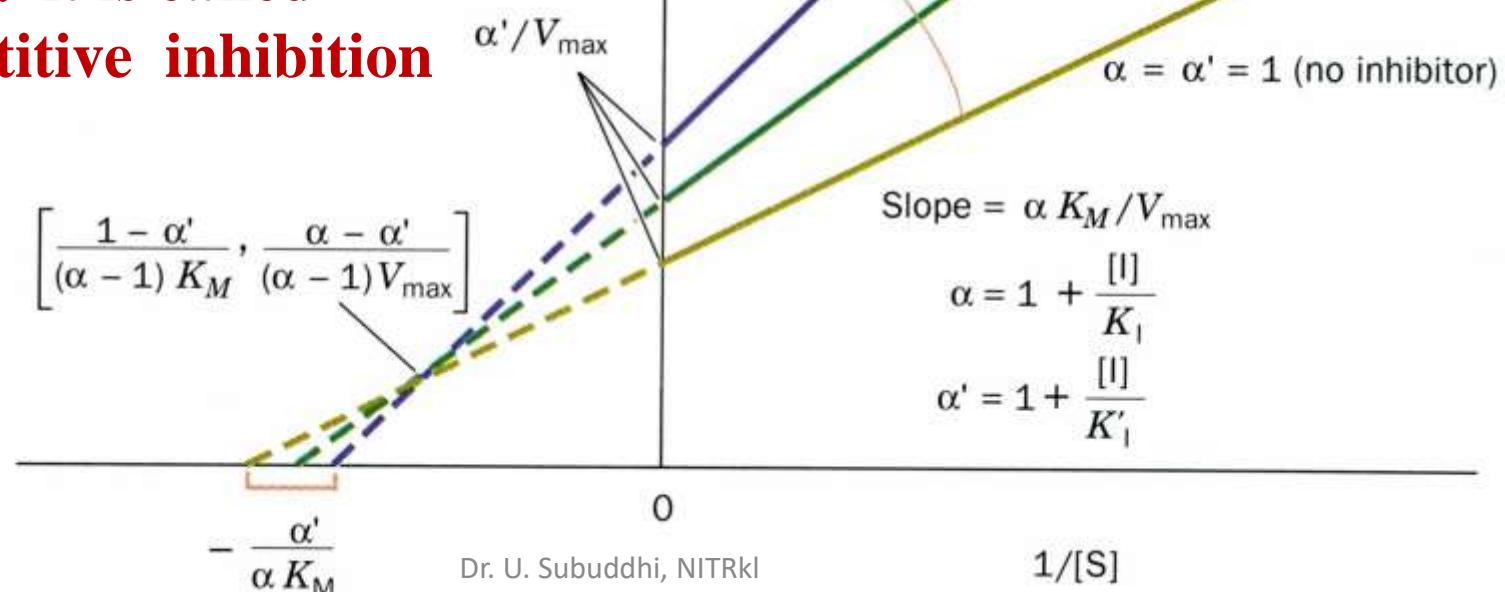
$$v_o = \frac{V_{max}[S]}{\alpha K_M + \alpha'[S]}$$

Mixed Inhibition: Lineweaver-Burke Plot

$$v_o = \frac{V_{max} [S]}{\alpha K_M + \alpha' [S]}$$

$$\frac{1}{v_0} = \left(\frac{\alpha K_M}{V_{max}} \right) \frac{1}{[S]} + \frac{\alpha'}{V_{max}}$$

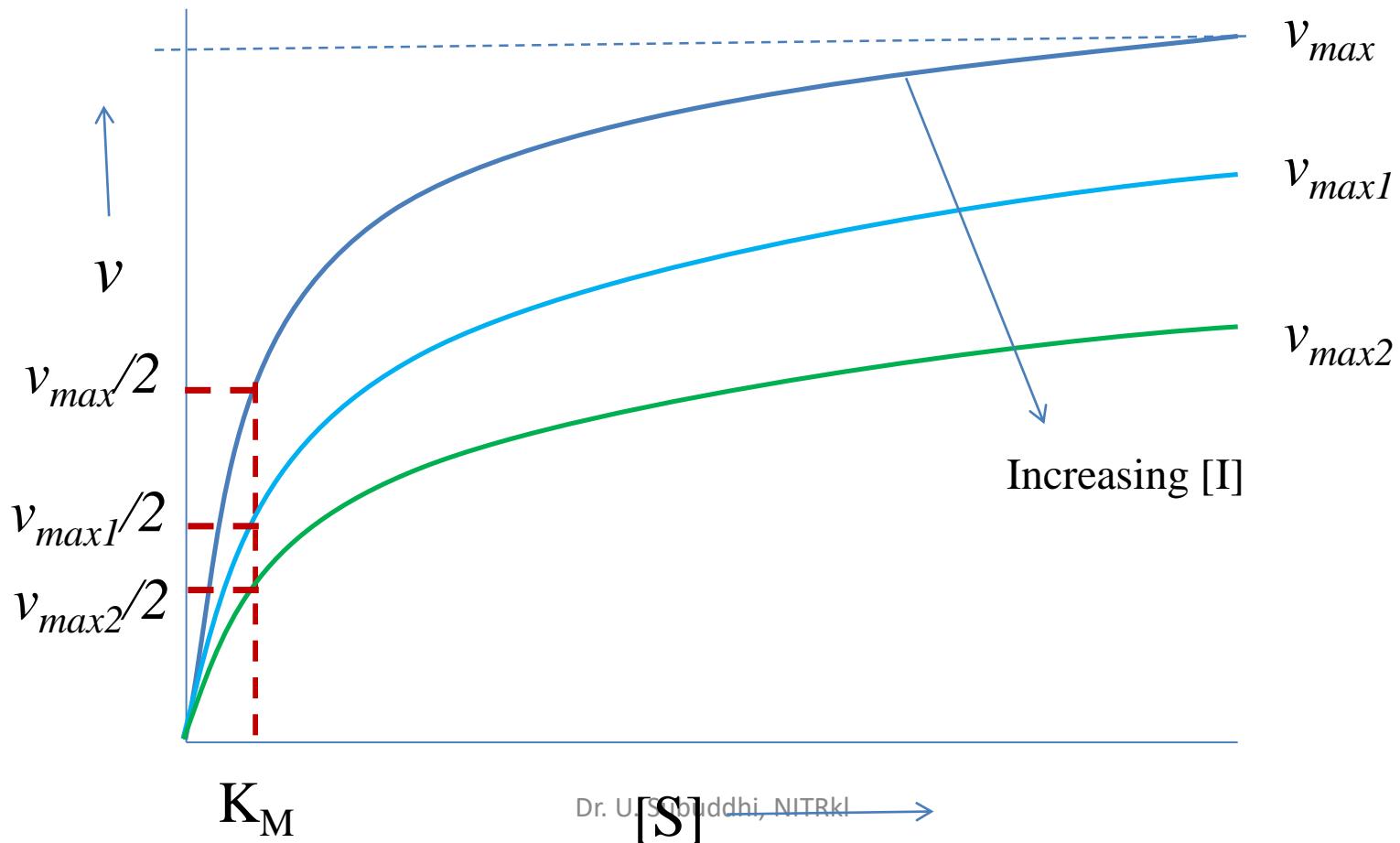
When $\alpha=\alpha'$ it is called
noncompetitive inhibition



When $\alpha=\alpha'$ it is called Noncompetitive inhibition

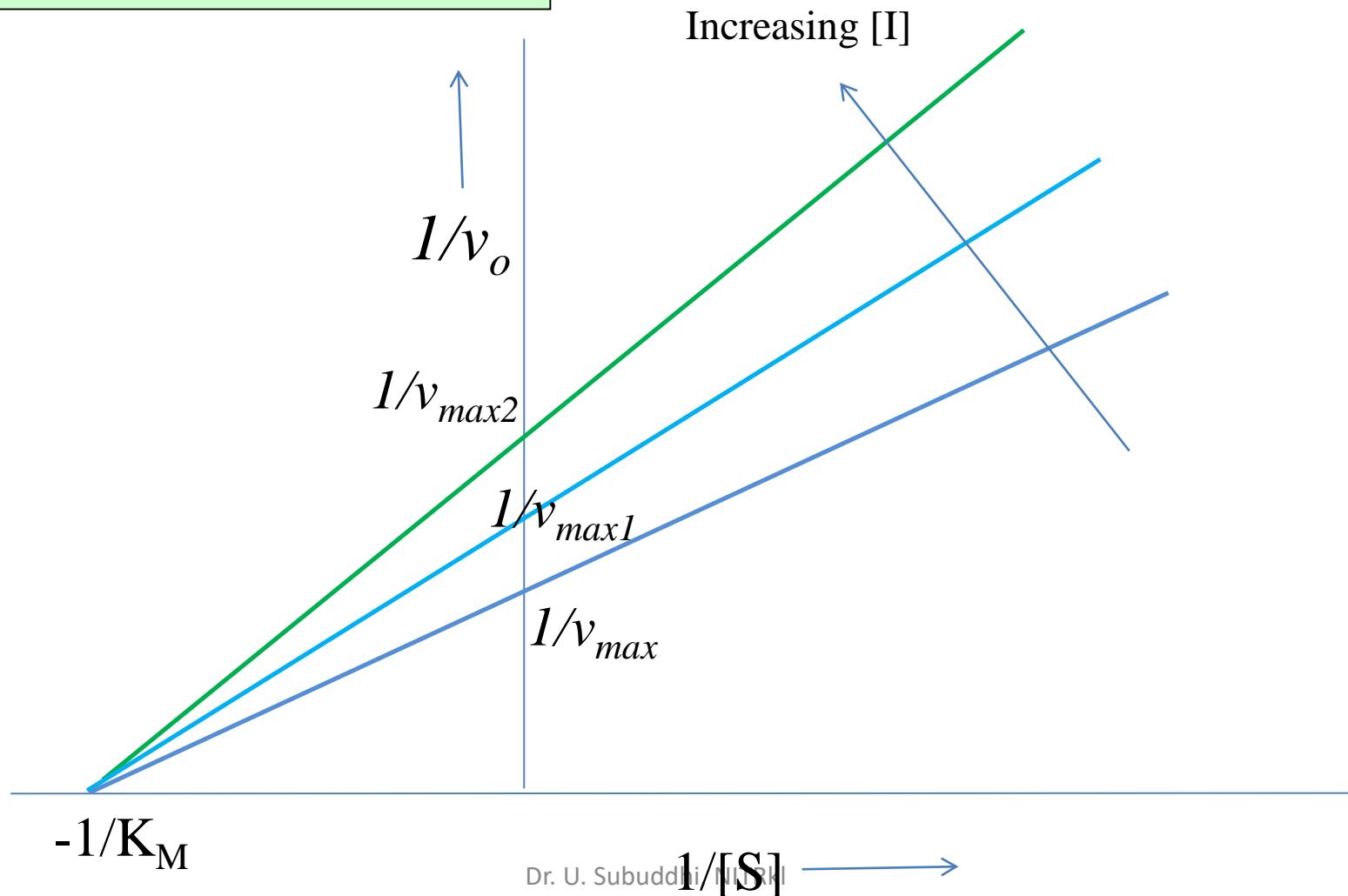
$$v_o = \frac{v_{\max} [S]}{\alpha K_M + \alpha' [S]}$$

$$v_o = \frac{v_{\max} [S]}{\alpha (K_M + [S])}$$



Noncompetitive Inhibition: Lineweaver-Burke Plot

$$\frac{1}{v_o} = \left(\frac{\alpha K_M}{v_{\max}} \right) \frac{1}{[S]} + \frac{\alpha}{v_{\max}}$$

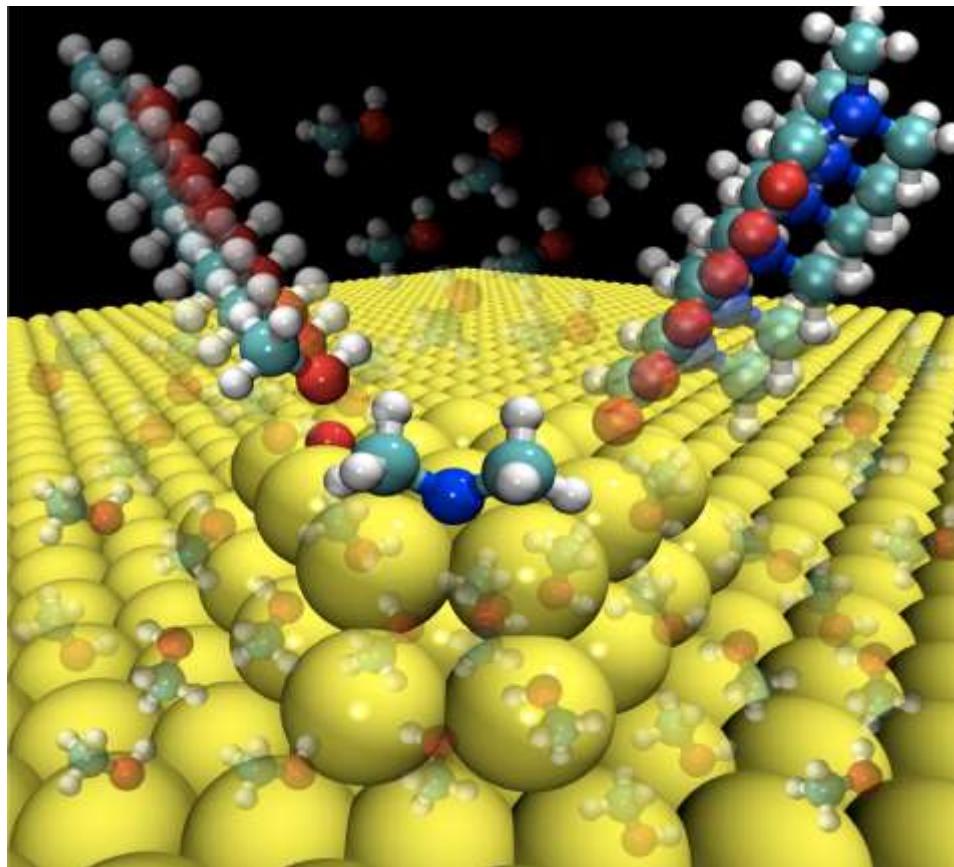


Effects of Inhibitors on the parameters of Michaelis-Menten equation

Type of Inhibition	V_{\max}^{app}	K_M^{app}
None	v_{\max}	K_M
Competitive	v_{\max}	αK_M
Uncompetitive	v_{\max}/α'	K_M/α'
Mixed	v_{\max}/α'	$\alpha K_M/\alpha'$
Noncompetitive	v_{\max}/α'	K_M

$$\alpha = \left(1 + \frac{[I]}{K_I} \right) \quad \alpha' = \left(1 + \frac{[I]}{K'_I} \right)$$

Heterogeneous Catalysis



- Surface Reaction: Solid catalyst, gaseous or liquid reactant

Heterogeneous Catalysis:

In general:

Solid phase serves as the **catalyst**, **gas/liquid** phase is the **Substrate**.

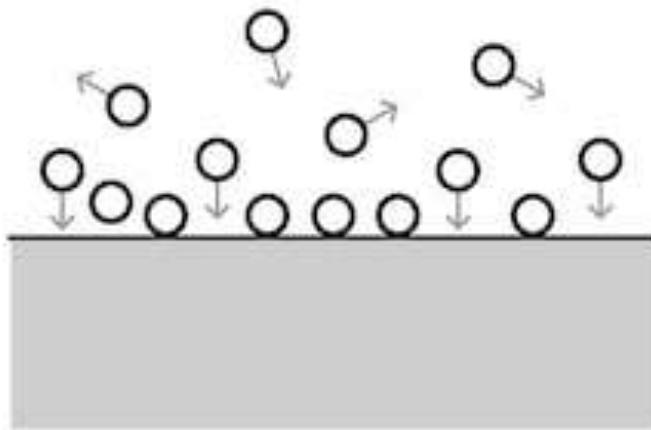
We would study heterogeneous catalysis between **solid** phase (**catalyst**) and **gas (substrate)**.

Such heterogeneous catalysis goes through **Solid-Gas intermediate**, which is roughly equivalent to the ES complex of enzyme catalysis.

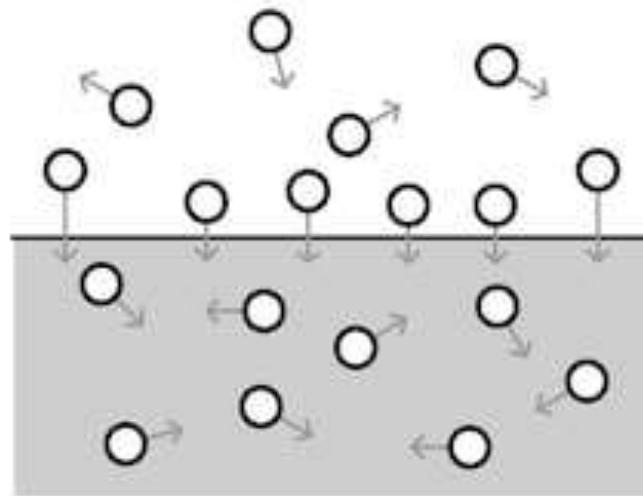


So in order to study a surface reaction we need to understand the adsorption process

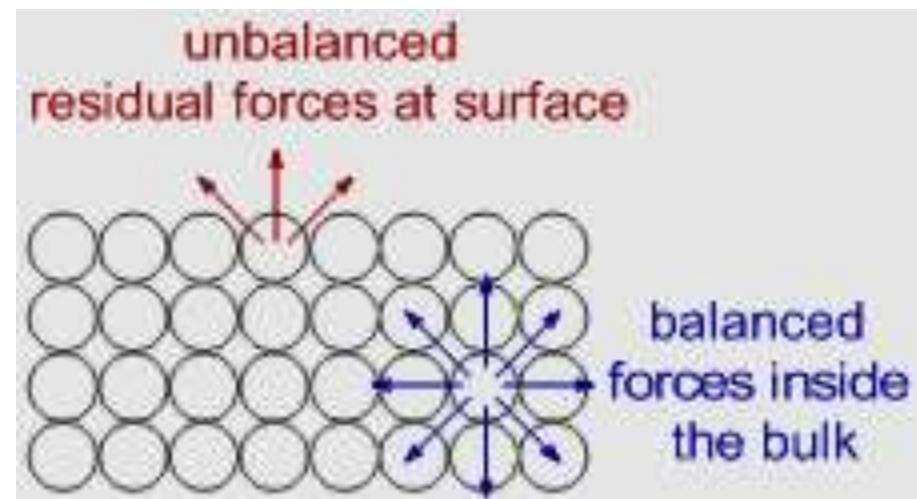
Adsorption Vs. Absorption



Adsorption



Absorption



Surface : Adsorbent

Gas/Liquid: Adsorbate

Adsorption is a spontaneous process
It is an exothermic process

Langmuir Adsorption Isotherm



In 1916, Irving Langmuir presented his model for the adsorption of species onto simple surfaces.

Langmuir was awarded the Nobel Prize in 1932 for his work concerning surface chemistry.

Langmuir adsorption isotherm is the most idealistic isotherm.

He hypothesized that a given surface has a certain number of equivalent sites to which a species can “stick”, either by physisorption or chemisorption.

His theory began when he postulated that gaseous molecules do not rebound elastically from a surface, but are held by it in a similar way to groups of molecules in solid bodies.

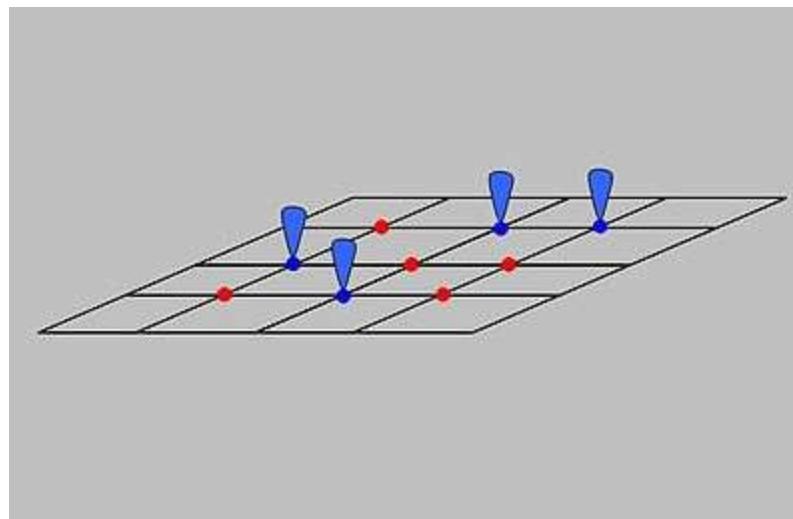
Basic Assumptions of the Model

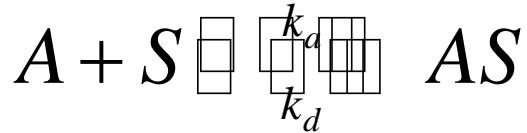
Adsorption can't proceed beyond monolayer coverage

All sites on the surface are equivalent and the surface is uniform and homogeneous

The ability of a molecule to adsorb at a given site is independent of the adjacent molecule i.e. there is no lateral interaction between the adsorbed molecules

The process of adsorption involves a dynamic equilibrium





k_a : rate constant of adsorption

k_d : rate constant of desorption

θ : fraction of surface sites that is occupied

$(1-\theta)$: fraction of surface sites that is free

$$\text{Rate of adsorption} = k_a [A] (1-\theta)$$

$$\text{Rate of desorption} = k_d \theta$$

At equilibrium: Rate of adsorption = Rate of desorption

$$k_a [A] (1-\theta) = k_d \theta$$

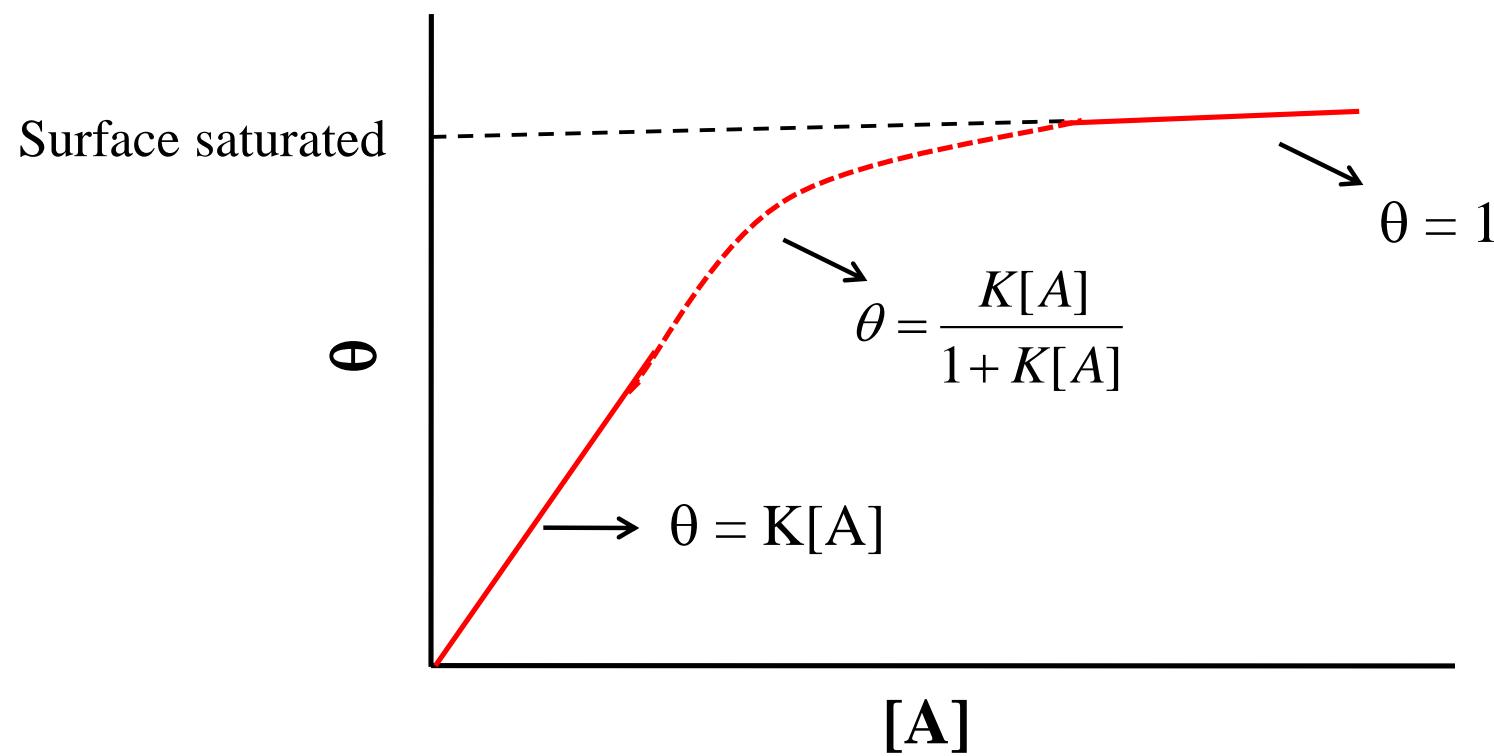
$$\frac{\theta}{1-\theta} = \frac{k_a}{k_d} [A] = K[A]$$

$K = k_a/k_d$ = equilibrium constant for the adsorption process

$$\boxed{\theta = \frac{K[A]}{1 + K[A]}}$$

$$\theta = \frac{K[A]}{1 + K[A]}$$

$$\theta = \frac{Kp_A}{1 + Kp_A}$$



Heterogeneous Catalysis Reactions

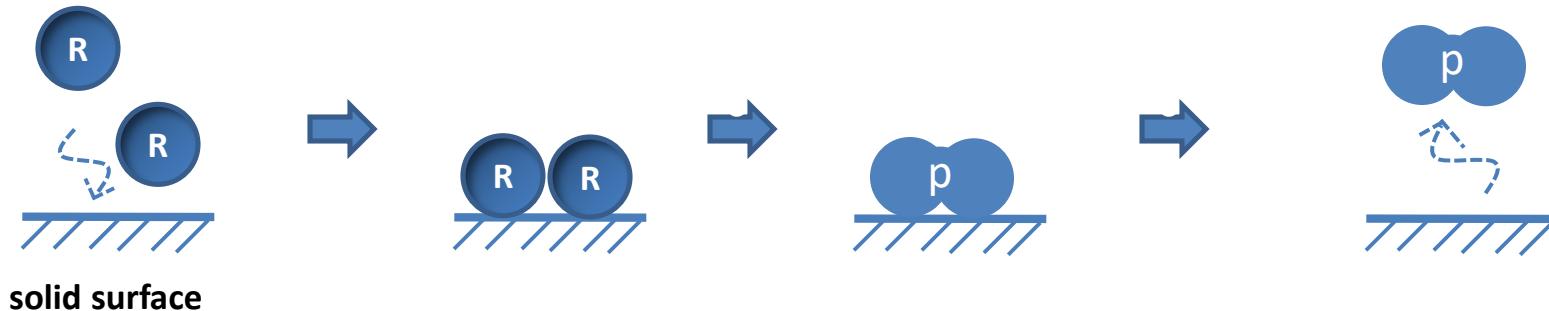
The different steps involved in a heterogeneous catalysis reaction are

1. Diffusion of the reactant molecules to the surface of the catalyst
2. Adsorption of the reactant on the surface of the catalyst
3. Reaction on the surface
4. Desorption of the product
5. Diffusion of the product to the bulk

Out of the five steps step 1 and 5 (diffusion) are very fast processes.

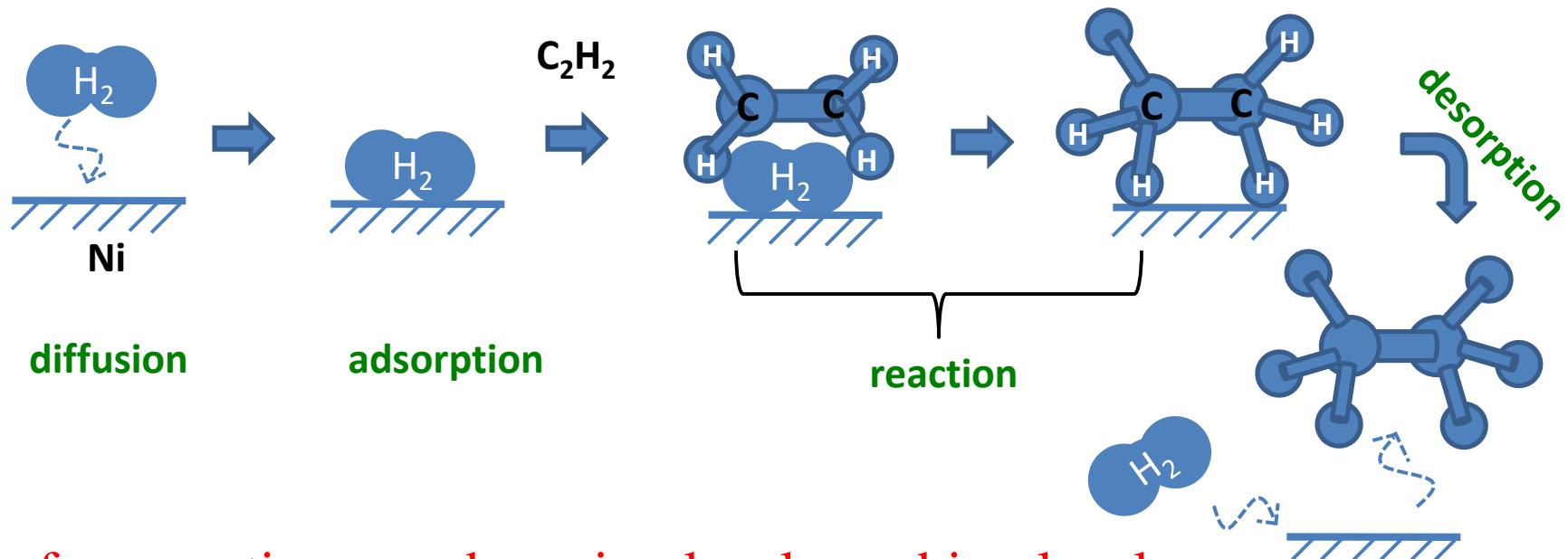
Steps 3 (reaction) and 4 (desorption) are often can not be differentiated *i.e.* the product formation and desorption happen simultaneously.

Heterogeneous Catalysis: Mechanistic steps



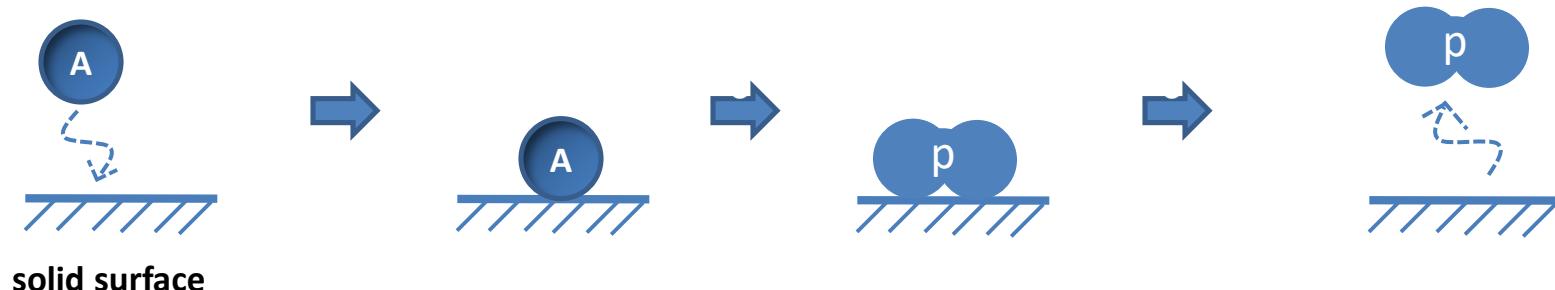
Steps: i) diffusion ii) adsorption iii) reaction iv) desorption

Real life example: hydrogenation of ethylene on Ni surface



Surface reactions can be unimolecular or bimolecular

Unimolecular Reaction: A single adsorbed molecule forms product



The rate of the reaction is proportional to the fraction of the surface that is occupied (Langmuir adsorption isotherm is followed)

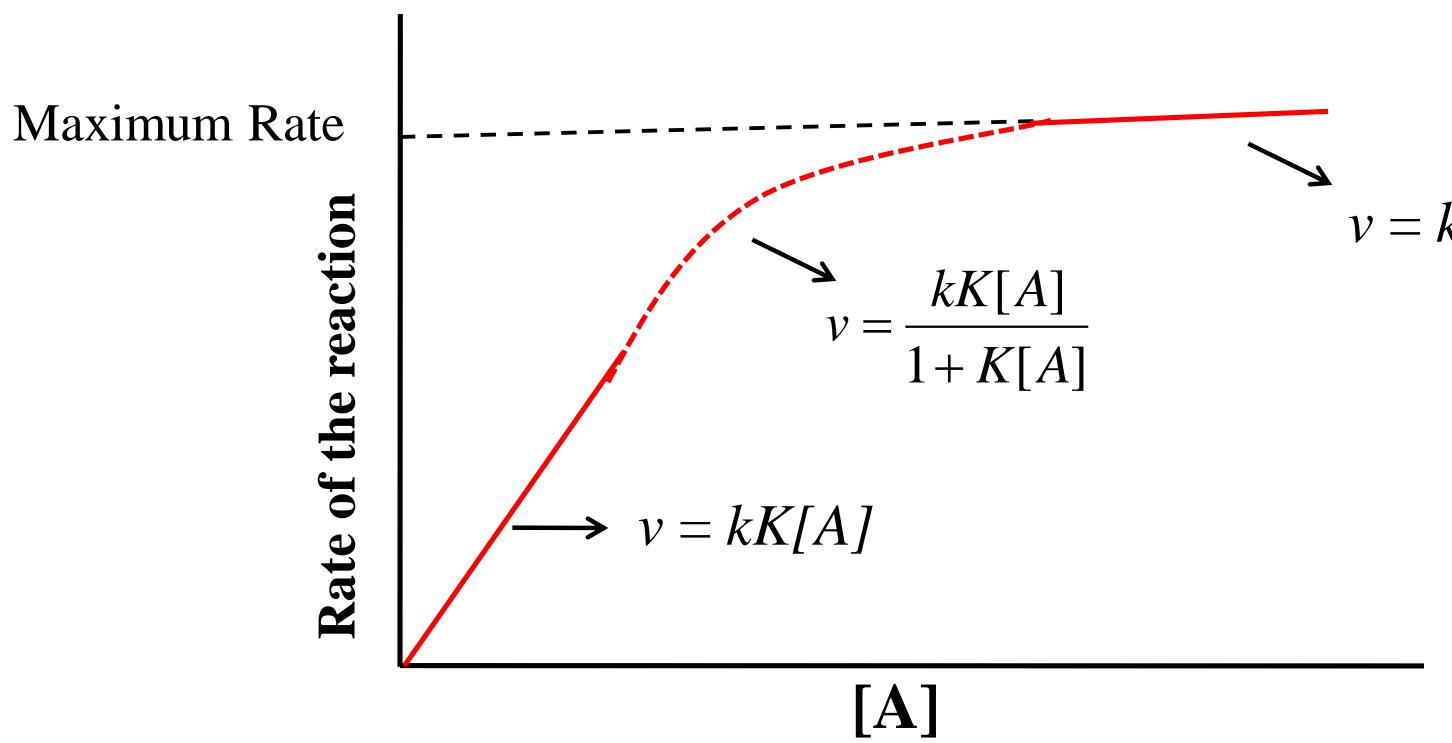
$$\text{Rate of the reaction} = v = k\theta = \frac{kK[A]}{1 + K[A]}$$

The dependence of v on $[A]$ is similar to that of θ

$$\text{Rate of the reaction} = v = k\theta = \frac{kKp_A}{1 + Kp_A}$$

Example: Decomposition of PH_3 on W

Decomposition of NH_3 on Fe



Case (i) : When $[A]$ or p_A is very small

First order kinetics

Case (ii) : When $[A]$ or p_A is very high

Zero order kinetics

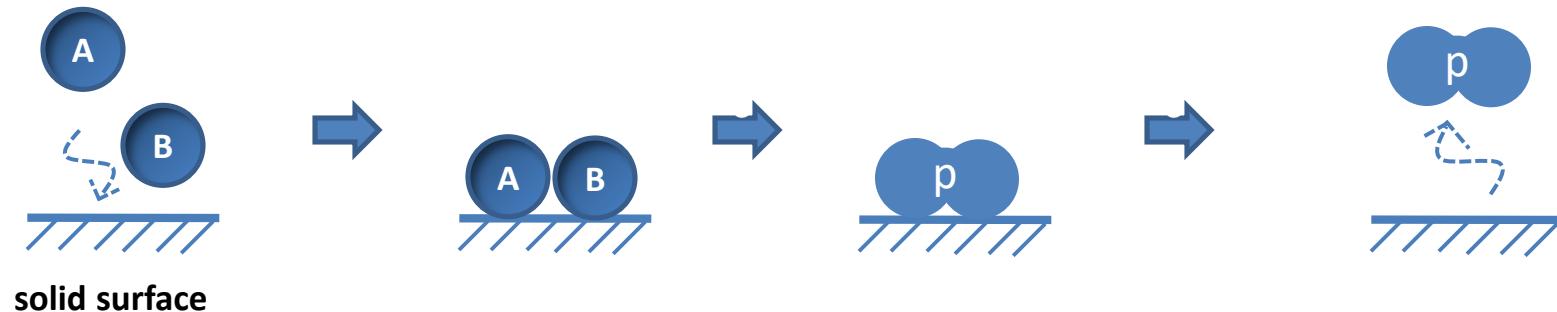
Case (iii) : When $[A]$ or p_A is neither very small or too high

Order is more than zero but less than 1 (*fractional order*)

Bimolecular Surface Reactions:

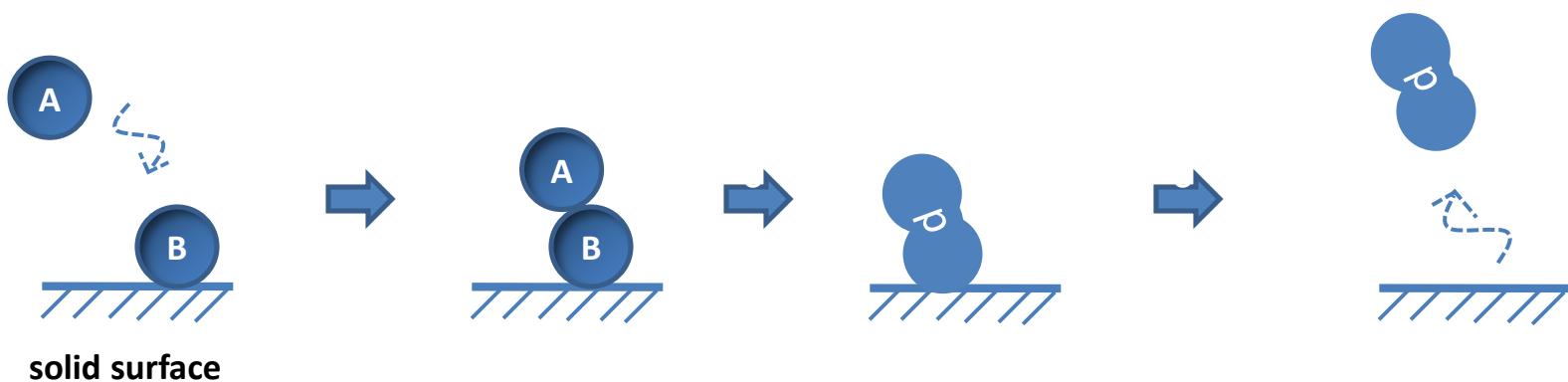
Langmuir-Hinshelwood mechanism

Simultaneous adsorption of two reactant molecules at adjacent sites and reaction between the two adsorbed neighboring molecules



Eley-Rideal mechanism

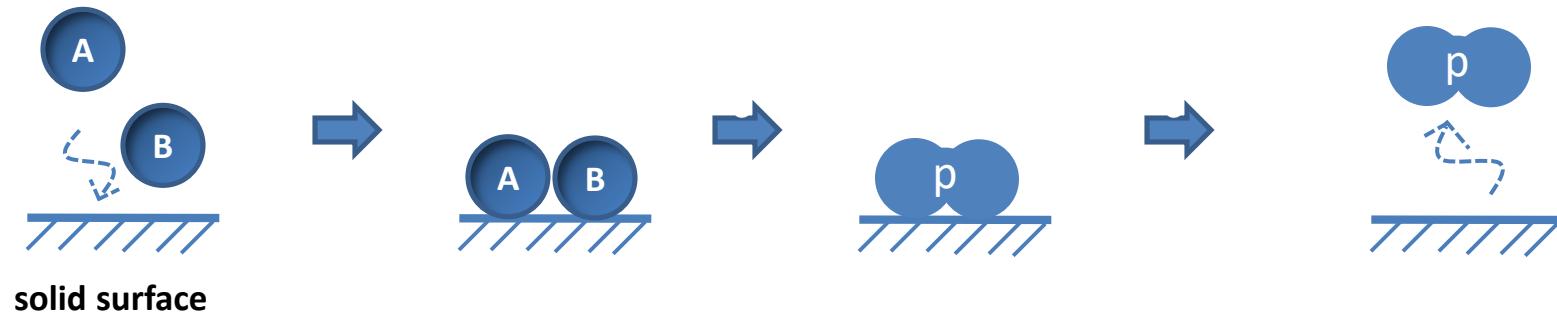
A gas-phase molecule reacts with another molecule adsorbed on the surface.



Bimolecular Surface Reactions:

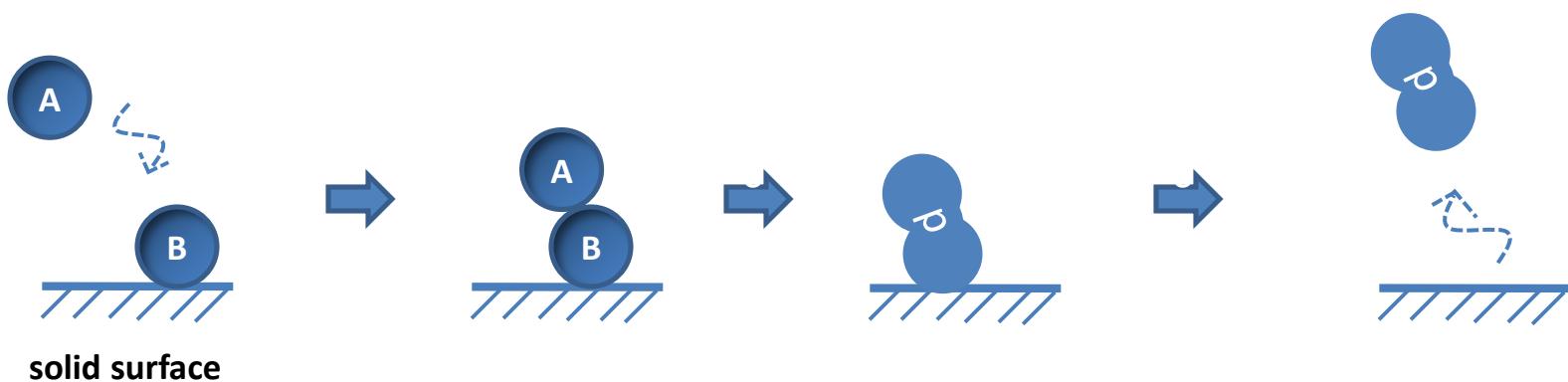
Langmuir-Hinshelwood mechanism

Simultaneous adsorption of two reactant molecules at adjacent sites and reaction between the two adsorbed neighboring molecules

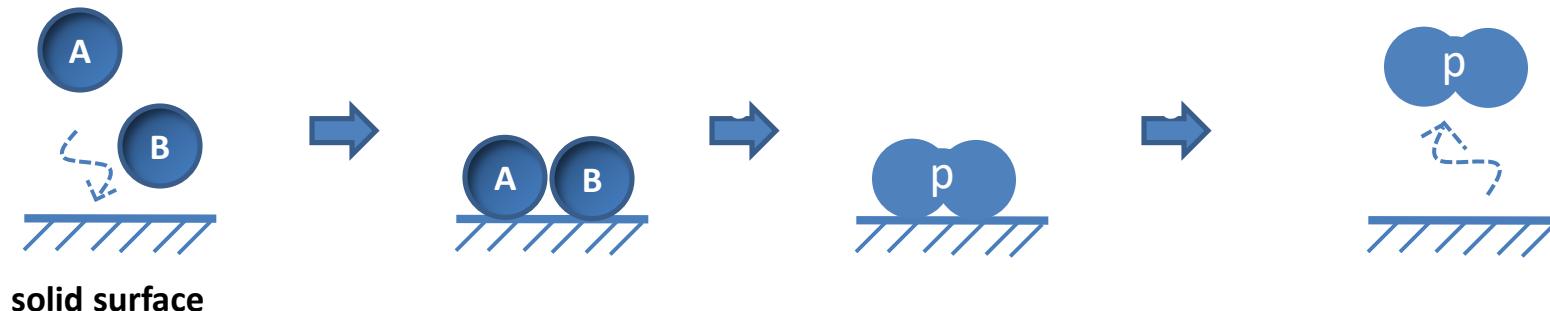


Eley-Rideal mechanism

A gas-phase molecule reacts with another molecule adsorbed on the surface.



Langmuir-Hinshelwood mechanism



Rate \propto fraction of molecules A and B that are adsorbed

$$\text{Rate} = v = k\theta_A \theta_B$$

A and B both adsorb on the catalyst surface so they compete with each other towards the available sites (Langmuir adsorption isotherm for two competing substrates)

Competitive Adsorption

θ_A = fraction of sites occupied by A, θ_B = fraction of sites occupied by B
Fraction of free sites available for adsorption = $1 - \theta_A - \theta_B$

$$\text{Rate of adsorption of A} = k_a^A [A] (1 - \theta_A - \theta_B)$$

$$\text{Rate of desorption of A} = k_d^A \theta_A$$

$$\text{At equilibrium } k_a^A [A] (1 - \theta_A - \theta_B) = k_d^A \theta_A$$

Rate of adsorption of B= $k_a^B[B](1 - \theta_A - \theta_B)$

Rate of desorption of B= $k_d^B\theta_B$

At equilibrium $k_a^B[B](1 - \theta_A - \theta_B) = k_d^B\theta_B$

$$\frac{\theta_A}{1 - \theta_A - \theta_B} = K_A[A]$$

$$\frac{\theta_B}{1 - \theta_A - \theta_B} = K_B[B]$$

$$\theta_A = \frac{K_A[A]}{1 + K_A[A] + K_B[B]}$$

$$\theta_B = \frac{K_B[B]}{1 + K_A[A] + K_B[B]}$$

The fraction of surface sites occupied by one substance is reduced if the amount of the other substance is increased i.e. the two substances are competing with each other for the surface sites

$$\text{Rate} = v = k \theta_A \theta_B$$

$$\theta_A = \frac{K_A[A]}{1 + K_A[A] + K_B[B]}$$

$$\theta_B = \frac{K_B[B]}{1 + K_A[A] + K_B[B]}$$

$$\text{Rate} = v = \frac{k K_A K_B [A][B]}{(1 + K_A[A] + K_B[B])^2}$$

$$\text{Rate} = v = \frac{k K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$

General Example: Catalytic conversion reaction in automobiles

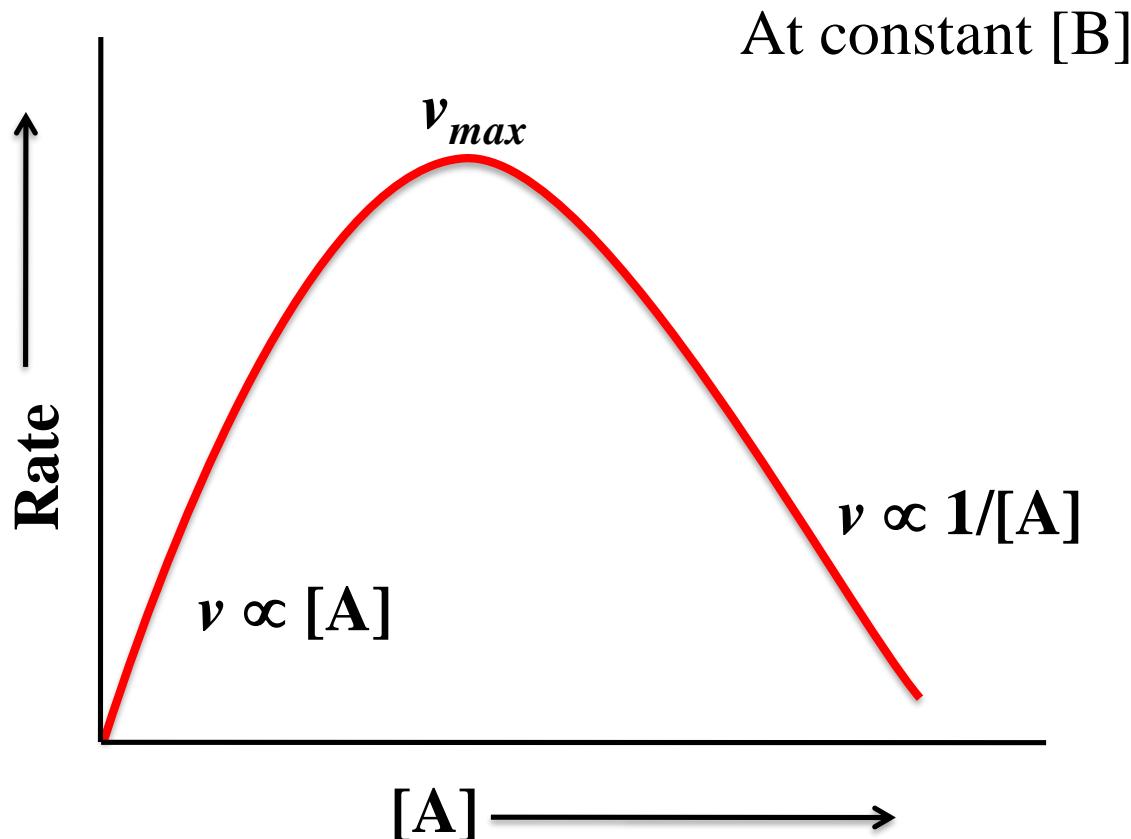
A special case: Both $K_A p_A \ll 1$ and $K_B p_B \ll 1$

Second order kinetics

Example: Hydrogenation of ethylene on Cu surface

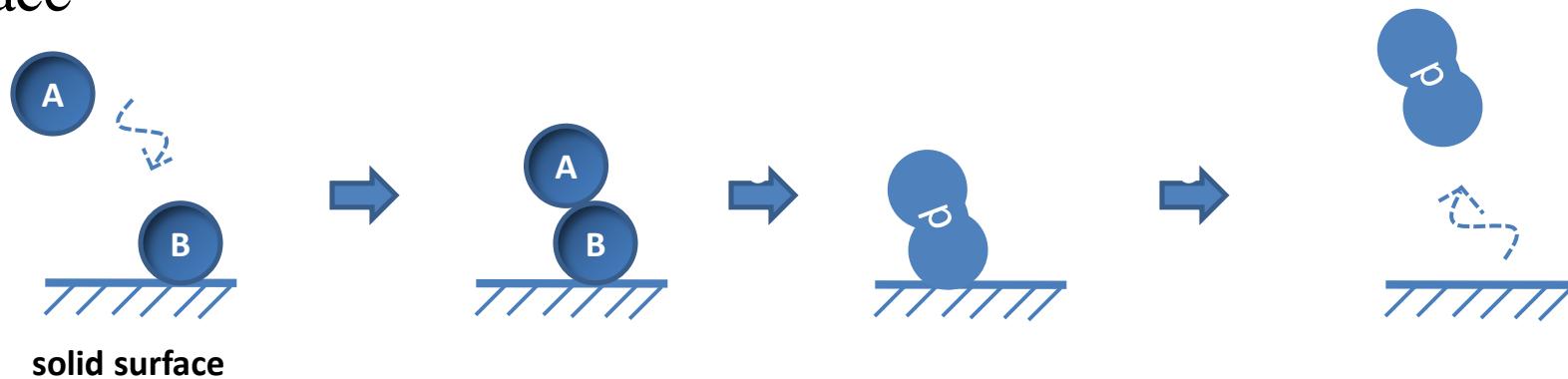
Langmuir-Hinshelwood mechanism:

$$\text{Rate } = v = \frac{k K_A K_B [A][B]}{(1 + K_A[A] + K_B[B])^2}$$



Eley-Rideal mechanism

A gas-phase molecule reacts with another molecule adsorbed on the surface



It is not necessary that A does not adsorb at all but even if A adsorbs it does not react with B i.e. adsorbed A molecules do not take part in the reaction only the free A in the gaseous medium reacts with the adsorbed B.

Eley-Rideal mechanism is not very common and often it is found to occur along with the other mechanism.

Example: Hydrogenation of ethylene on Ni surface

There are two conditions

1. If only one reactant adsorbs and the other one remains unadsorbed in the gaseous medium

$$Rate = v = k[A]\theta_B$$

$$v = \frac{k[A]K_B[B]}{1 + K_B[B]}$$

$$Rate = v = kp_A\theta_B$$

$$v = \frac{kK_B p_A p_B}{1 + K_B p_B}$$

2. If both the reactants adsorb on the catalyst surface

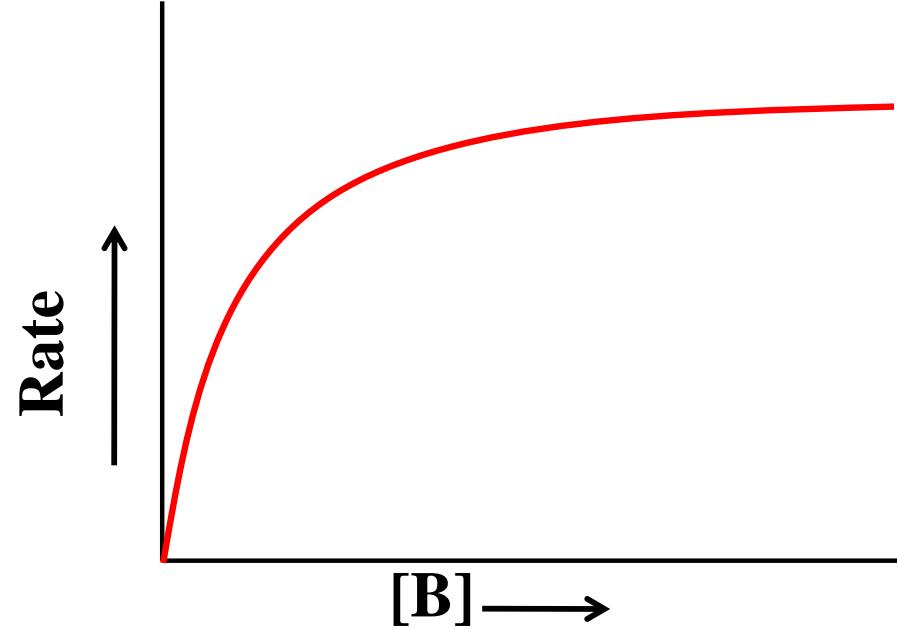
$$Rate = v = k[A]\theta_B$$

$$v = \frac{k[A]K_B[B]}{1 + K_A[A] + K_B[B]}$$

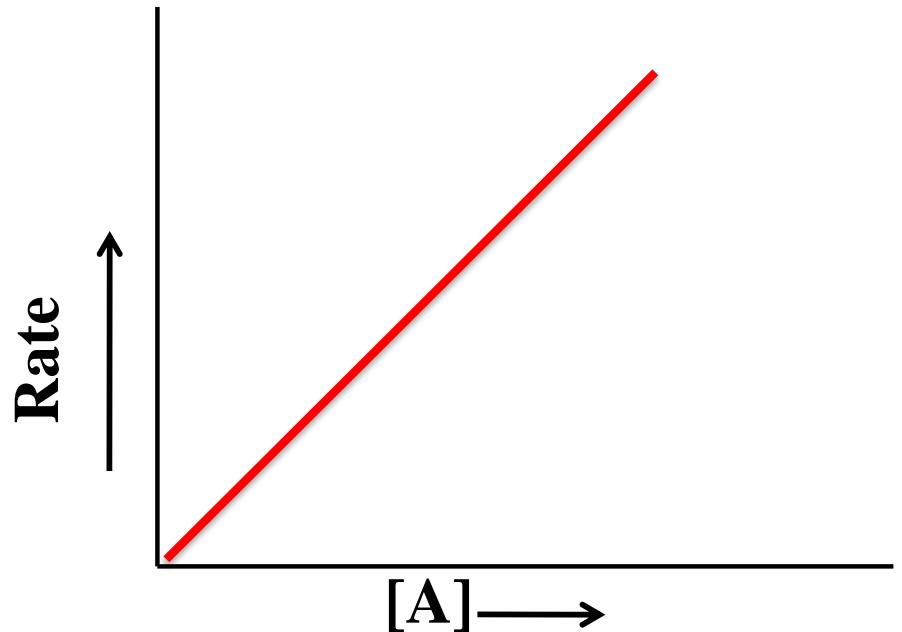
$$Rate = v = kp_A\theta_B$$

$$v = \frac{kK_B p_A p_B}{1 + K_A p_A + K_B p_B}$$

The Eley-Rideal mechanism



$$v = \frac{k[A]K_B[B]}{1 + K_B[B]}$$



Industrial application of heterogeneous catalysis

Solid catalysts	Function	Examples
Metals	Hydrogenation, Dehydrogenation	Fe, Ni, Pt, Ag
Semiconducting oxides & sulfides	Oxidation Desulfurization	NiO, ZnO, MgO, MoS ₂
Insulating oxides	Dehydration	Al ₂ O ₃ , SiO ₂ , MgO
Acids	Polymerization Isomerization Cracking Alkylation	Alumino silicates, (Zeolites) Silico-alumino- phosphate

STEREOCHEMISTRY

Dr Sabita Patel

Department of Chemistry

NIT Rourkela, 769008

Ph: 0661-2462660, 9861414910

Email: sabitap@nitrkl.ac.in

Syllabus

- Chirality,
- Configuration and conformation,
- Geometrical isomerism,
- Optical isomerism,
- Enantiomers and Diastereomers,
- Projection formulas,
- Interconversion of projection formulas,
- D-L and R-S nomenclature (CIP rules),
- Erythro and threo nomenclature.
- *dl*- and *meso* compounds,
- Atropisomerism,
- Stereospecific and stereoselective reactions,
- Conformations vrs. reactivity of cycloalkanes

SUGGESTED BOOKS

- 1. Organic Chemistry: Jonathan Clayden, Nick Greeves, Stuart Warren, 2nd Edition Oxford University Press.**
- 2. March's Advanced Organic Chemistry, M. B. Smith and Jerry March, Wiley Publication 6th edition.**
- 3. Stereochemistry of Organic Compounds(Principles and Application), D. Nasipuri, New age International (P) Ltd.**
- 4. Stereochemistry (Conformation and Mechanism, P. S. Kalsi, New age International (P) Ltd.**

Introduction

Stereochemistry is the study of the static and dynamic aspects of the three-dimensional shapes of molecules. In other sense it is the chemistry in space and describes the chemistry as a function of molecular geometry.

Stereochemistry is also known as 3D chemistry because the prefix "stereo-" means "three-dimensionality".

Beginning of organic stereochemistry was made by French Physicist **Biot (1815)** who found that certain organic molecules rotate the plane of a polarized light in solution or in gaseous phase: a property known as **optical activity**.

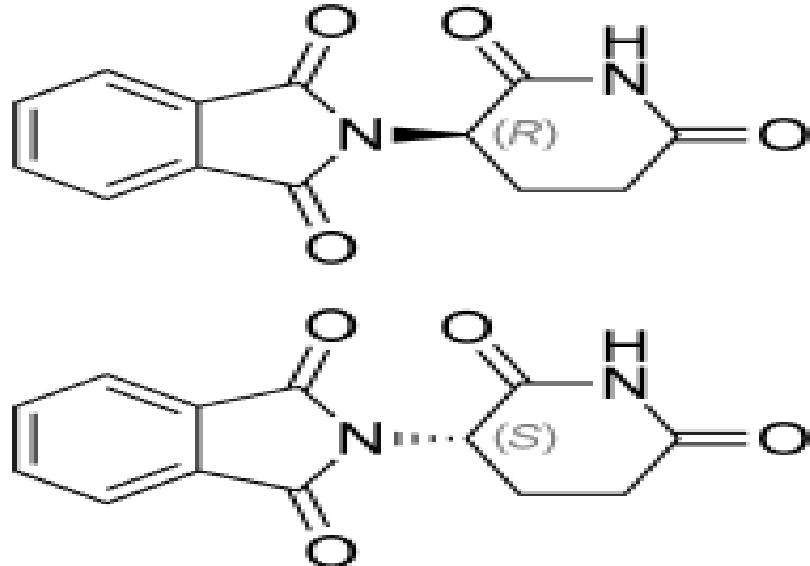
In 1848, Louis Pasteur ([Father of organic stereochemistry](#)), ascribed this property to the presence of some dissymmetric grouping of atoms in a molecule.

Later van't Hoff and Le Bel (1874) laid the foundation of organic stereochemistry by postulating the tetrahedral geometry of carbon compounds and thus added a third dimension to a 2-dimensional chemistry of earlier days.

Thalidomide is a drug, first prepared in 1957 in Germany, prescribed for treating morning sickness in pregnant women.

Primarily prescribed as a sedative or hypnotic, thalidomide also claimed to cure "anxiety, insomnia, gastritis, and tension"

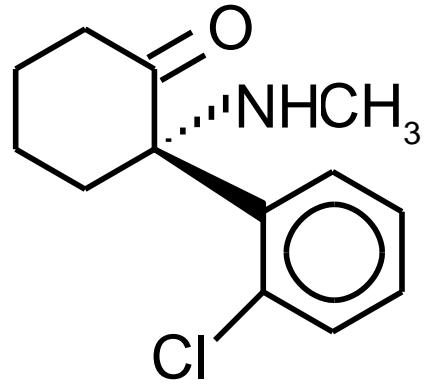
Shortly after the drug was sold in West Germany, between 5,000 and 7,000 infants were born with phocomelia (malformation of the limbs).



(S)-isomer: birth defects

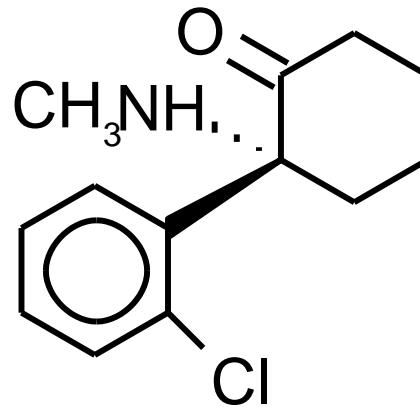
Thalidomide is racemic; while R-thalidomide is the bioactive form of the molecule, the individual enantiomers can racemize to each other due to the acidic hydrogen at the chiral centre. The racemization process can occur in vivo.

The properties of many drugs depends on their stereochemistry:



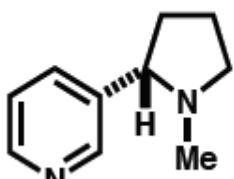
(S)-ketamine

Anesthetic

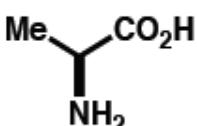


(R)-ketamine

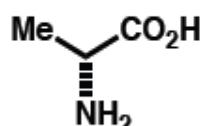
Hallucinogen



nicotine
toxin / stimulant

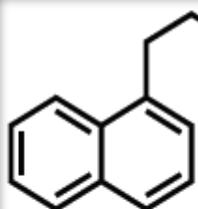


L-alanine
mammalian amino acid

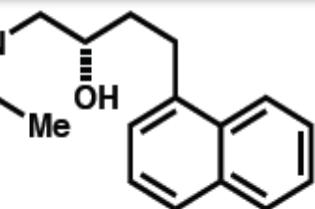
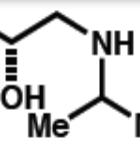


D-alanine
bacterial cell wall

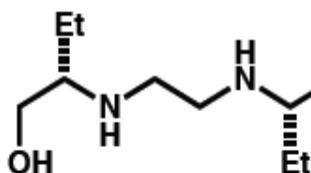
- Nature yields an enormous variety of chiral compounds
- Each enantiomer can have very different effects as highlighted below
- As a result we must have methods to control stereochemistry



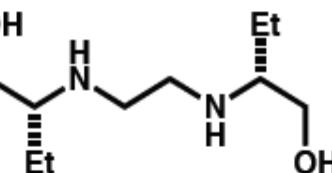
(-) -propanolol
 β -blocker for heart disease



(+)-propanolol
contraceptive

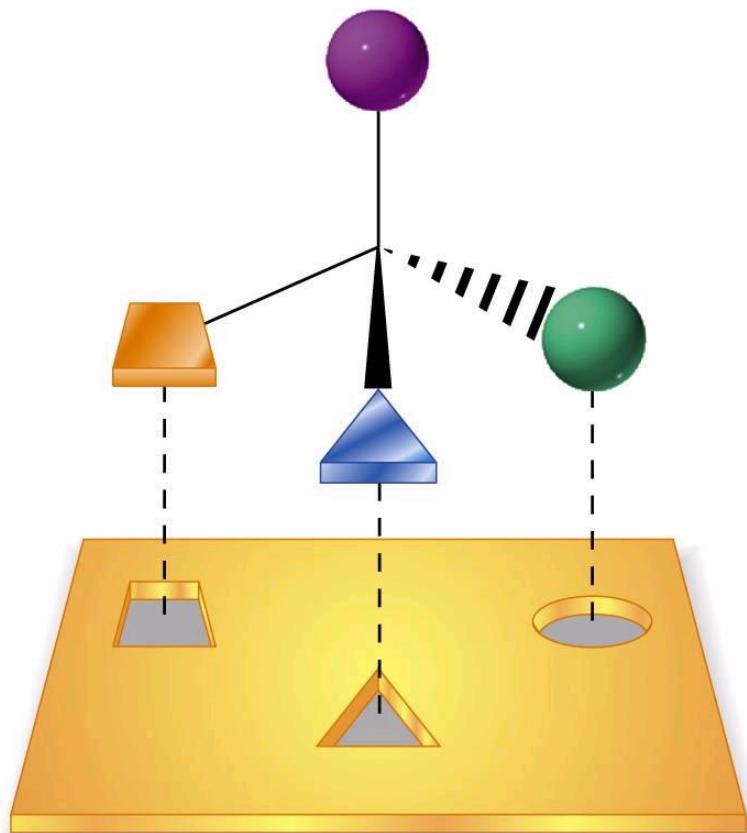


Ethambutol
tuberculostatic (anti-TB)

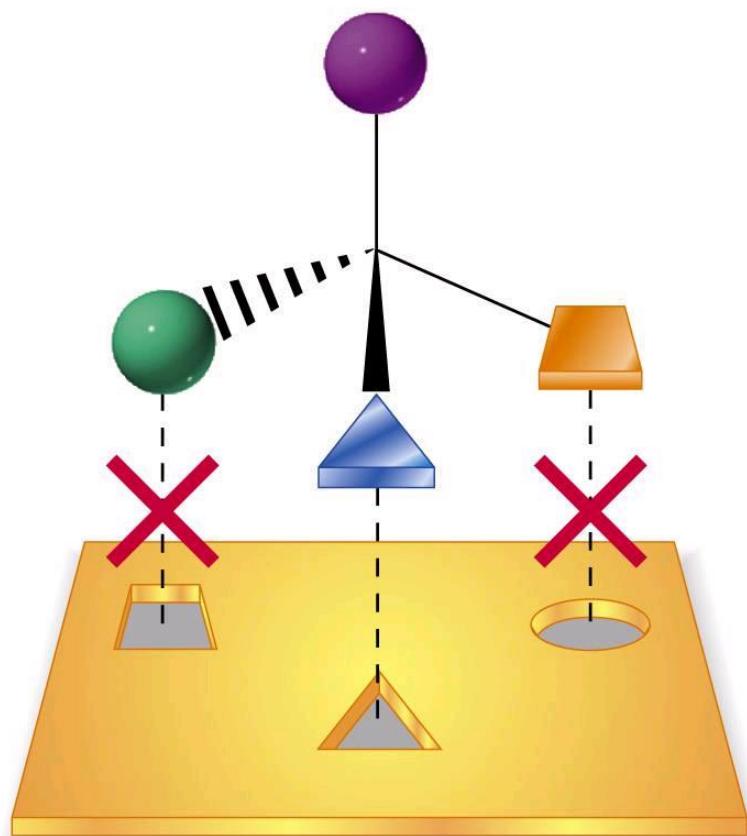


(R,R)-enantiomer
causes blindness

R enantiomer



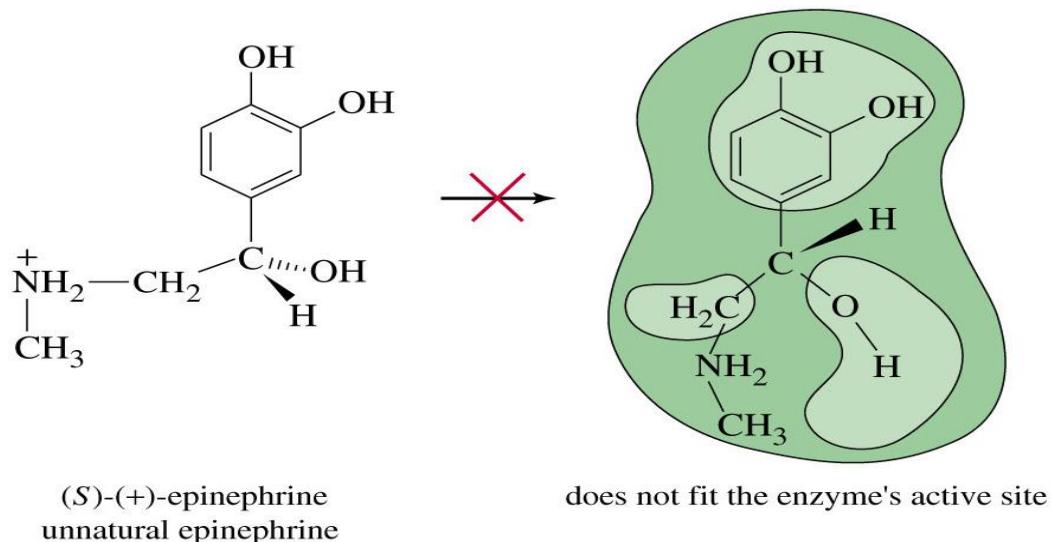
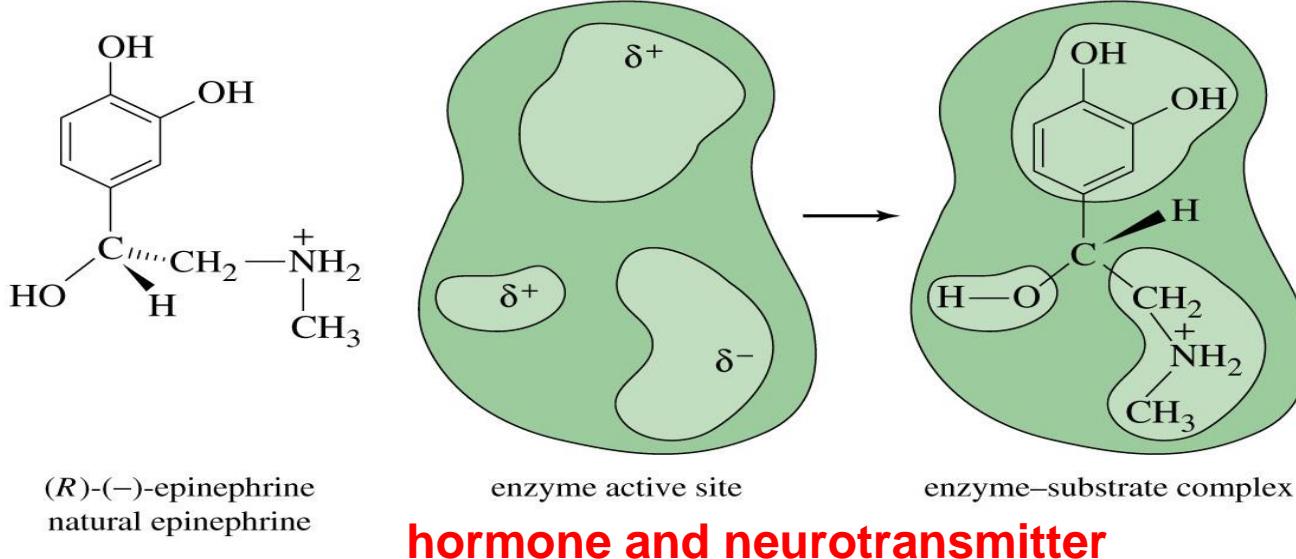
S enantiomer



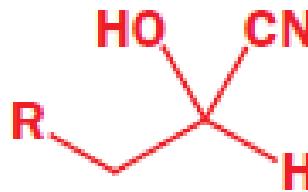
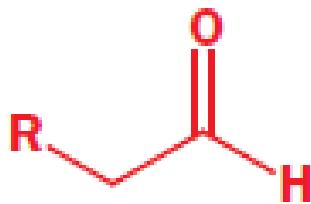
binding site of the receptor

binding site of the receptor

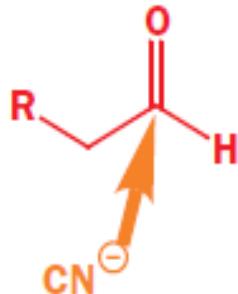
- Enzymes are capable of distinguishing between stereoisomers:



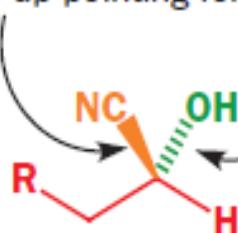
Some compounds can exist as a pair of mirror-image forms



cyanide approaching from front face of carbonyl group

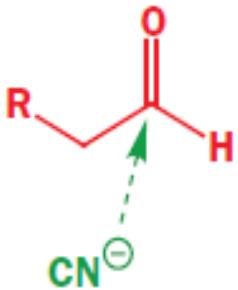


nitrile ends up pointing forward

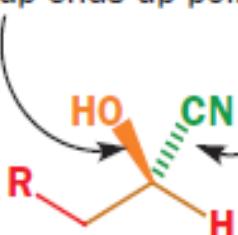


hydroxyl group ends up pointing back

cyanide approaching from back face of carbonyl group

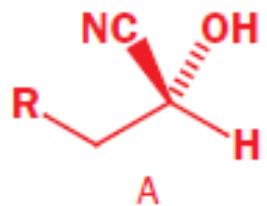


hydroxyl group ends up pointing forward

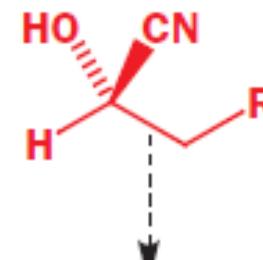
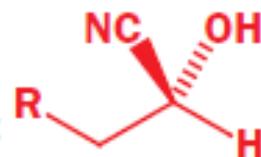


nitrile ends up pointing back

The structures are **nonsuperimposable**—so they are not identical. They are **mirror images** of each other.



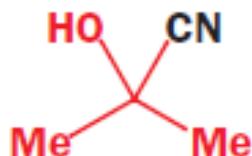
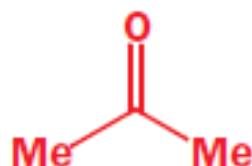
reflect this
molecule in an
imaginary mirror:



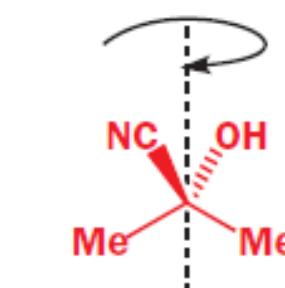
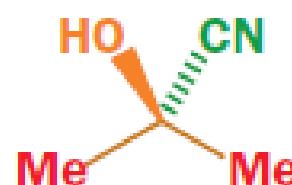
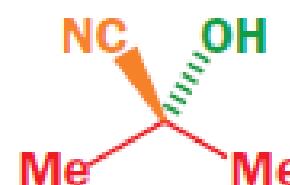
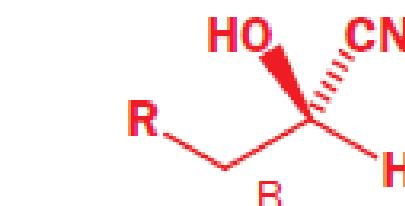
new
"mirror
image"
molecule

Enantiomers and chirality

- Enantiomers are structures that are not identical, but are mirror images of each other
- Structures are chiral if they cannot be superimposed upon their mirror image



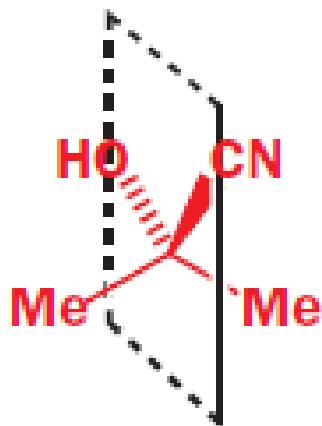
- Achiral structures are superimposable on their mirror images



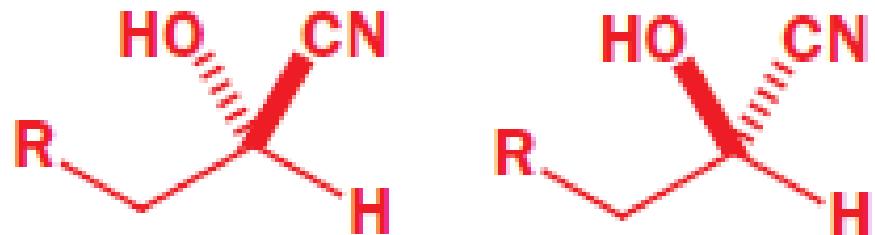
rotate about this axis

What is the essential difference between these two compounds that one is superimposable on its mirror image and other is not? The answer is symmetry or plane of symmetry

A plane through the molecule that divides the molecule into two parts that are mirror images of each other.



plane of symmetry
runs through
central carbon,
OH and CN

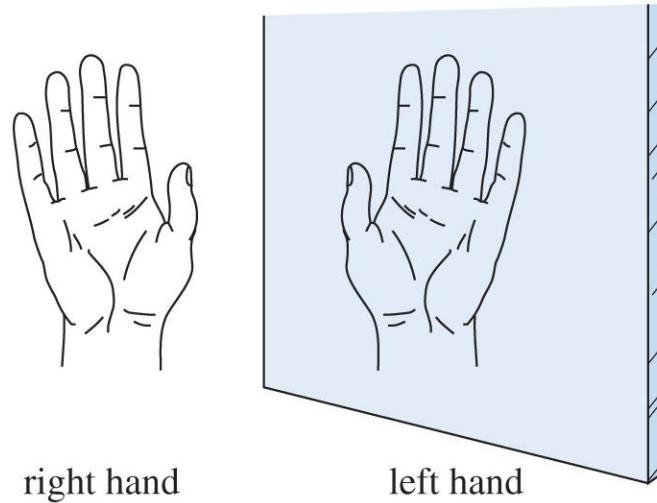


No plane of symmetry
Thus contain two enantiomers

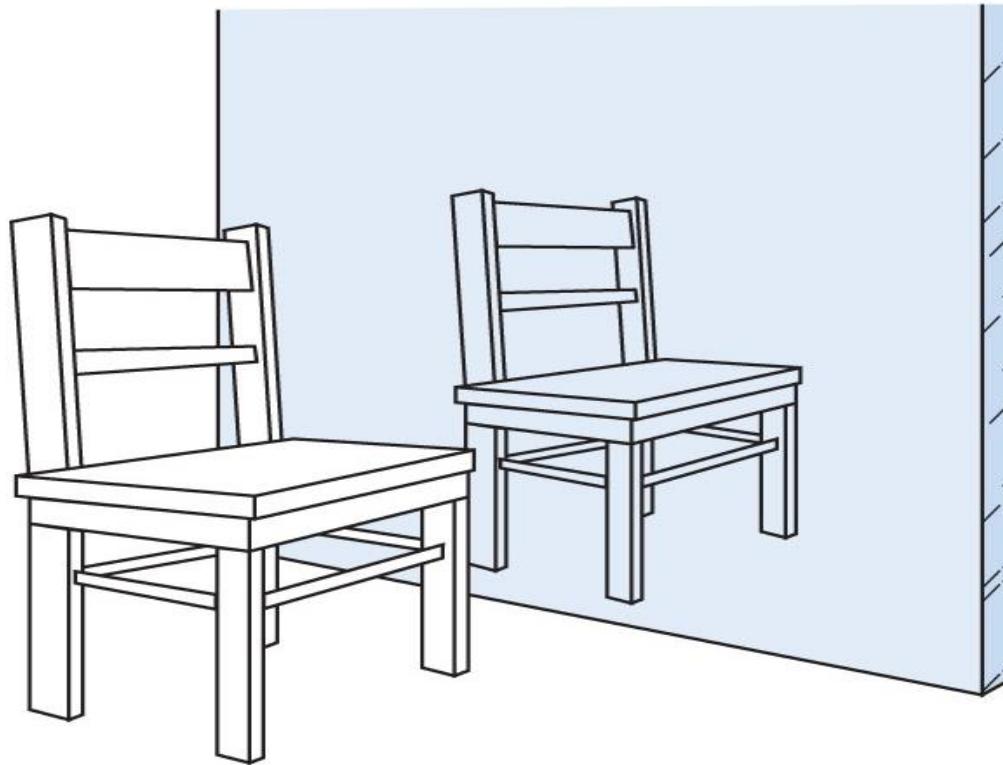
Planes of symmetry and chirality

- Any structure that has no plane of symmetry can exist as two mirror-image forms termed as *enantiomers*
- Any structure with a plane of symmetry cannot exist as two enantiomers

Chirality



- “Handedness”: Right-hand glove does not fit the left hand.
- An object is **chiral** if its mirror image is different from the original object.

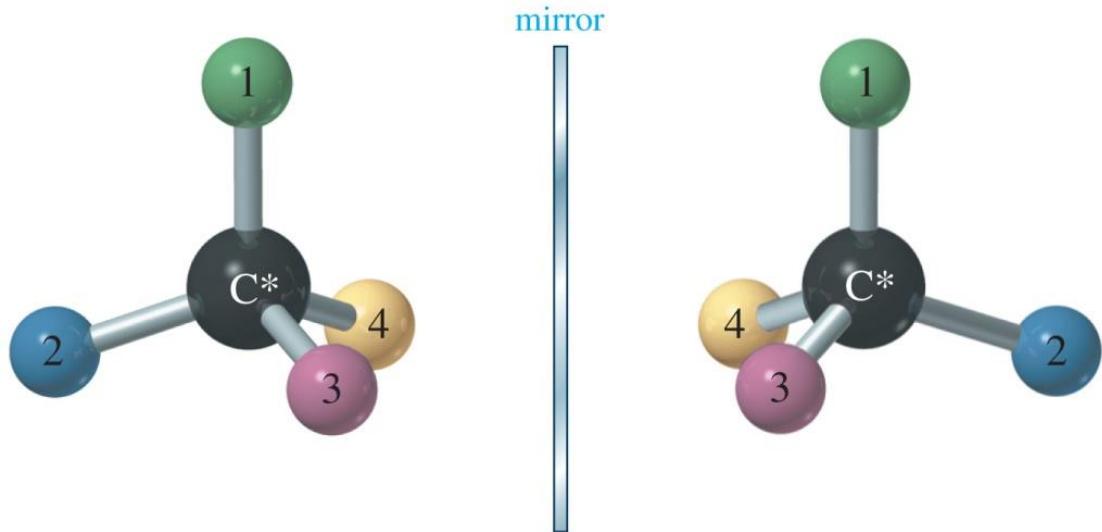


© 2013 Pearson Education, Inc.

Achiral

- Mirror images that can be superposed are *achiral* (not chiral).

Chiral Carbon Atom



© 2013 Pearson Education, Inc.

- Also called **asymmetric carbon atom**, **Stereogenic** or **chiral center**
- Carbon atom that is bonded to four different groups it will not have a plane of symmetry is chiral.
- Its mirror image will be a different compound (**enantiomer**).

To summarize

- A structure with a plane of symmetry is achiral and superimposable on its mirror image and cannot exist as two enantiomers
- A structure without a plane of symmetry is chiral and not superimposable on its mirror image and can exist as two enantiomers

Enantiomers are isomers; In particular, enantiomers are a type of isomer called **stereoisomers**, because the isomers differ not in the connectivity of the atoms, but only in the overall shape or arrangement of atoms/groups of the molecule.

Do the compounds
have the same molecular
formulae ?

NO

Not isomers

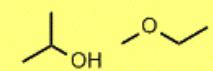
YES

Isomers

Do the compounds have the atoms
connected in the same order ?

NO

Constitutional



YES

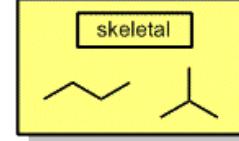
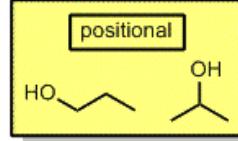
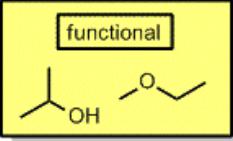
Stereoisomers

Can the compounds be
interconverted by rotation
about single bonds ?

functional
groups

locations for functional
groups or substituents

backbone



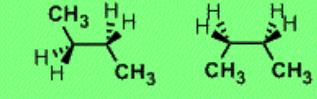
NO

Configurational

Is the isomerism due to
restricted rotation ?

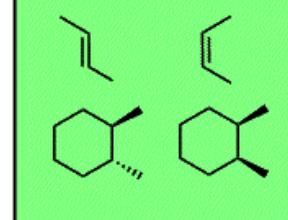
YES

Conformational



YES

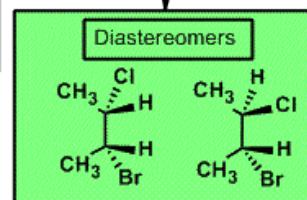
cis-trans
(geometric)



NO

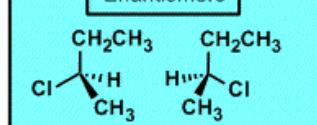
Optical

Are the compounds
non-superimposable
mirror images ?



YES

Enantiomers



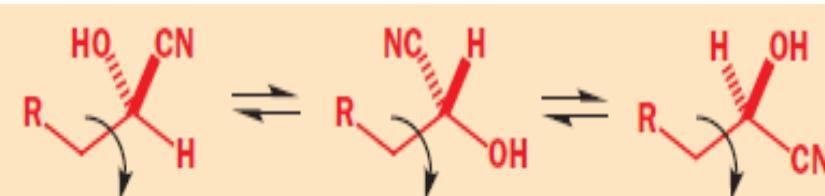
Configuration and Conformation

If two stereoisomers really are different molecules: they cannot be interconverted without breaking a bond somewhere. We therefore say that they have different configurations.



two configurations: going from one enantiomer to the other requires a bond to be broken

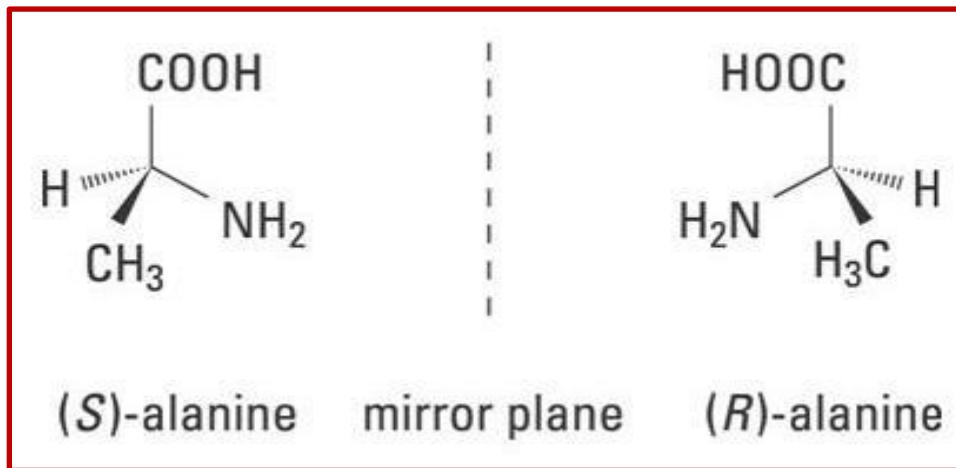
But any molecule can exist in a number of conformations: two conformations differ only in the temporary way the molecule happens to arrange itself, and can easily be interconverted just by rotating around bonds



three conformations of the same enantiomer: getting from one to the other just requires rotation about a bond: all three are the same molecule

Is there a chemical difference between two enantiomers?

Take (*S*)-alanine (alanine extracted from plants) and (*R*)-alanine (the enantiomer found in bacterial cell walls) as examples.



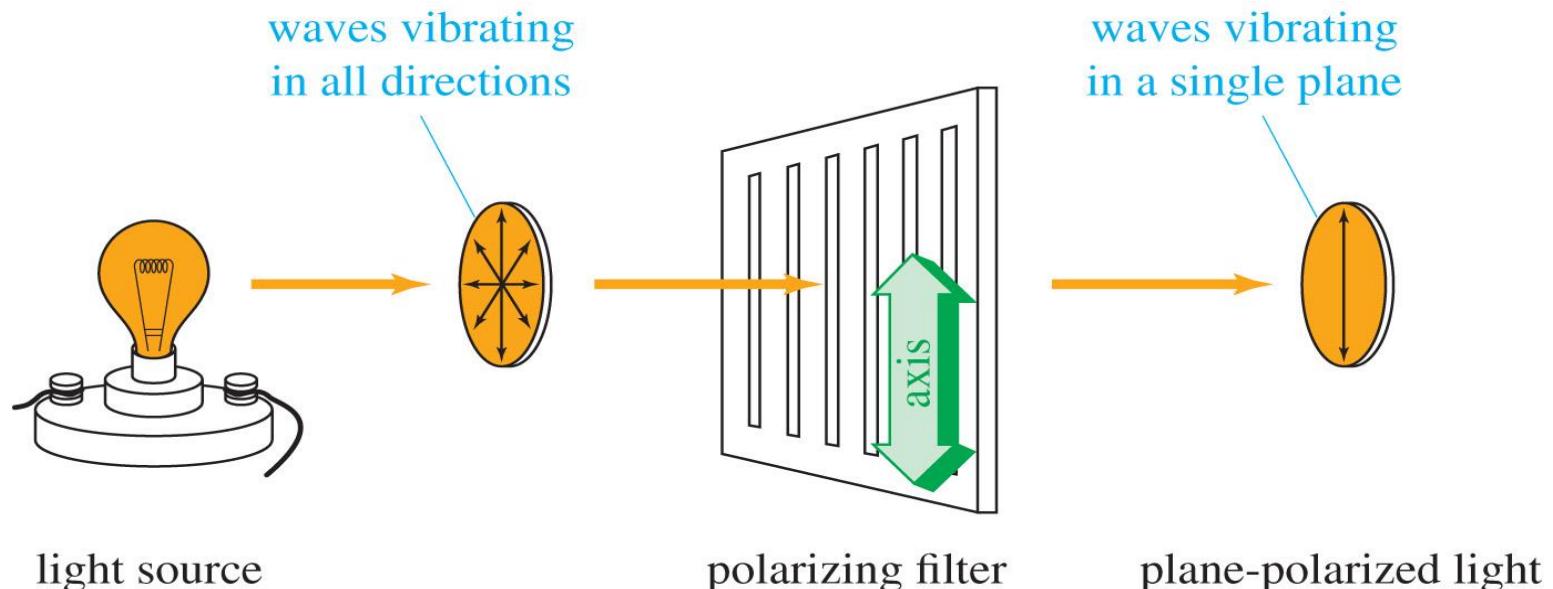
They both have identical NMR spectra, identical IR spectra, and identical physical properties, identical chemical properties in achiral environment with two important exceptions.

If you shine plane-polarized light through a solution of (*S*)-alanine, you will find that the light is rotated to the right. A solution of (*R*)-alanine rotates plane-polarized light to the left (same magnitude but opposite direction). Racemic alanine, on the other hand, lets the light pass unrotated.

Different interaction (Reactivity) with other chiral molecules.

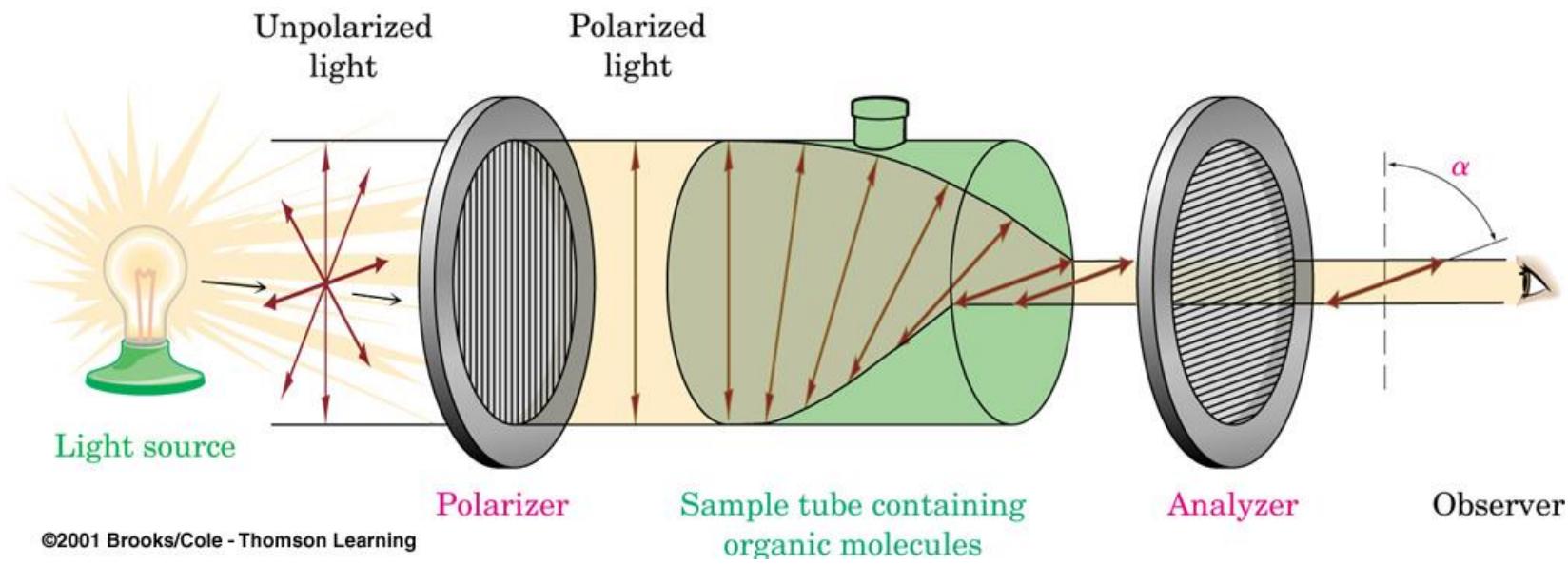
The rotation of plane-polarized light is known as optical activity.

Plane-polarized light is composed of waves that vibrate in only one plane.



© 2013 Pearson Education, Inc.

Enantiomers rotate the plane of polarized light in opposite directions, but same number of degrees.



Clockwise
Dextrorotatory (+) or d

Counterclockwise
Levorotatory (-) or l

The optical rotation is dependent upon the substance, the concentration, the path length through the sample, and the wavelength of light.

Specific Rotation $[\alpha]_D$: a standardized value for the optical rotation

$$[\alpha]_{\lambda}^T = \frac{\alpha}{l \cdot c}$$

α = optical rotation in degrees

l = path length in dm

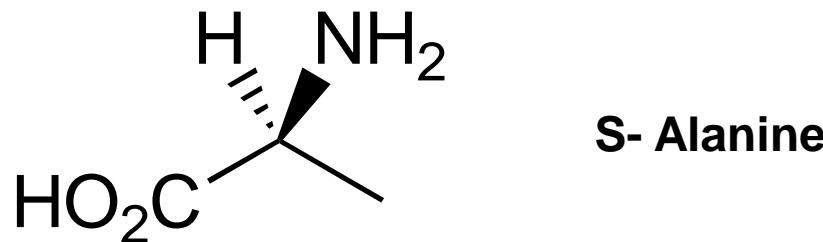
c = concentration of sample in g/ mL

T = temperature in °C

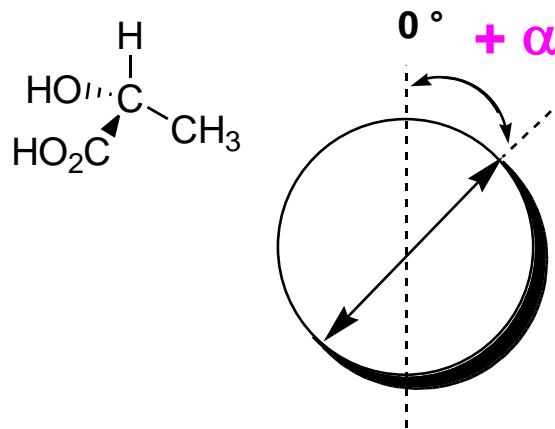
λ = wavelength of light, usually D for the
D-line of a sodium lamp (589 nm)

The specific rotation is a physical constant of a chiral molecule.

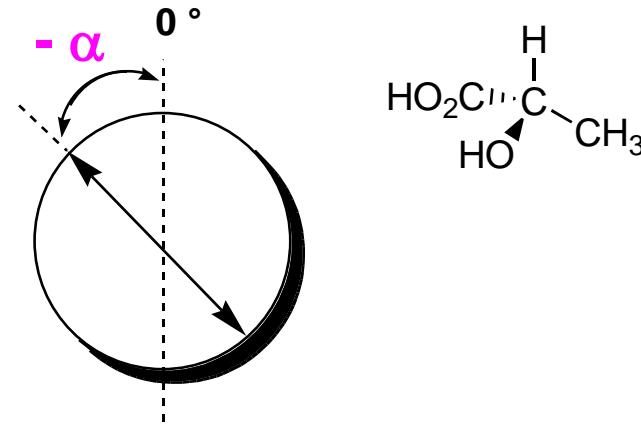
The $[\alpha]_D$ may also depend upon solvent, therefore the solvent is usually specified.



$$[\alpha]_D^{20} = +14.5^\circ \text{ (c 10, 6N HCl)}$$



dextrorotatory (*d*): rotates light to the right (clockwise)



levorotatory (*l*): rotates light to the left (counterclockwise)

α :angle (in degrees) plane polarized light is rotated by an optically active sample. Expressed in degrees.

Enantiomers will rotate plane polarized light the same magnitude (α) but in opposite directions (+ or -).

Used to calculate the purity of samples

90% (+) + 10% (-)

will rotate light 80% of pure (+)

75% (+) + 25% (-) will rotate light 50% of pure (+)

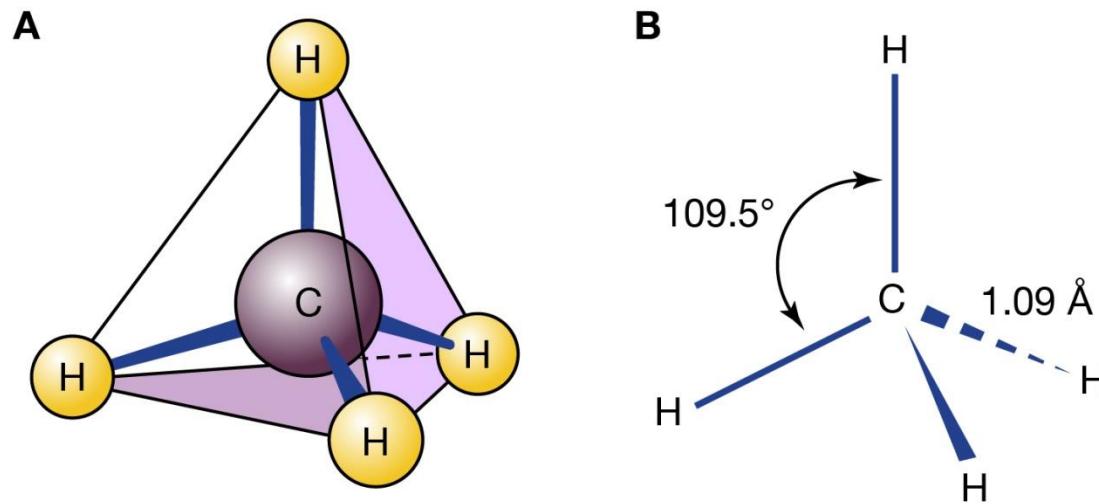
50% (+) + 50% (-) will be optically inactive

50:50 mixture of enantiomers (+/-): racemate or racemic mixture.

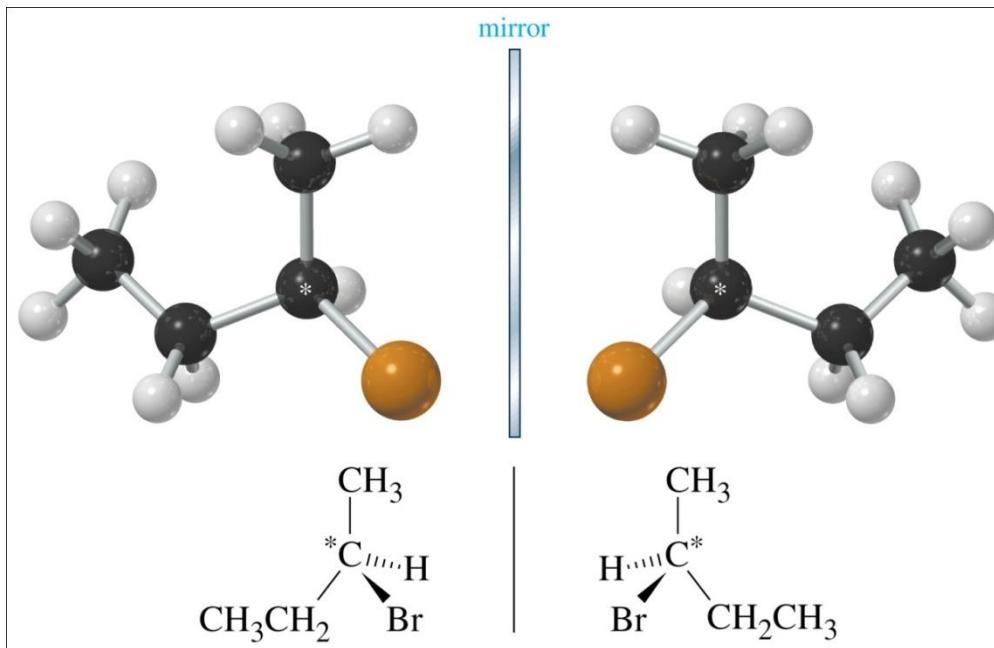
Each individual molecule is chiral, however the bulk property of the substance is achiral, if it is in an achiral environment.

Molecular representation of stereochemical molecules

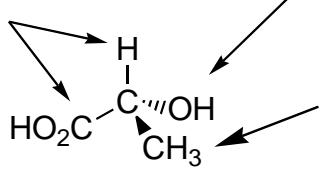
Since stereochemistry refers to molecules in three dimensions, appropriate modes of representations of 3D molecules on 2D paper is essential.



Flying wedge notation (mostly used for single asymmetric center)



In the plane of the paper
and in the same plane
as the tetrahedral carbon
(adjacent position off the
tetrahedral carbon)



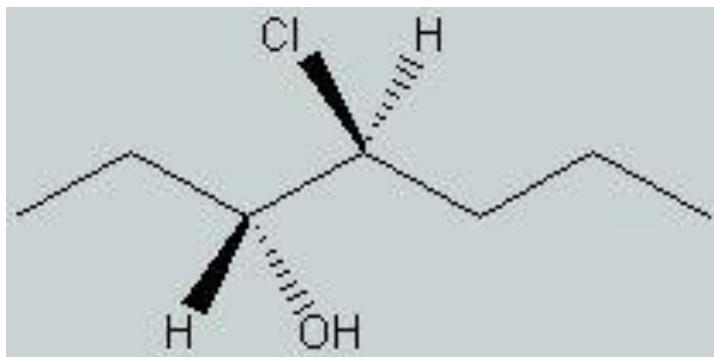
Dash: projecting behind
the plane of the paper
away from you

Wedge: projecting out
of the plane of the paper
toward you

Dash and Wedge are on
adjacent position off the
tetrahedral carbon

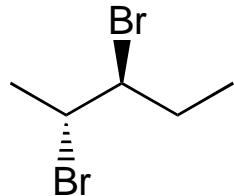
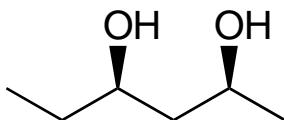
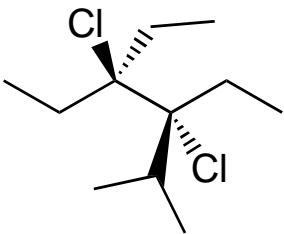
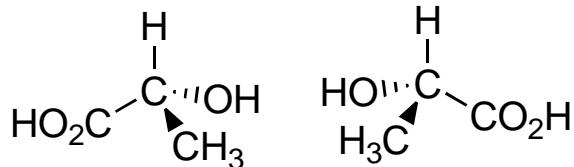
Stereoisomes with more than one chiral centers

- Ex:-This molecule has no plane or center of symmetry, so it is a **chiral** molecule. The *third* and *fourth* carbons from the left are **stereocenters**, because they are each bonded to four different groups.

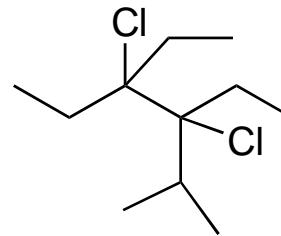
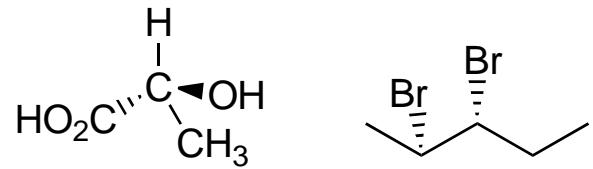


draw the carbon backbone in the plane of the paper, and draw substituents either coming towards you (with wedges) or going away from you (with dashes). Note that each carbon should look like a tetrahedron.

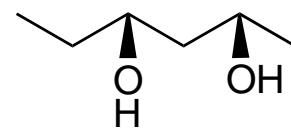
- A **chiral** molecule with **stereocenters** has 2^n different forms.
- This molecule has four different forms. So it has two stereocenter so 2^2 ,of four different form.



Correct



Incorrect

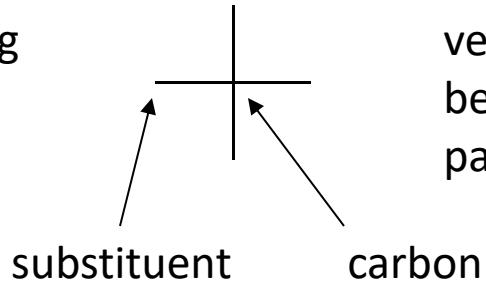


- Interchanging any two groups inverts the stereochemistry.
- The “double-switch” does not change the stereochemistry.

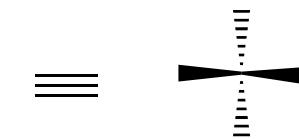
Fischer Projection formulae: representation of a three-dimensional molecule as a flat structure.

A tetrahedral carbon is represented by two crossed lines:

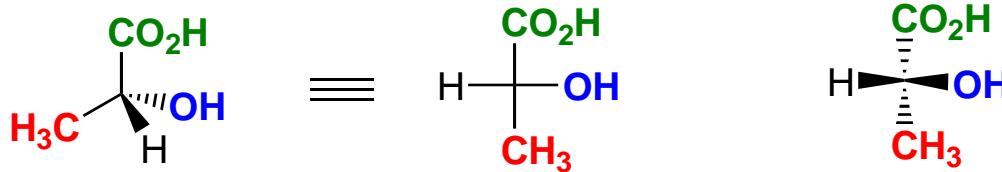
horizontal line is coming
out of the plane of the
page (toward you)



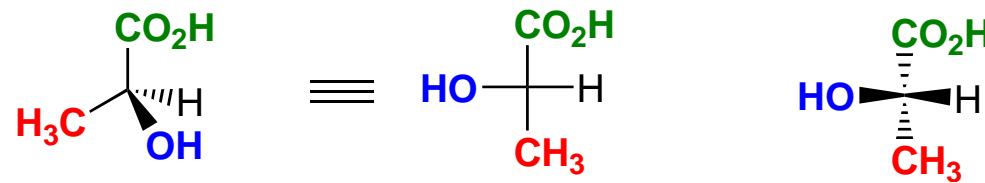
vertical line is going back
behind the plane of the
paper (away from you)



(R)-lactic acid

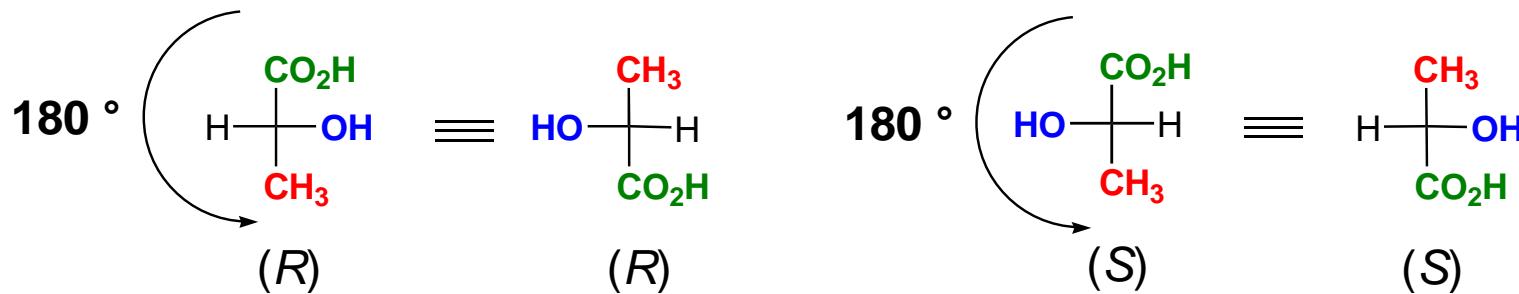


(S)-lactic acid

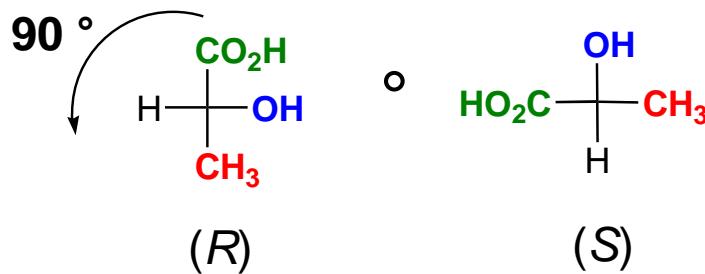


Manipulation of Fischer Projections

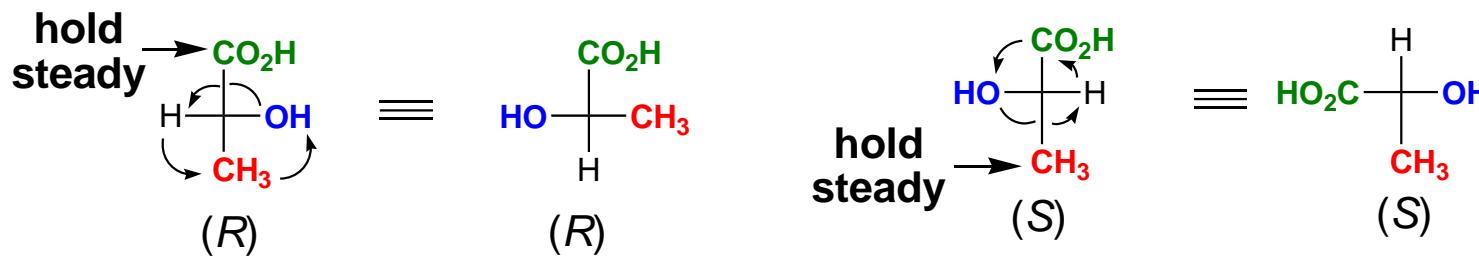
1. Fischer projections can be rotated by 180° only!



a 90° rotation inverts the stereochemistry and is not permissible

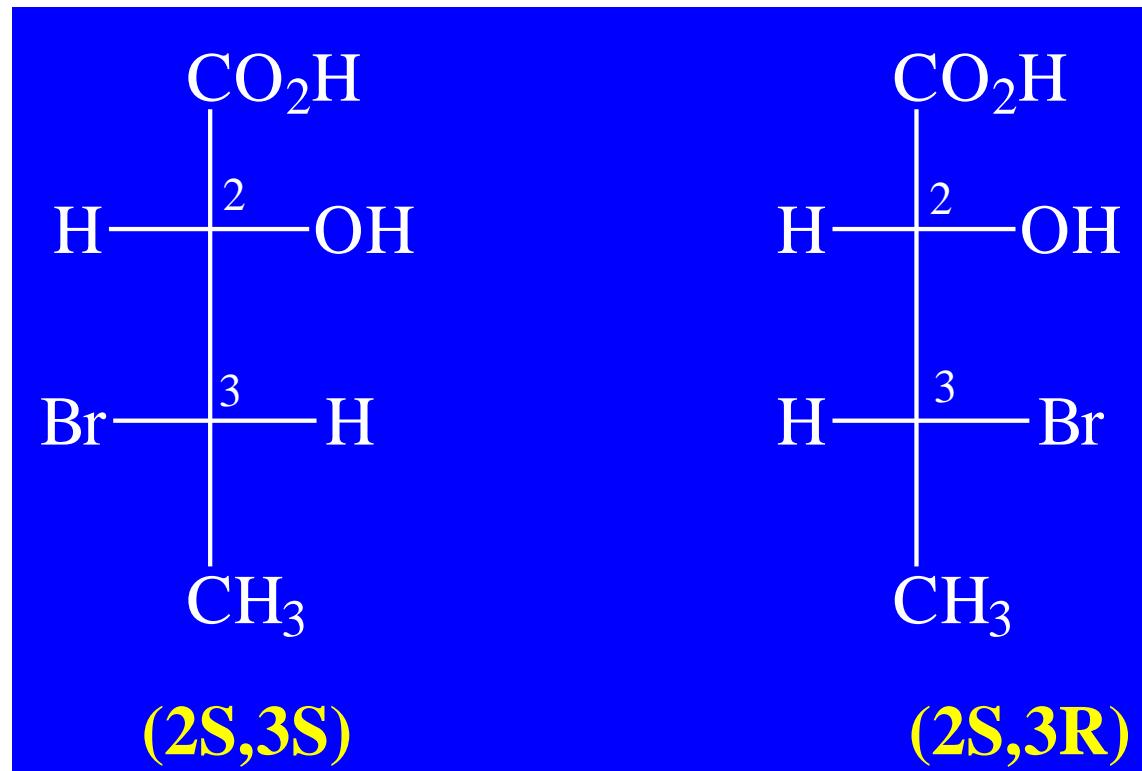


2. If one group of a Fischer projection is held steady, the other three groups can be rotated clockwise or counterclockwise.



Fischer Projections with 2 Chiral Centers

By convention :Longest carbon chain in the vertical position, keeping the most oxidized one at the top.

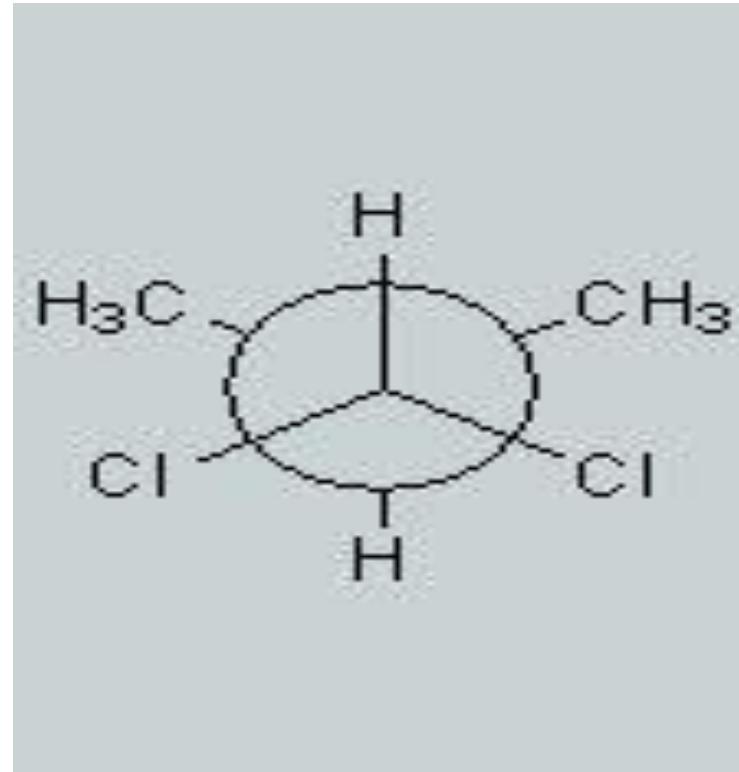


Newman Projections

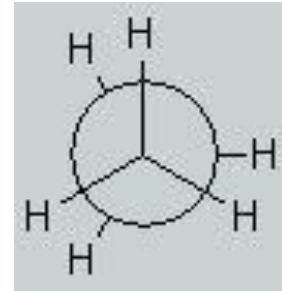
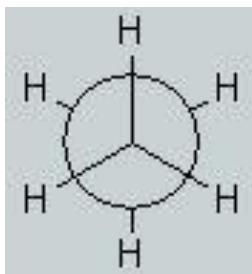
- **Newman Projections**

are used mainly for determining conformational relationships.

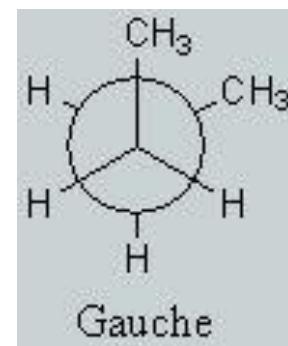
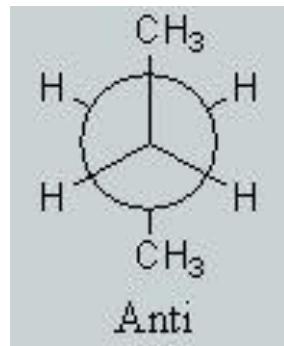
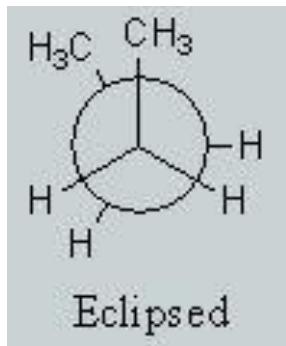
Recall that conformers are molecules that can be converted into one another by a rotation around a single bond.



- The front carbon of this bond is represented by a dot, and the back carbon is represented by a large circle. The three remaining bonds are drawn as *sticks* coming off the dot (or circle), separated by one another by 120 degrees. A **Newman Projection** can be drawn such that the groups on the front carbon are *staggered* (60 degrees apart) or *eclipsed* (directly overlapping) with the groups on the back carbon.

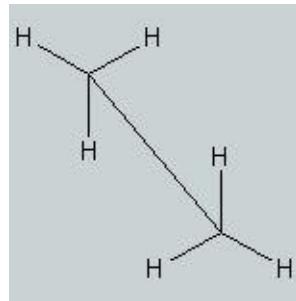


- **Newman Projections** can be made for butane, such that its *eclipsed*, *gauche*, and *anti* conformations can be seen.

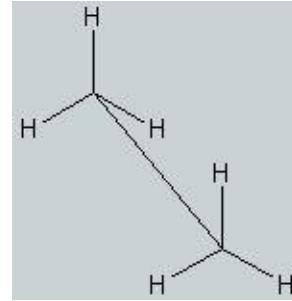


Sawhorse Projections

- **Sawhorse Projections** are very similar to Newman Projections, but are used more often because the carbon-carbon bond that is compressed in a Newman Projection is fully drawn out in a **Sawhorse Projection**.
- **Sawhorse Projections** are useful for determining enantiomeric or diasteromeric relationships between two molecules.



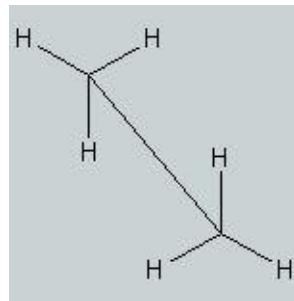
staggered



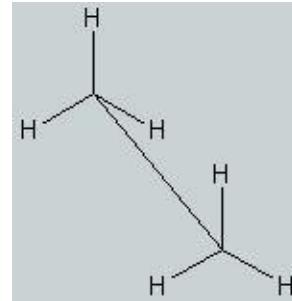
eclipsed

Sawhorse Projections

- **Sawhorse Projections** are very similar to Newman Projections, but are used more often because the carbon-carbon bond that is compressed in a Newman Projection is fully drawn out in a **Sawhorse Projection**.
- **Sawhorse Projections** are useful for determining enantiomeric or diasteromeric relationships between two molecules.

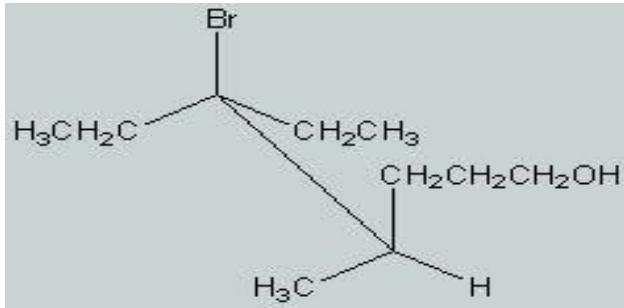


staggered



eclipsed

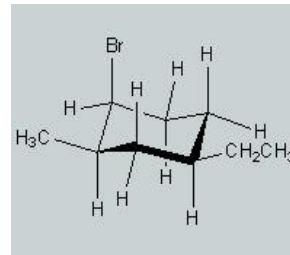
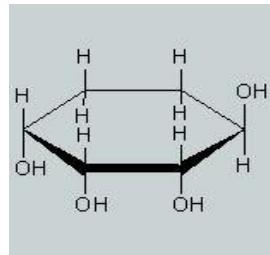
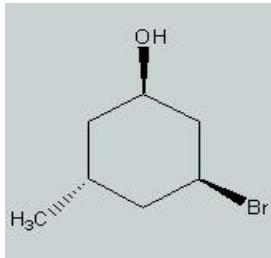
- Consider the following molecules and determine whether the **Sawhorse Projection** is staggered or eclipsed, how many carbons are in the longest chain of the molecule, and what other groups are connected to the front and back carbons?



- This **Sawhorse Projection** is *eclipsed*. The longest chain in the molecule most likely always contains the bond you are looking down. There are *seven* carbons in the longest chain, two from the ethyl group on the back carbon, three from the propanol group on the front carbon, and two connecting carbons from the **Sawhorse Projection**. Therefore, the remaining groups are *a hydrogen and a methyl group* on the front carbon and *a bromine and an ethyl group* on the back carbon.

Cyclic Structures

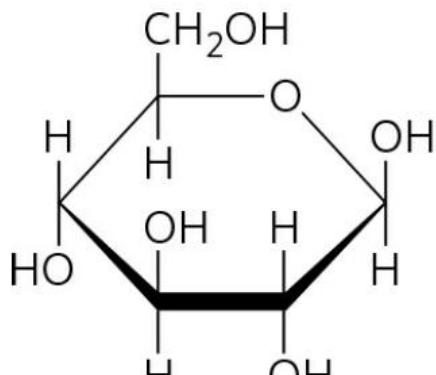
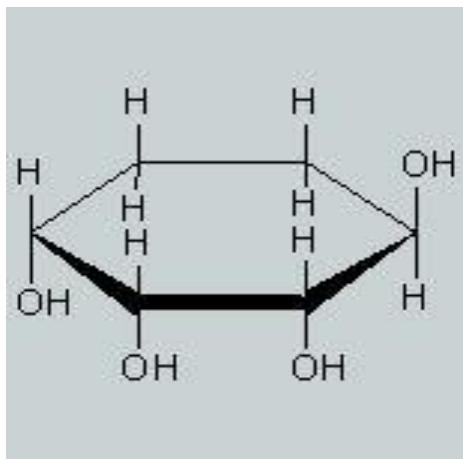
- From left to right, these structures are the *Wedge-Dash Notation*, the *Haworth Projection*, and the *Chair Conformation*.



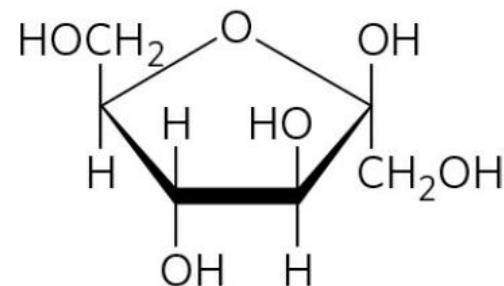
- First one is cyclic wedge-dash notation. In the structure above, the methyl group is behind the page. Since there must be four bonds to each carbon, and two *sticks* and one *dash* have already been drawn in, the remaining hydrogen must be *wedged*.

Haworth Projections

- **Haworth Projections** are similar to the cyclic Wedge-Dash notation, in that the ring itself is drawn as planar. The groups on a **Haworth Projection** are simply oriented perpendicular to the plane of the ring, either up or down. It is important to note that two groups that are both oriented up or both oriented down are *cis* to one another.



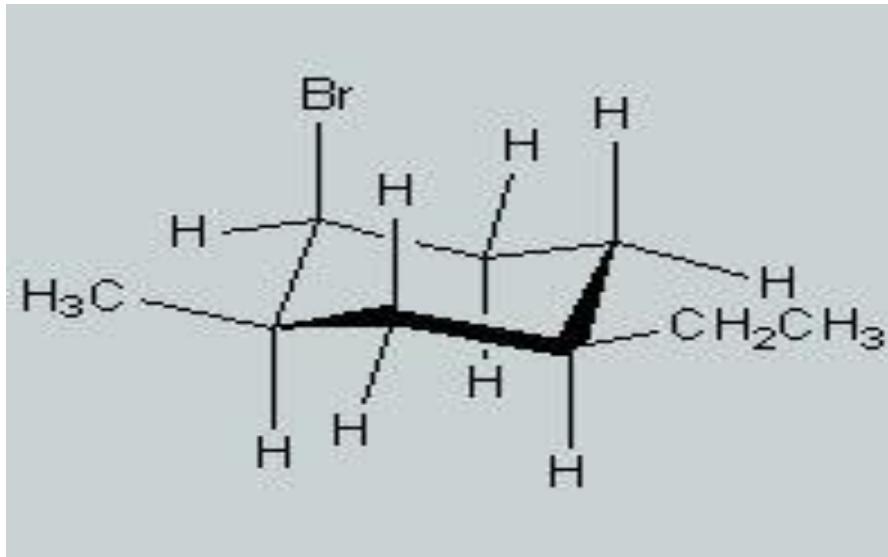
β -D-Glucopyranose



β -D-Fructofuranose

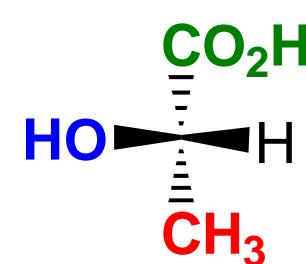
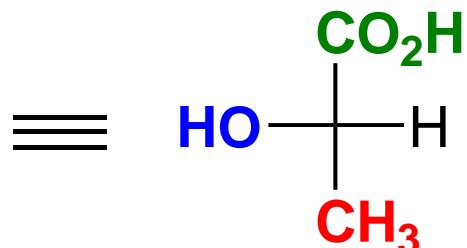
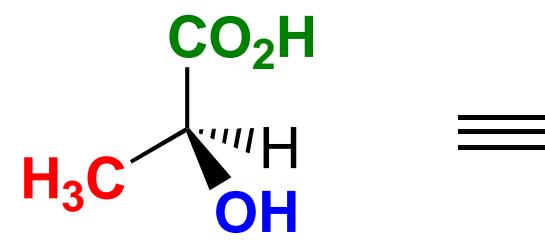
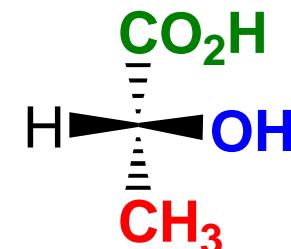
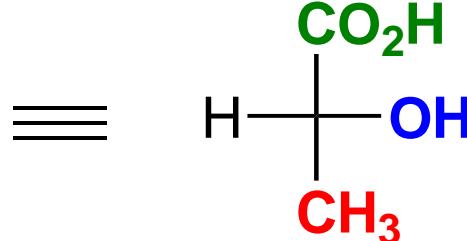
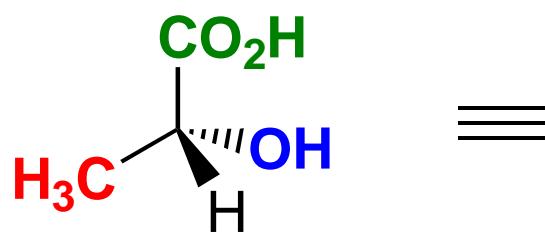
Chair Conformation

- **Chair Conformations** are the most accurate representations of how cyclohexane rings are actually oriented in space. They appropriately reflect the angles between the carbons in the ring and the positions of the groups on each carbon in the ring.

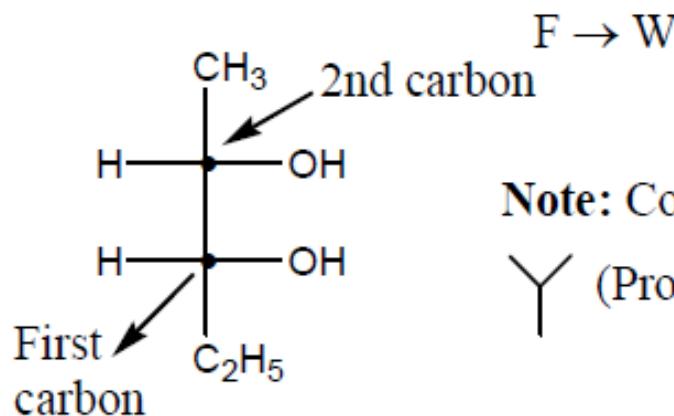


Conversion of projection formula

- Conversion of Fisher to Wedge.

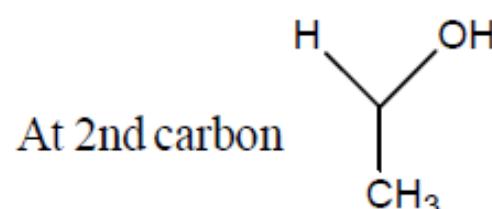
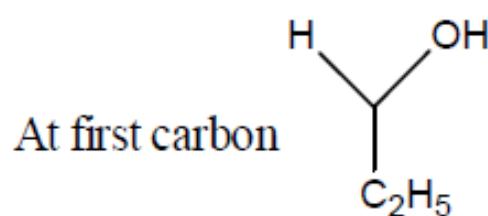


• Conversion Fischer to sawhorse

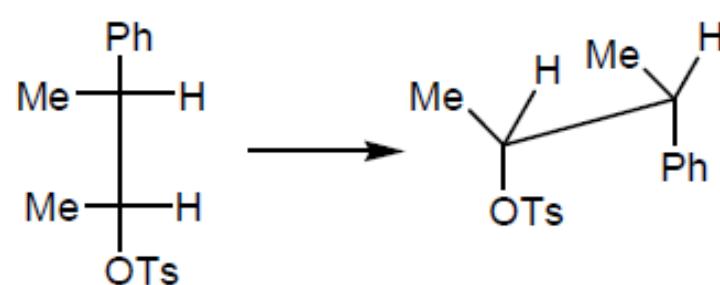
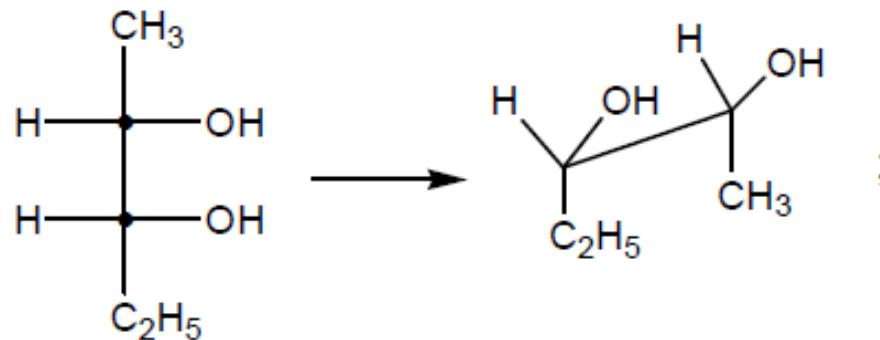


Note: Consider at first carbon shape like

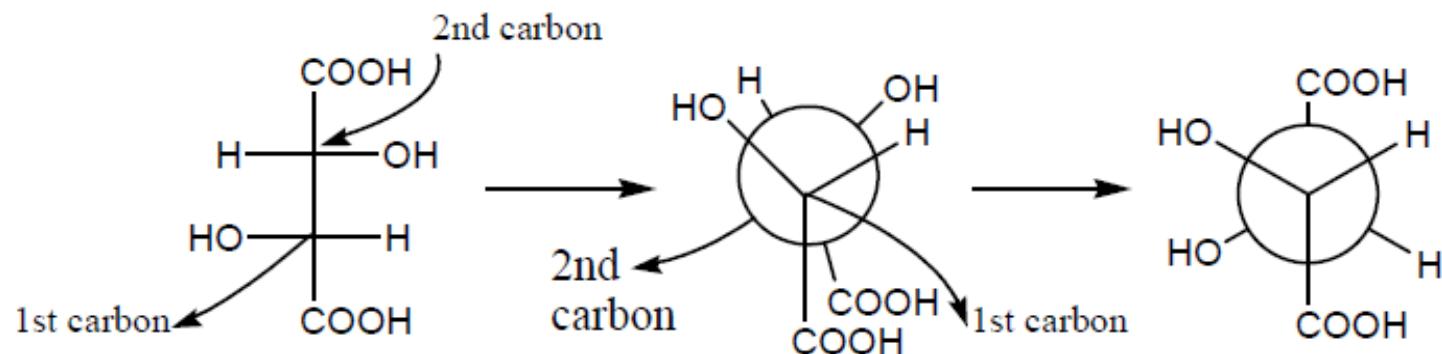
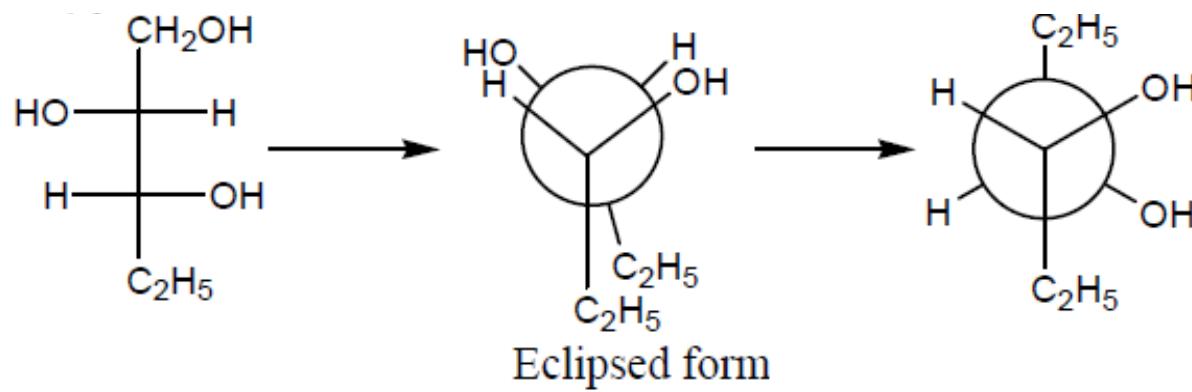
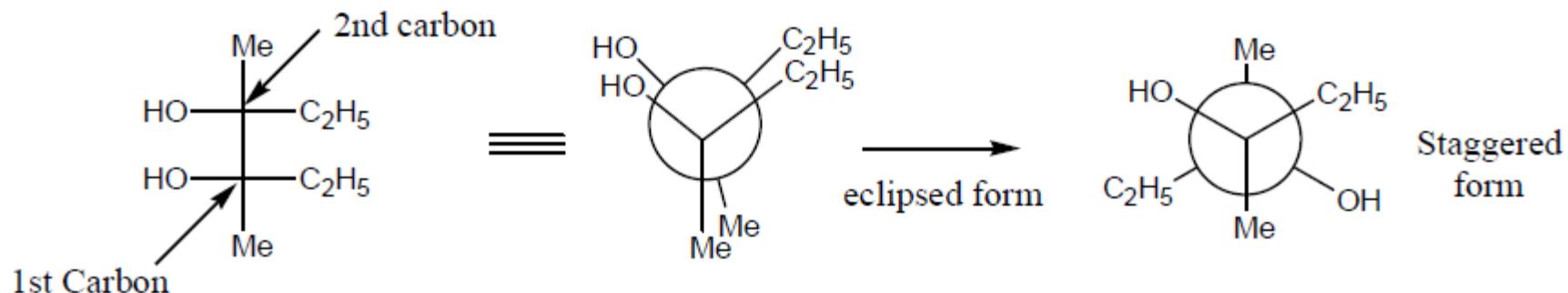
(Pronounced 'Y')



and then combine these two by a straight line like



• Conversion Fischer to Newmann



Configurational Nomenclature

- Appropriate configurational descriptors (name or symbol) is necessary to distinguish two stereoisomers.
- One must know which structures belong to which enantiomers.

Fischer's D and L Nomenclature

R and S (CIP Nomenclature)

Threo and Erythro nomenclature

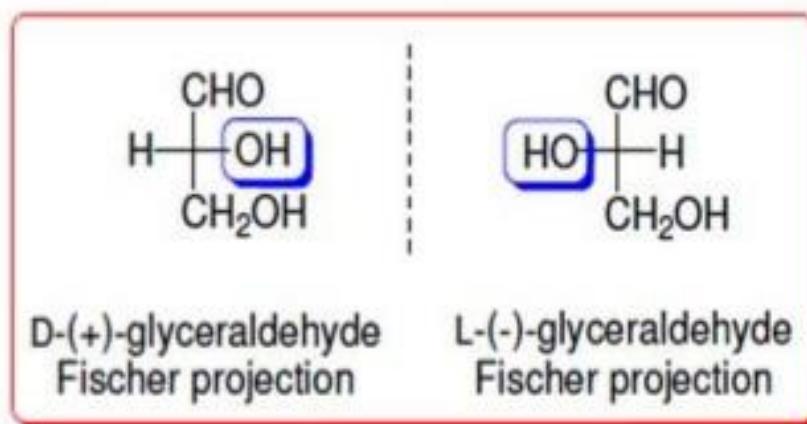
Cis-trans and E Z nomenclature

Fischer Projections and the D/L Notation:

- ✓ The first system for doing this was developed by **Fischer and Rosanoff** around 1900.
- ✓ **Fischer first** developed a method for drawing carbohydrates in two-dimensions, and a convention with respect to orientation, so as to indicate their three dimensional structures, so-called ***Fischer projections***.
- ✓ Fischer and Rosanoff then devised a notation for designating the configurations of stereogenic centres, depicted in Fischer projections, as either **D or L**.

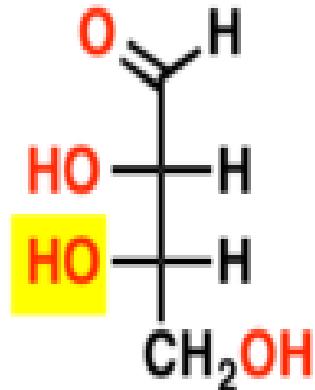
The symbols **D and L** *DO NOT* relate to the sign of rotation of an optically active molecule which is designated (+)- (or *d*) and (-)- (or *l*).

Example: D (+)-glyceraldehyde was defined as being D because the OH group attached to the C-2 is on the right hand side (RHS) of the molecules when drawn in its correct Fischer projection (in which the CHO group appears at the top). Its enantiomer L (-)-glyceraldehyde was defined as L because the OH group is on the left hand side (LHS).

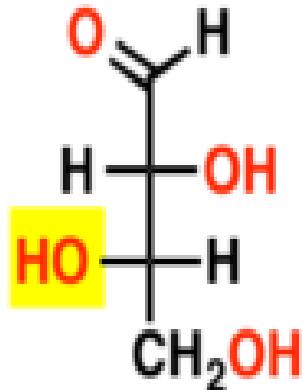


In carbohydrates, in general, the OH group attached to the penultimate carbon atom in the chain determines the assignment of D or L. Thus (+)-glucose has the D-configuration and (+)-ribose has the L-configuration.

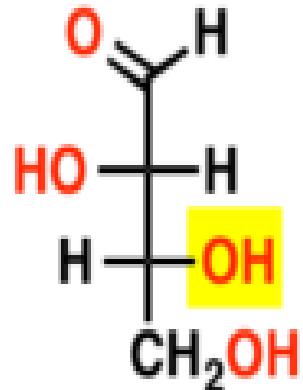
Four carbon sugars (aldotetroses)



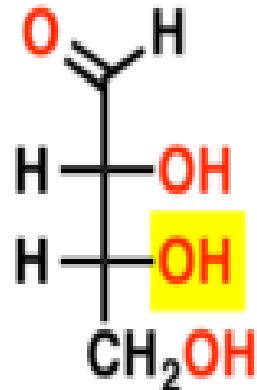
L-Erythroose



L-Threose

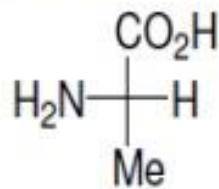


D-Threose

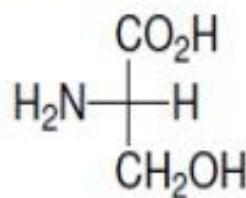


D-Erythroose

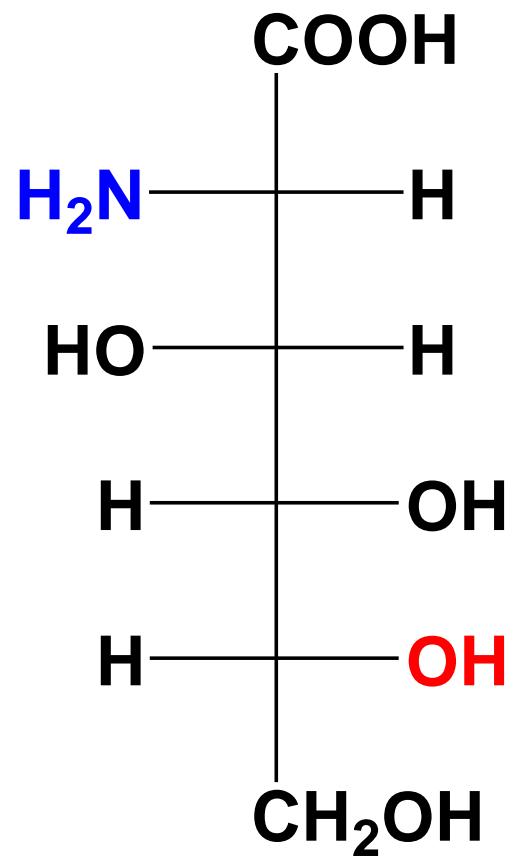
The notation was extended to α -amino acids : L enantiomers are those in which the NH₂ group is on the LHS of the Fischer projection in which the carboxyl group appears at the top. Conversely, the D enantiomers are those in which the NH₂ group is on the RHS. Thus (+)-alanine and (-)-serine are L-amino acids.



L-(+)-alanine
Fischer projection



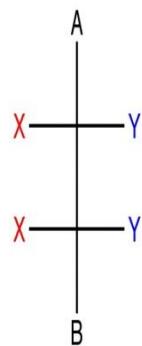
L-(-)-serine
Fischer projection



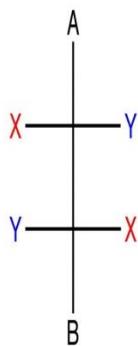
D_g or L_s 2-amino-2-deoxymannoic acid

Erythro and Threo nomenclature

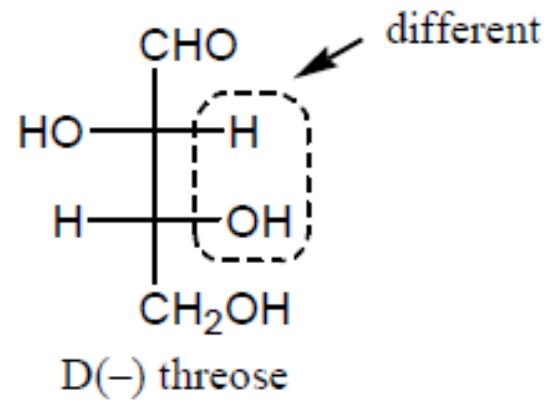
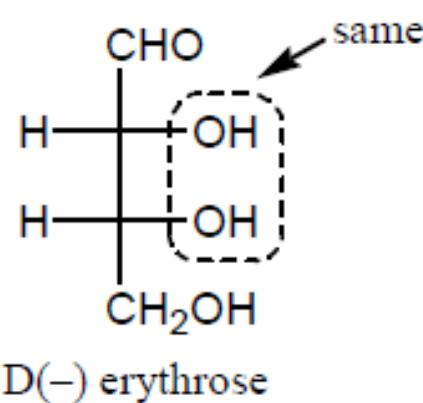
- Erythro diastereomers have similar group on same side of the Fischer Projection.
- Threo diastereomers have similar group on the opposite side of the Fischer projection.



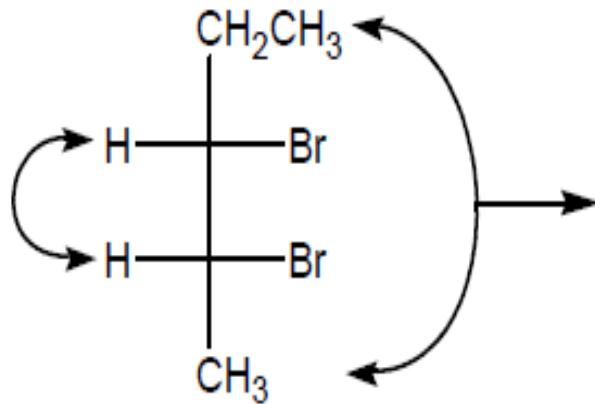
erythro isomer



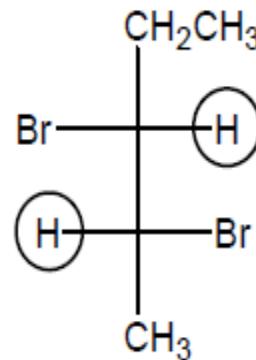
threo isomer



- Ex:



These two are different group on the two asymmetric carbon placed at top and bottom.



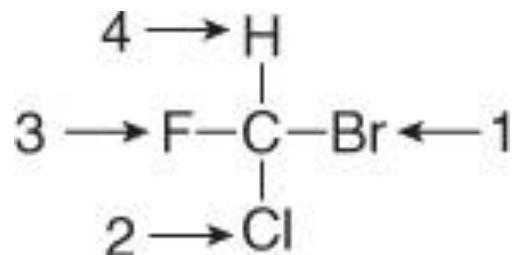
- (1) Two asymmetric carbon should be there
- (2) On two asymmetric carbon, two of the groups are the same and the third is different.

R/S Nomenclature

Cahn-Ingold-Prelog system (CIP)

Labeling Stereogenic Centers with *R* or *S*

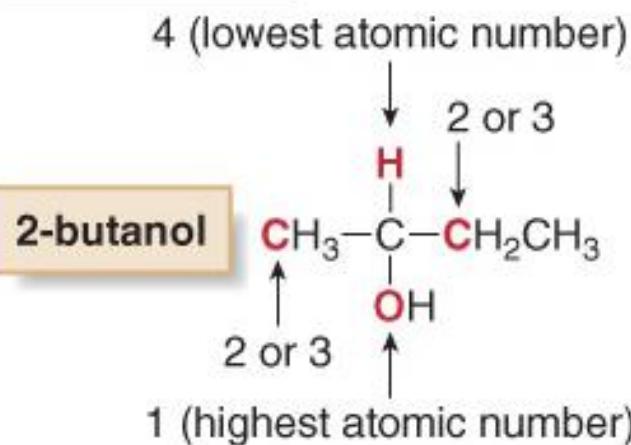
- To designate enantiomers as *R* or *S*, priorities must be assigned to each group bonded to the stereogenic center, in order of decreasing atomic number. The atom of highest atomic number gets the highest priority (1).



Priority Rules for Naming Enantiomers (R or S)

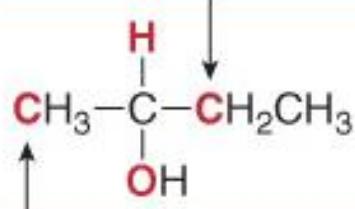
- If two atoms on a stereogenic center are the same, assign priority based on the atomic number of the atoms bonded to these atoms. One atom of higher priority determines the higher priority.

Following rule 1:



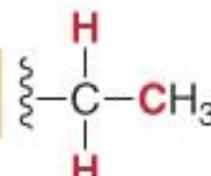
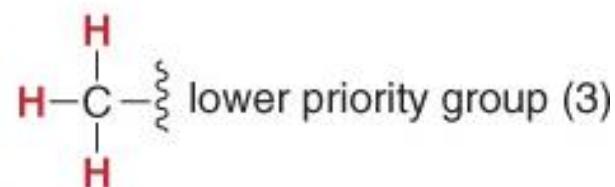
Adding rule 2:

This C is bonded to 2 H's and 1 C.



higher priority group (2)

This C is bonded to 3 H's.



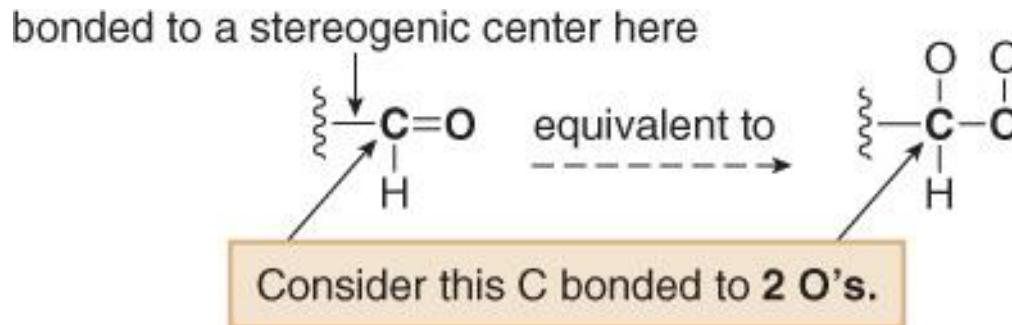
Priority of Isotopes on a Stereogenic Center

- If two isotopes are bonded to the stereogenic center, assign priorities in order of decreasing mass number. Thus, in comparing the three isotopes of hydrogen, the order of priorities is:

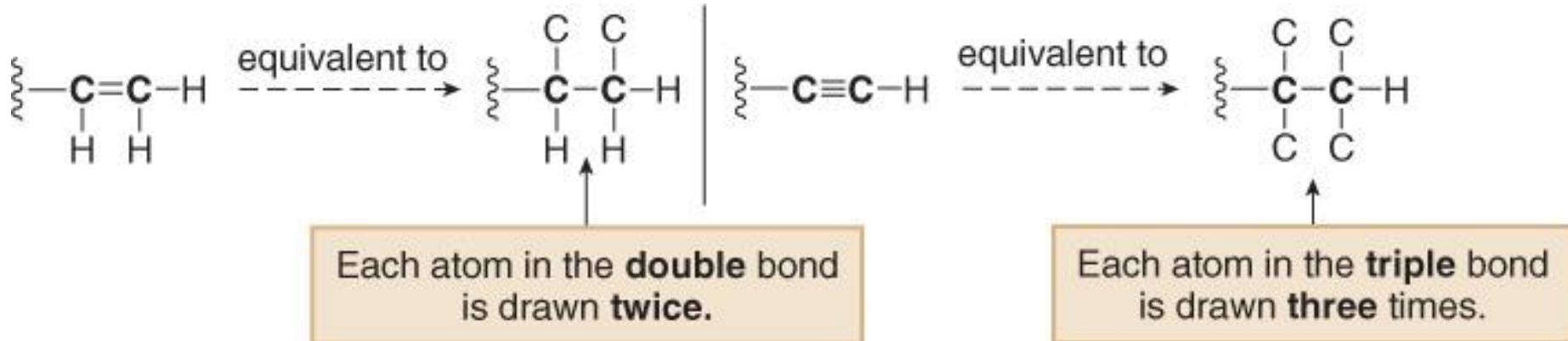
	Mass number	Priority
T (tritium)	3 (1 proton + 2 neutrons)	1
D (deuterium)	2 (1 proton + 1 neutron)	2
H (hydrogen)	1 (1 proton)	3

Priority Rules for Multiple Bonds in (R or S) Labeling

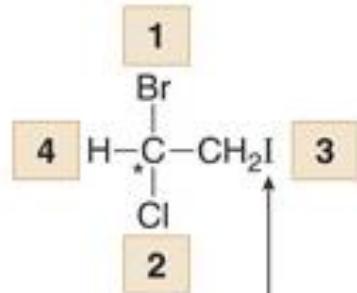
- To assign a priority to an atom that is part of a multiple bond, treat a multiply bonded atom as an equivalent number of singly bonded atoms. For example, the C of a C=O is considered to be bonded to two O atoms.



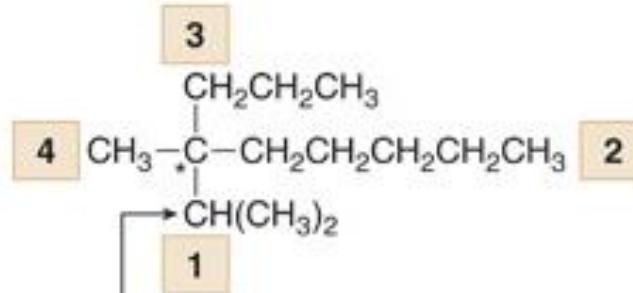
- Other common multiple bonds are drawn below:



Examples Assigning Priorities



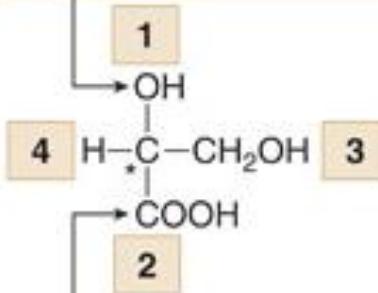
I is NOT bonded directly to the stereogenic center.



This is the highest priority C since it is bonded to 2 other C's.

[* = stereogenic center]

highest atomic number = highest priority

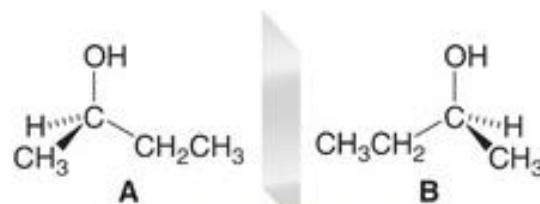


This C is considered bonded to 3 O's.

R or S Enantiomers

How To Assign R or S to a Stereogenic Center

Example Label each enantiomer as R or S.



two enantiomers of 2-butanol

Step [1] Assign priorities from 1 to 4 to each group bonded to the stereogenic center.

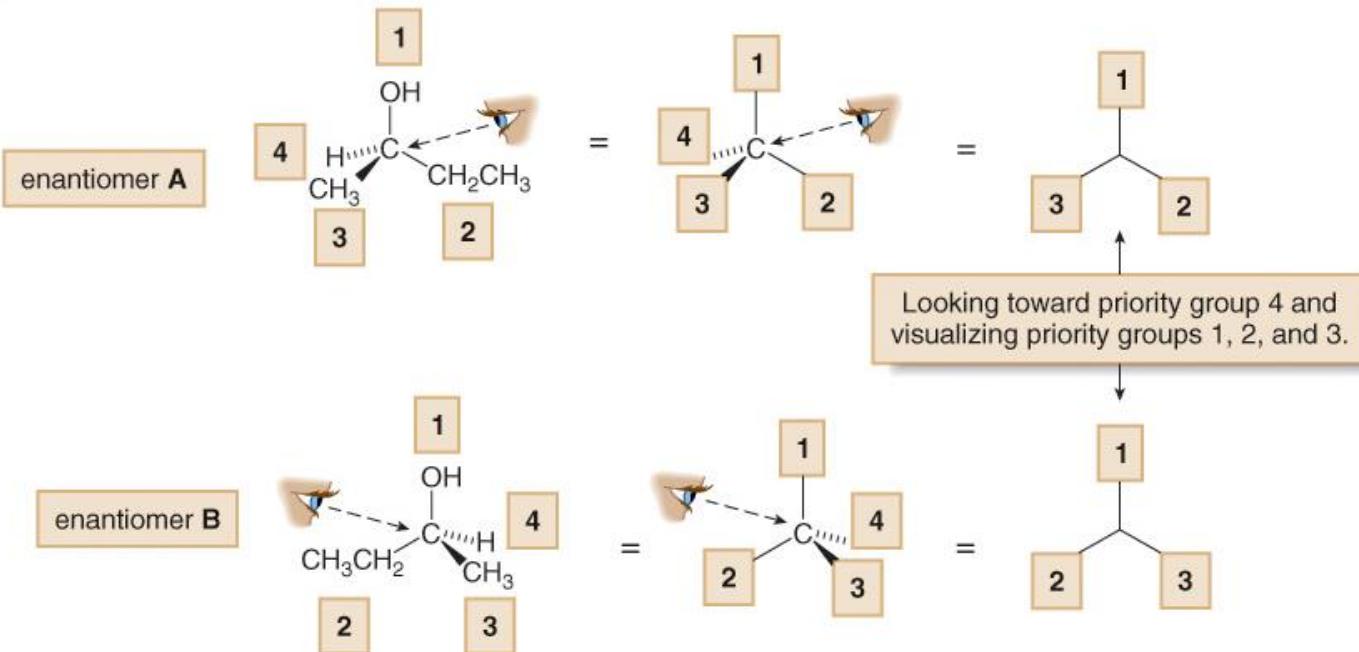
- The priorities for the four groups around the stereogenic center in 2-butanol were given in rule 2, on page 167.

-OH	-CH ₂ CH ₃	-CH ₃	-H		
1	2	3	4		
highest			lowest		
Decreasing priority					

Positioning the Molecule for R/S Assignment

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).

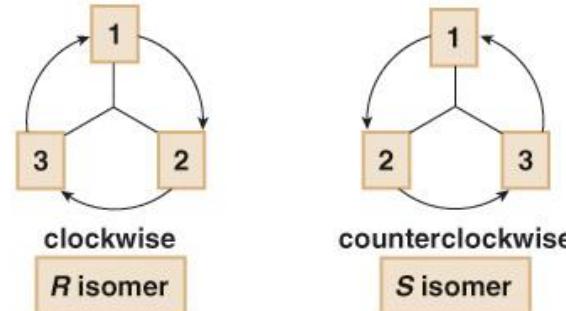
- For each enantiomer of 2-butanol, look toward the lowest priority group, drawn behind the plane, down the C–H bond.



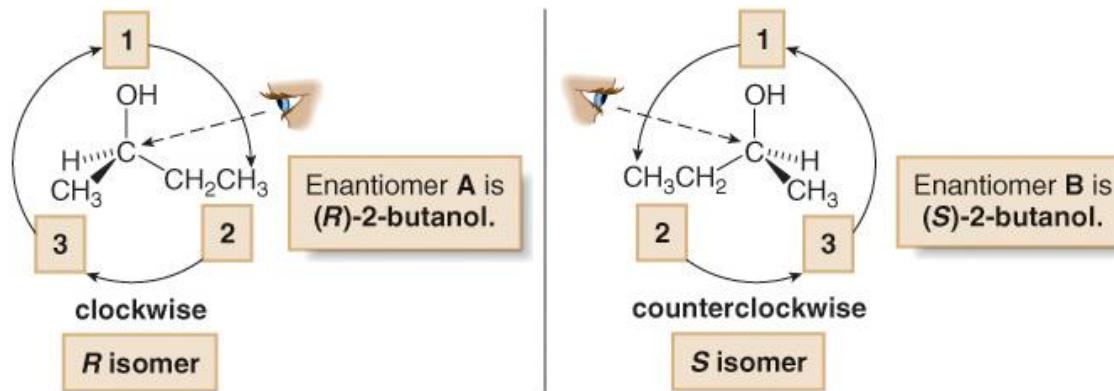
Step [3]

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**.



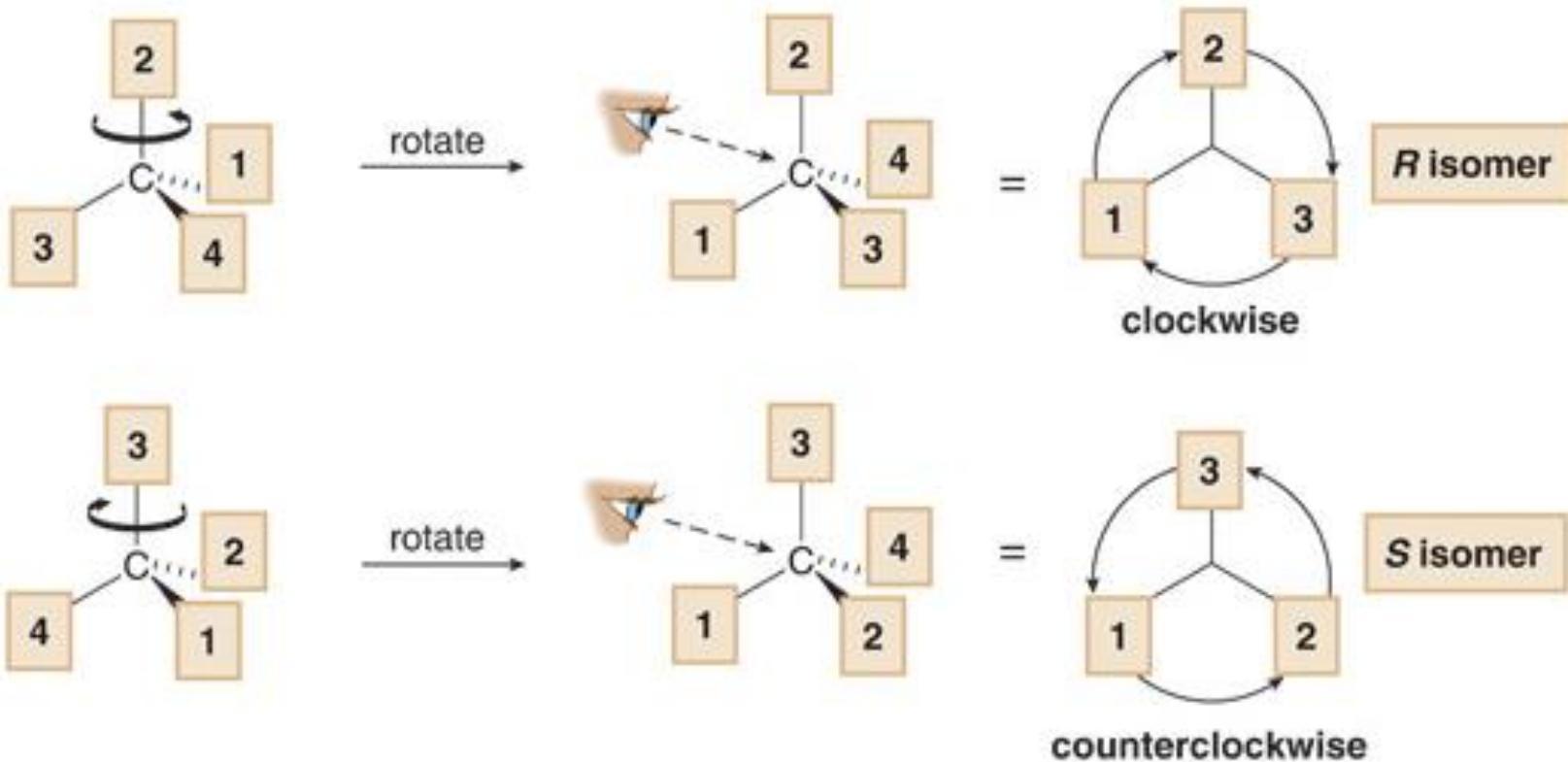
- The letters *R* or *S* precede the IUPAC name of the molecule. For the enantiomers of 2-butanol:



R-enantiomer (Clockwise Rotation)

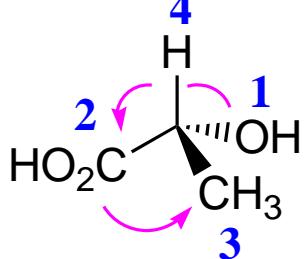
S-enantiomer (Counterclockwise Rotation)

Manipulation of Chiral Molecules



Switching any two groups on a molecule with a single stereogenic center, converts the molecule into its enantiomer.

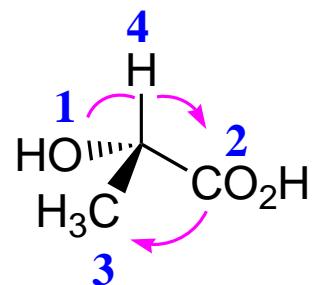
Or use the “Hand Rule.” Orient the lowest priority group up. Point your thumb in the direction of the lowest priority group. If you need to use your *right hand* so that your fingers point in the direction of the group priorities in the order 1→2→3, then the stereogenic center is assigned R (“rectus” or *right*). If your *left hand* is required so that your fingers point in the direction of the group priorities 1→2→3, the the stereogenic center is assigned S (“sinister” or *left*).

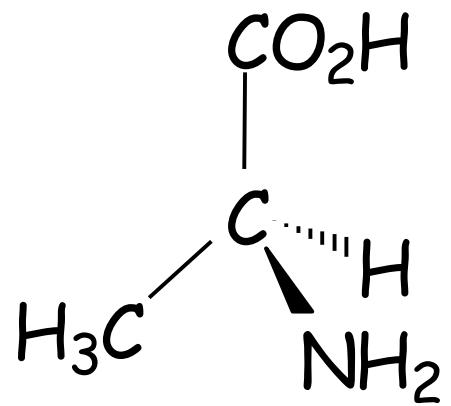


(R)-(-)-Lactic acid
(Right Hand)

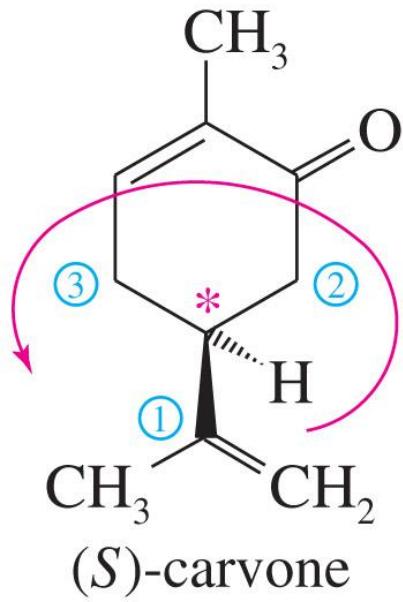


(S)-(+)-Lactic acid
(Left Hand)

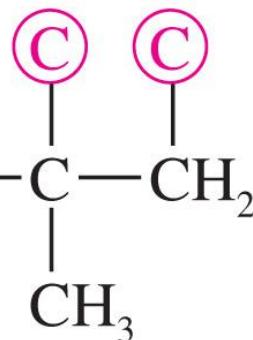




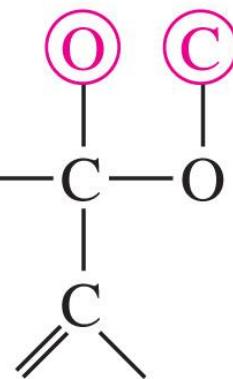
(S)-alanine



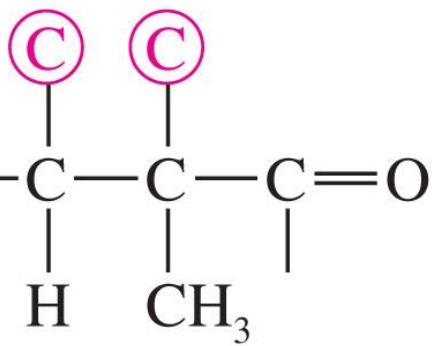
Group ①:



Group ②:

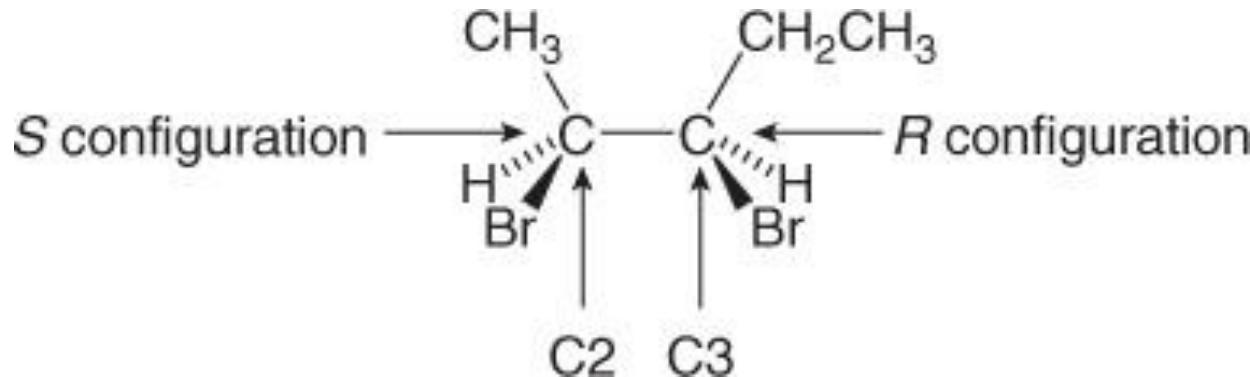


Group ③:



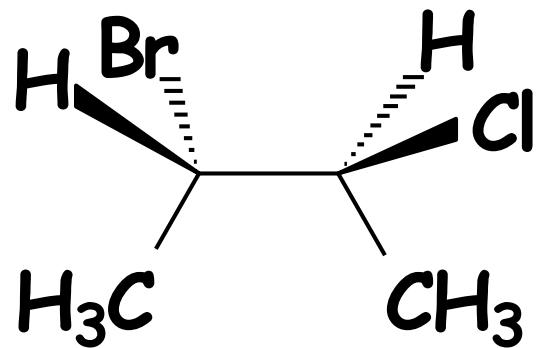
R and S Assignments in Compounds with Two or More Stereogenic Centers.

- When a compound has more than one stereogenic center, the *R* and *S* configuration must be assigned to each of them.



One stereoisomer of 2,3-dibromopentane

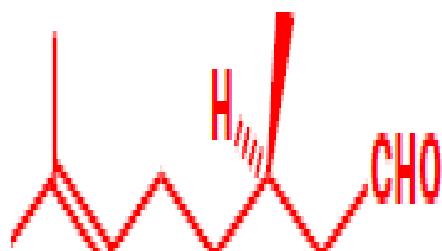
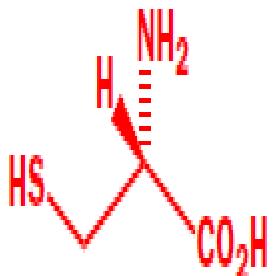
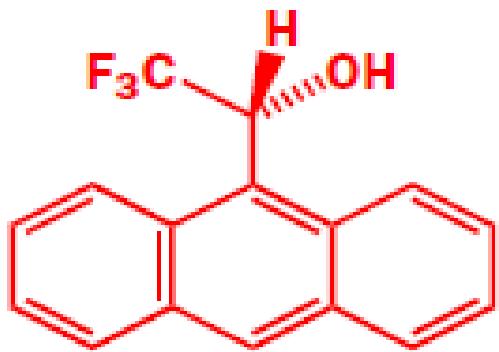
The complete name is **(2*S*,3*R*)-2,3-dibromopentane**



(2*S*, 3*S*)-2-bromo-3-chlorobutane

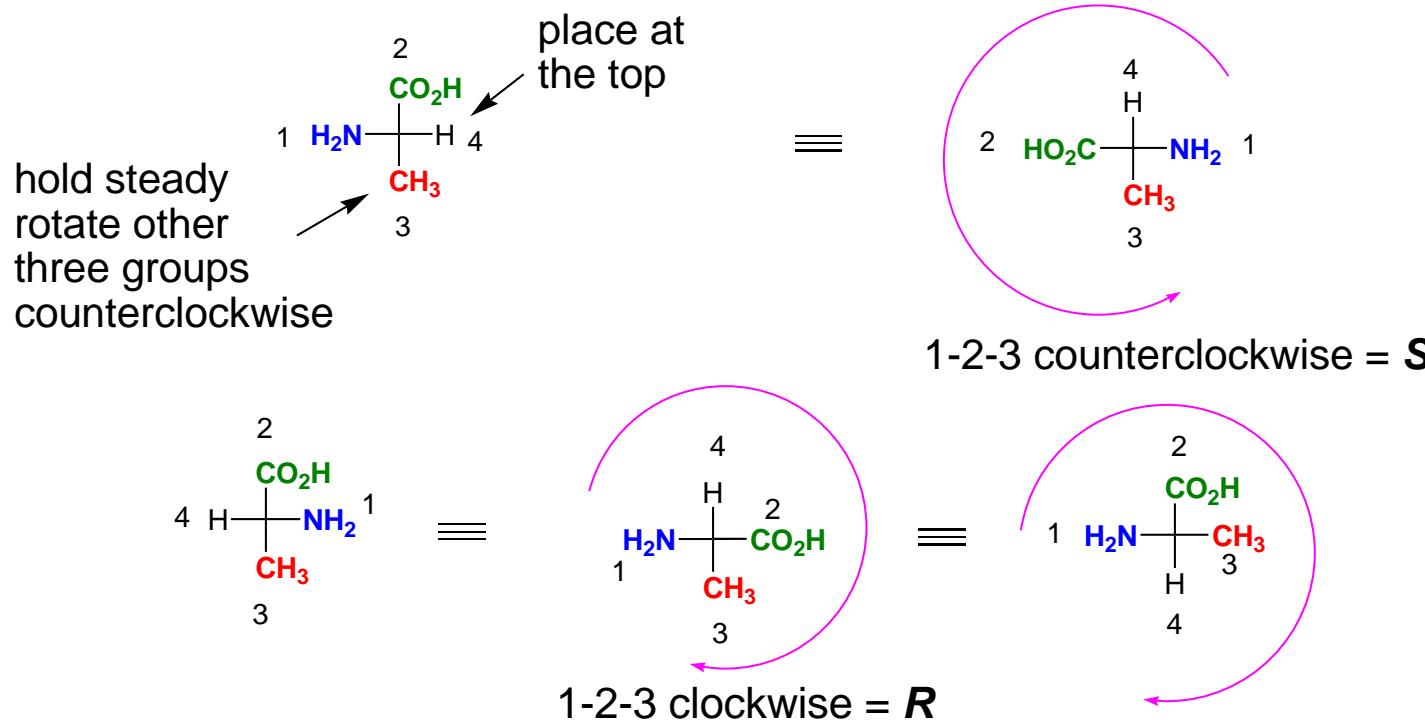
Questions

Assign a configuration R or S to these compound.



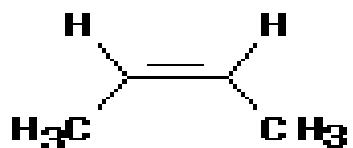
Assigning R and S Configuration to Fischer Projections

1. Assign priorities to the four substituents according to the Cahn-Ingold-Prelog rules
2. Perform the two allowed manipulations of the Fischer projection to place the lowest priority group at the top (or bottom). **Very Good rule: Vertical is good**
3. If the priority of the groups $1 \rightarrow 2 \rightarrow 3$ are clockwise then assign the center as *R*, if $1 \rightarrow 2 \rightarrow 3$ are counterclockwise then assign the center as *S*.

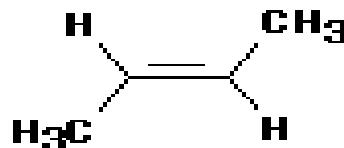


E/Z nomenclature

- IUPAC system for **naming** alkene isomers, called the **E-Z** system, is based on the same priority **rules**. The general strategy of the **E-Z** system is to analyze the two groups at each end of the double bond.
- Higher priority group at one end of the double bond and the higher priority group at the other end of the double bond are on the **same** side (**Z**, from German zusammen = together) or on **opposite** sides (**E**, from German entgegen = opposite) of the double bond.

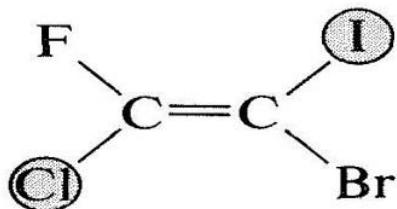


cis-2-butene
(Z)-2-butene

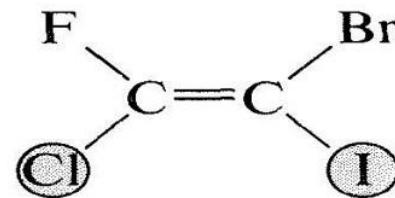


trans-2-butene
(E)-2-butene

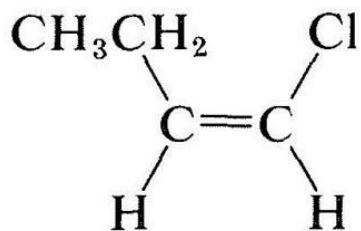
- Ex:



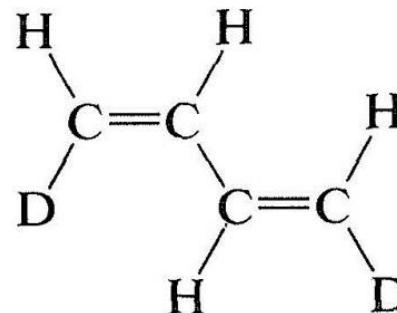
priority groups
on opposite sides
E configuration



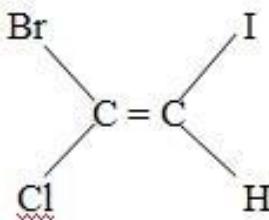
priority groups
on same side
Z configuration



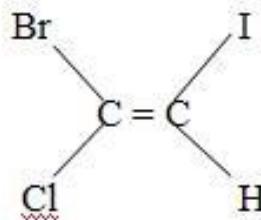
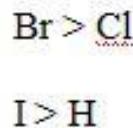
(*Z*)-1-chloro-1-butene



(*1Z,3E*)-1,3-butadiene-1,4-*d*₂



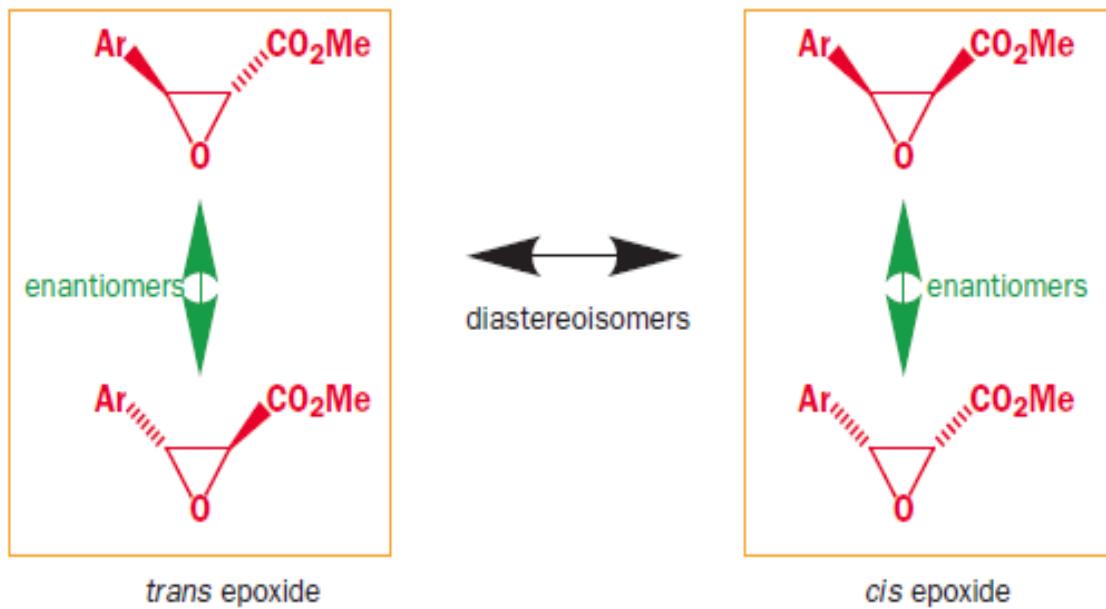
Z form



E- form

Diastereoisomers

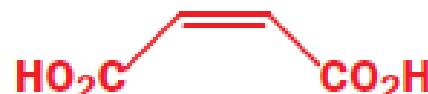
- **Diastereoisomers are stereoisomers that are not mirror images.**
Two diastereoisomers are different compound, and have different relative stereochemistry.
- Diastereoisomers may be achiral or chiral.
- Diastereoisomers can arise when structures have more than one stereogenic center.



butenedioic acids



fumaric acid

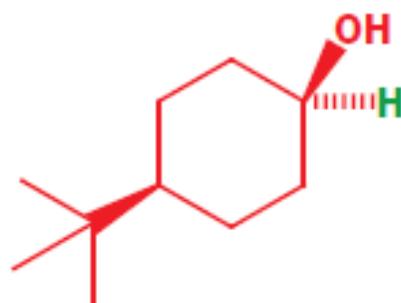


maleic acid

trans-butenedioic acid (fumaric acid)
m.p. 299–300 °C

cis-butenedioic acid (maleic acid)
m.p. 140–142 °C

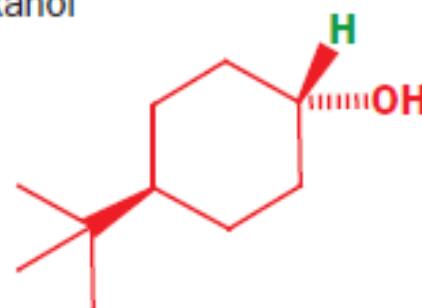
4-*t*-butylcyclohexanol



cis 4-*t*-butylcyclohexanol

mp 82–83 °C

¹H NMR: δ_H of green proton 4.02



trans 4-*t*-butylcyclohexanol

mp 80–81 °C

¹H NMR: δ_H of green proton 3.50

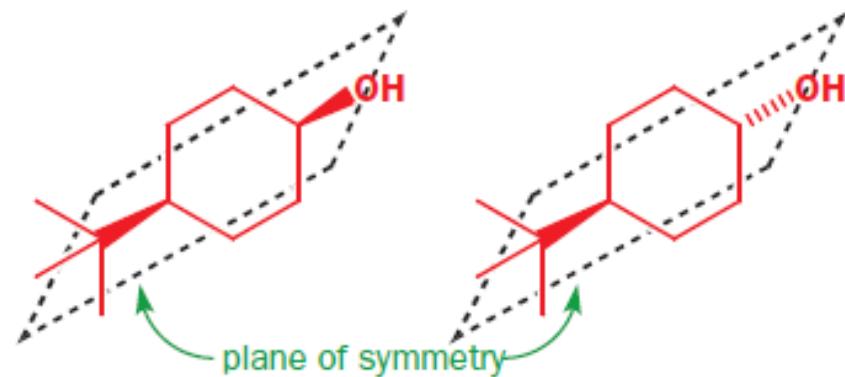
Diastereoisomers can be chiral or achiral

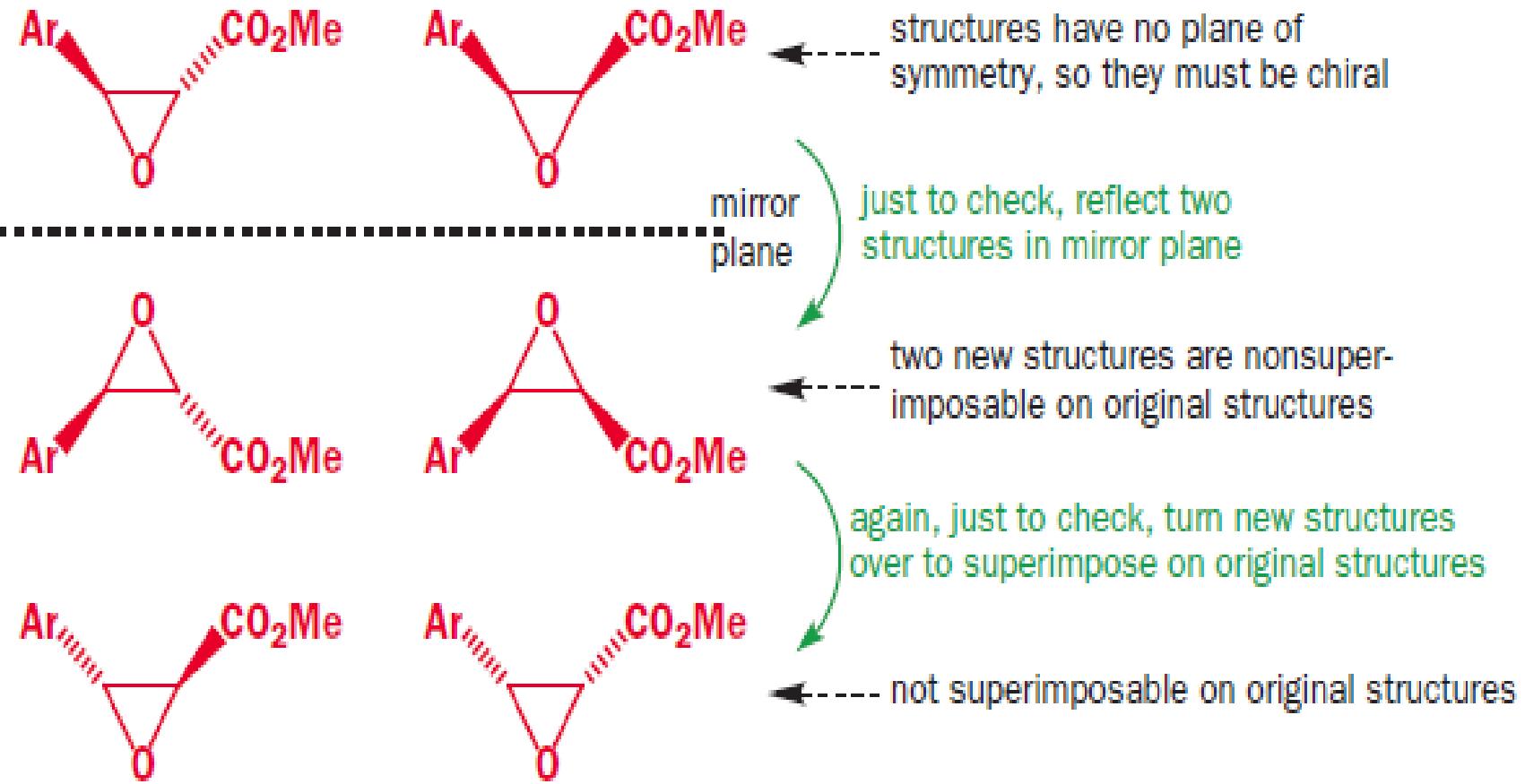


fumaric acid

maleic acid

plane of symmetry in plane of page





- The above pair of diastereoisomers are chiral because they don't have plane of symmetry.

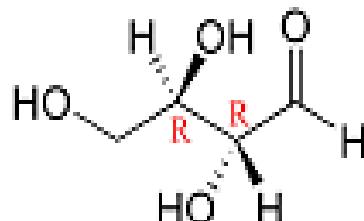
Converting enantiomers and diastereoisomers

- To go from one enantiomer to another both steriogenic centers are inverted.
- To go from one diastereoisomers to another only one of the two is inverted.

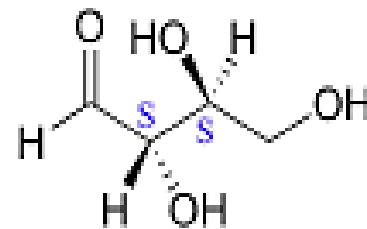


Examples

enantiomers

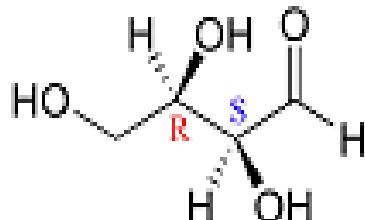


D-erythroose

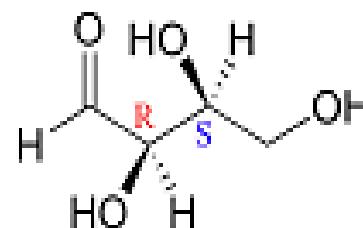


L-erythrose

diastereomers



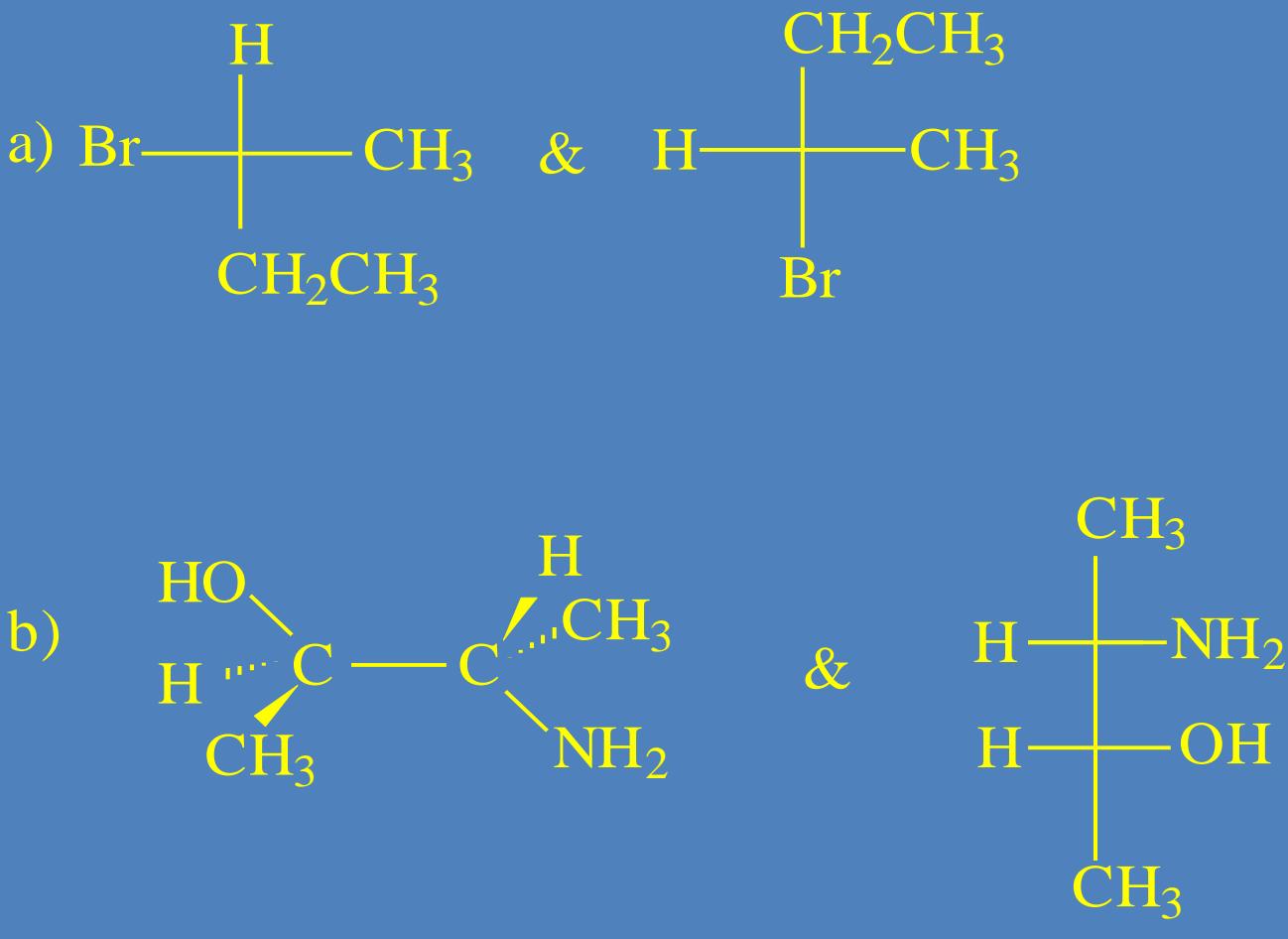
D-threose



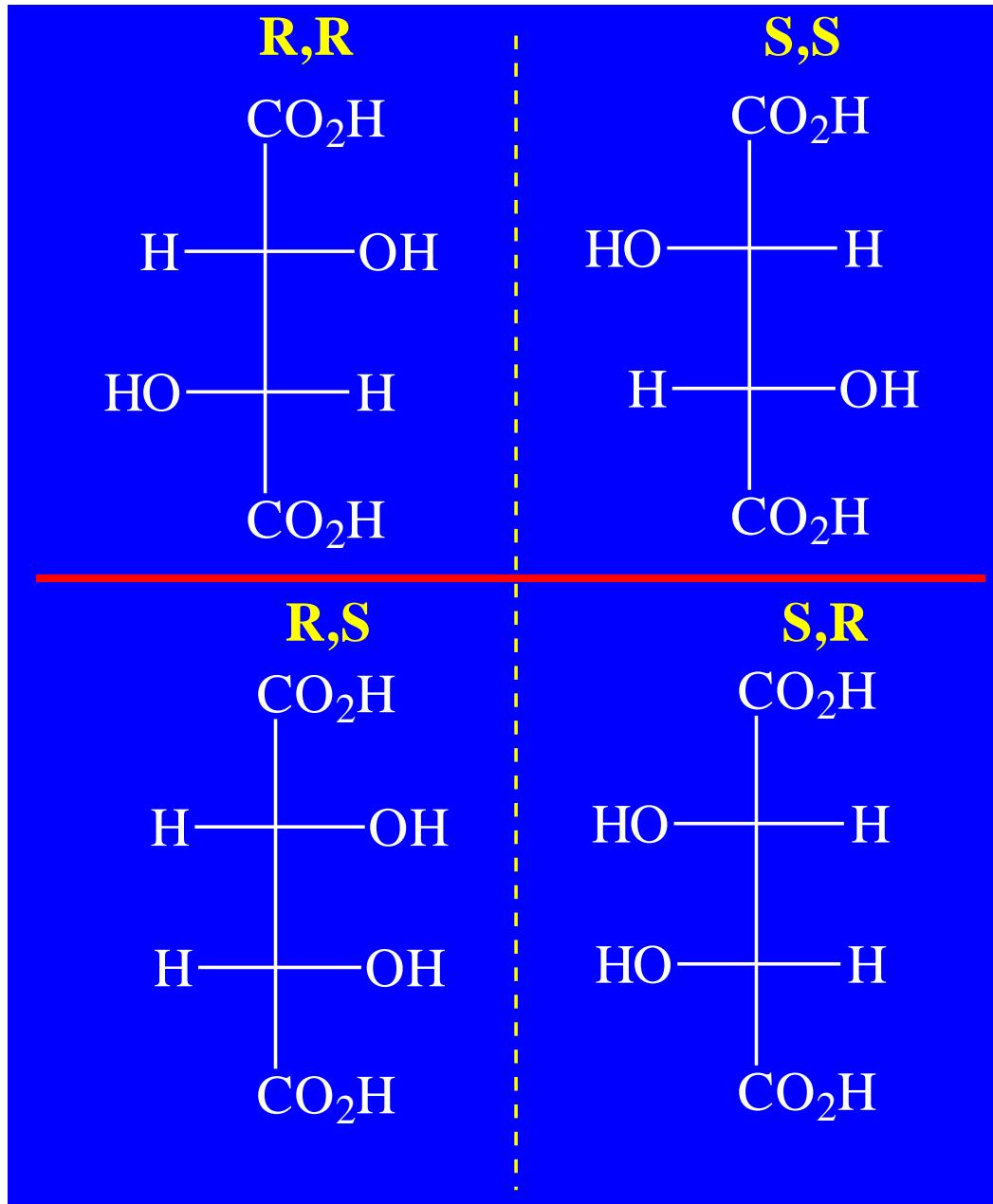
L-threose

enantiomers

Identical, Enantiomers or Diastereomers?



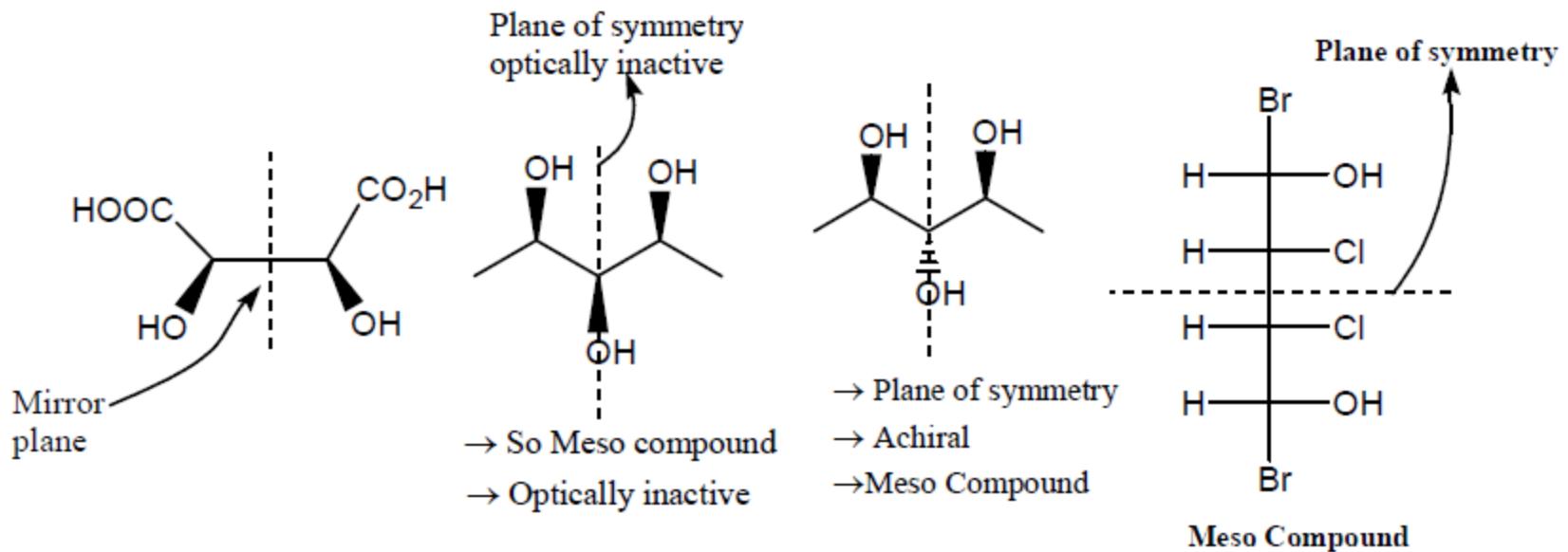
Tartaric Acids



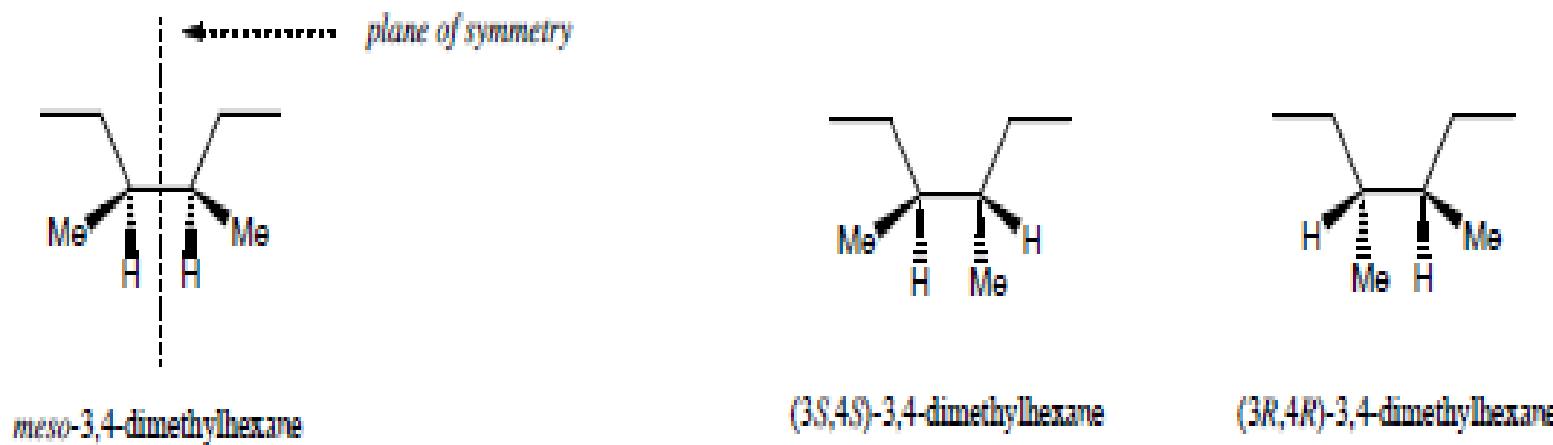
Meso compound

- Compounds that contain stereogenic center but achiral are called Meso compound.

For example:



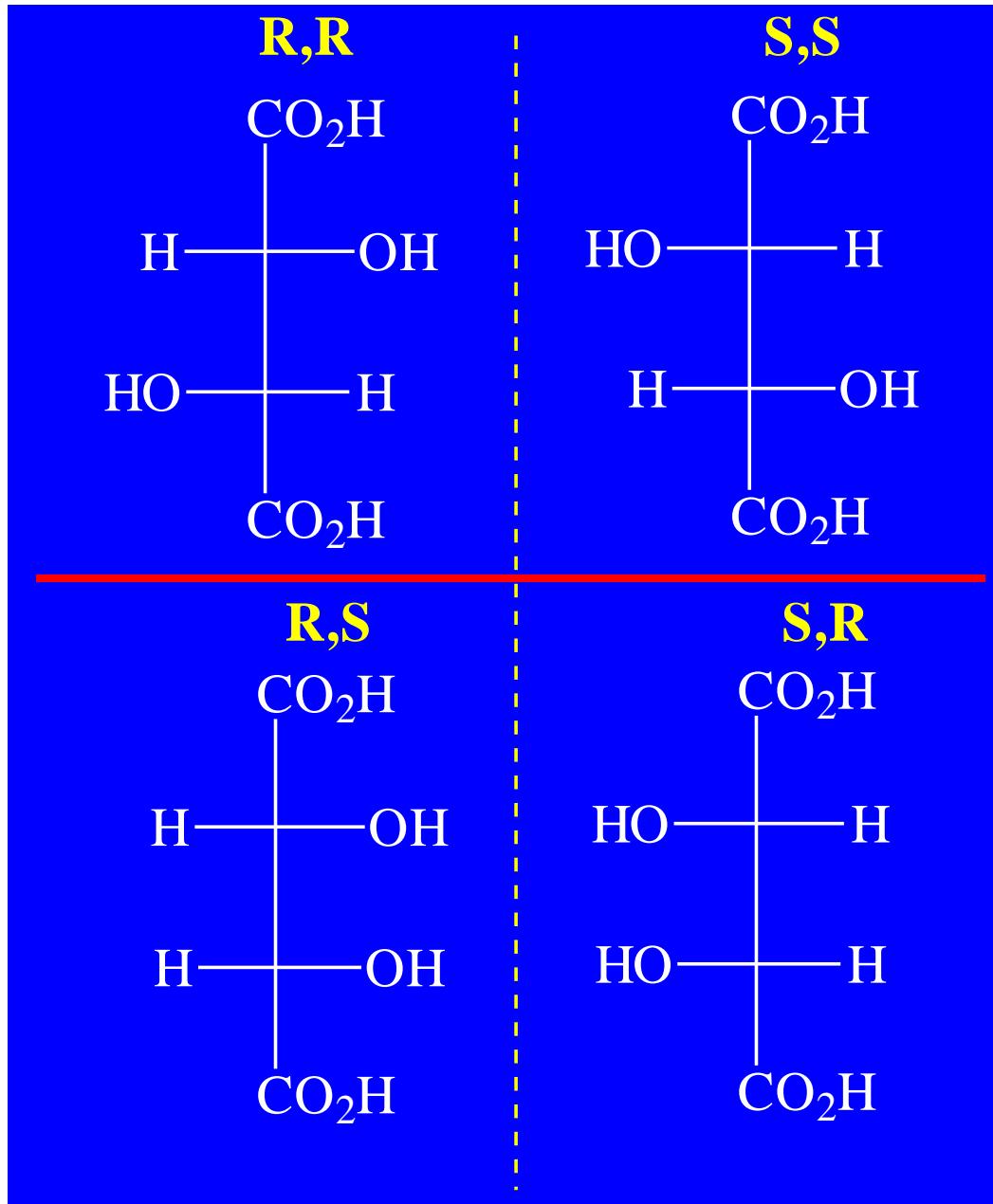
- The best way to identify a meso compound is to prove that it is superimposable with its mirror image. However, a quick test is to see if it contains a plane of symmetry:



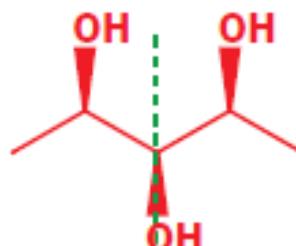
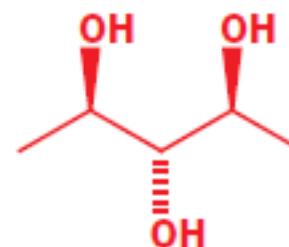
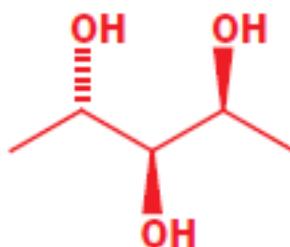
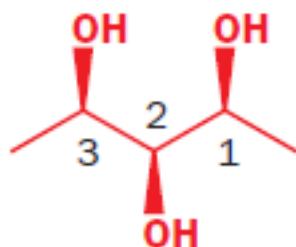
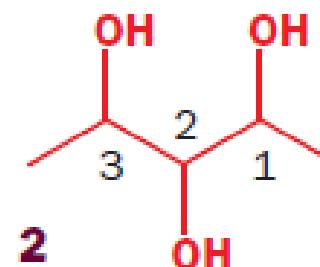
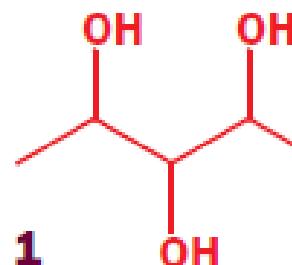
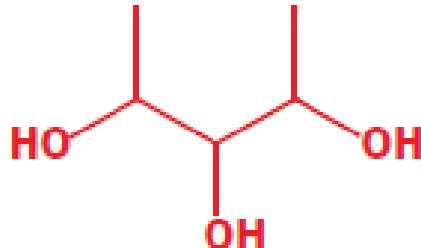
Compounds containing a plane of symmetry are achiral!

No plane of symmetry

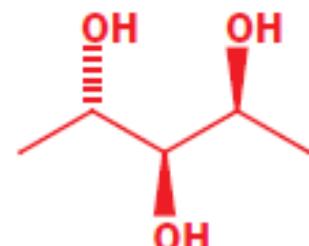
Tartaric Acids



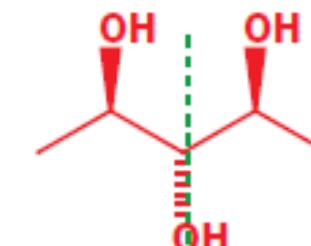
Investigating the stereochemistry of a compound



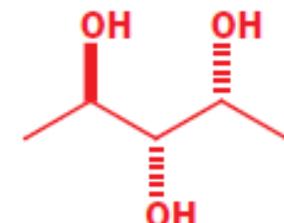
plane of symmetry
achiral (*meso*)



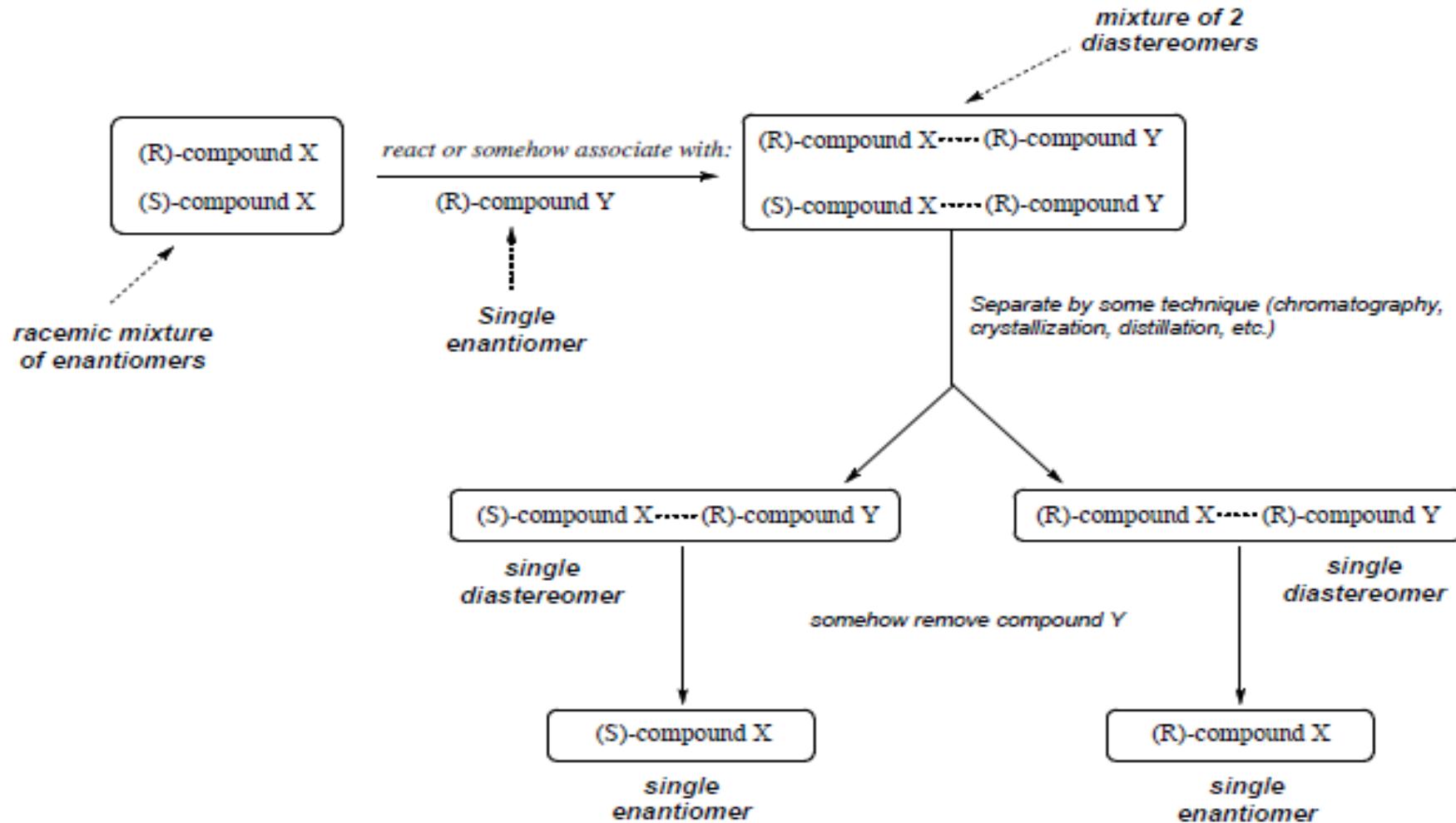
chiral



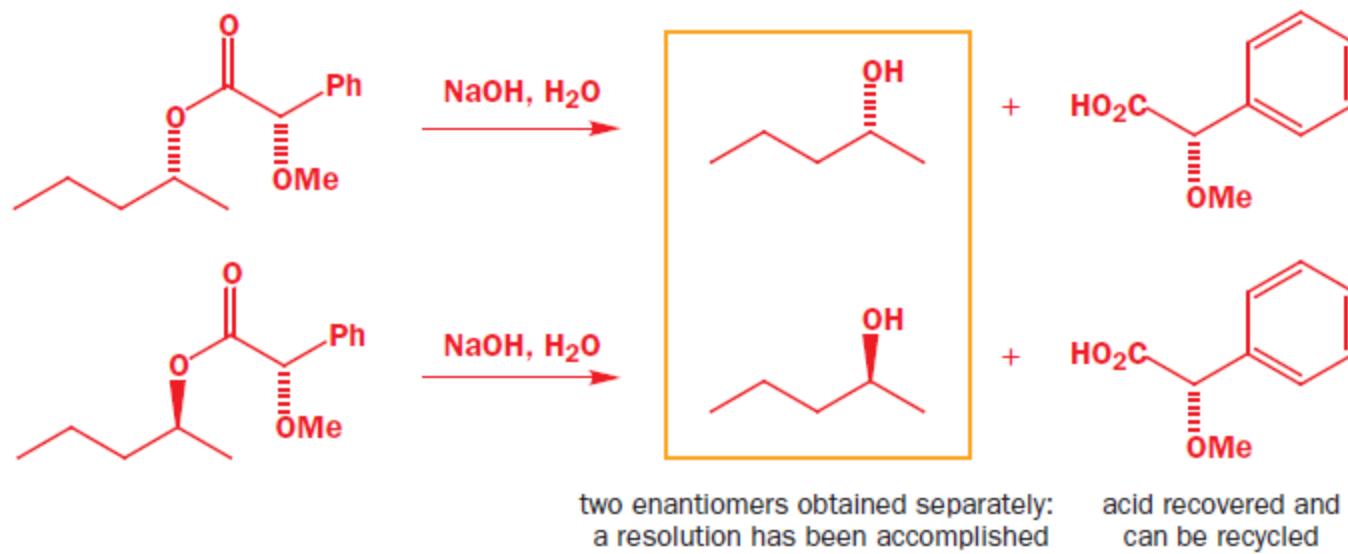
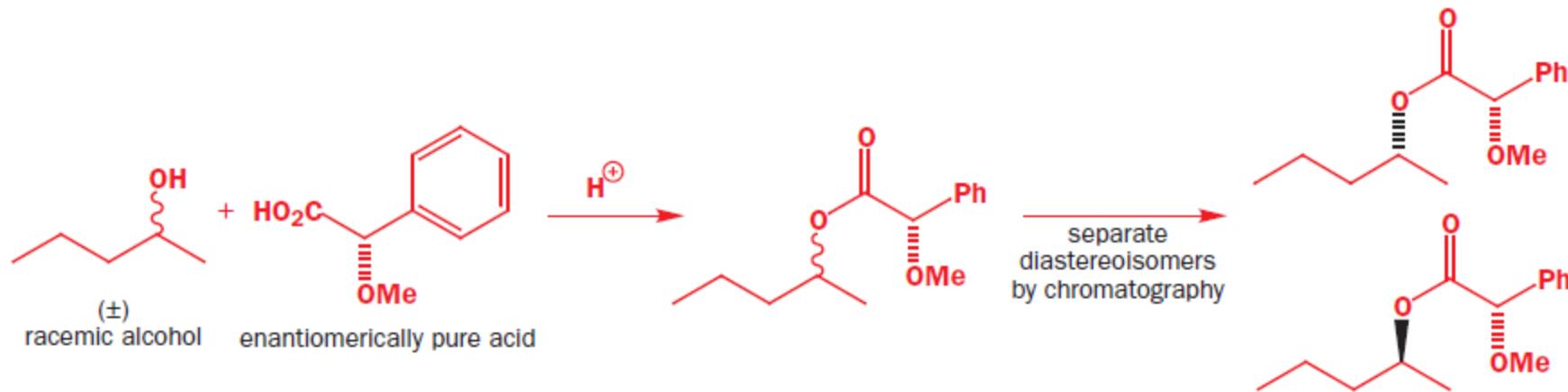
plane of symmetry
achiral (*meso*)



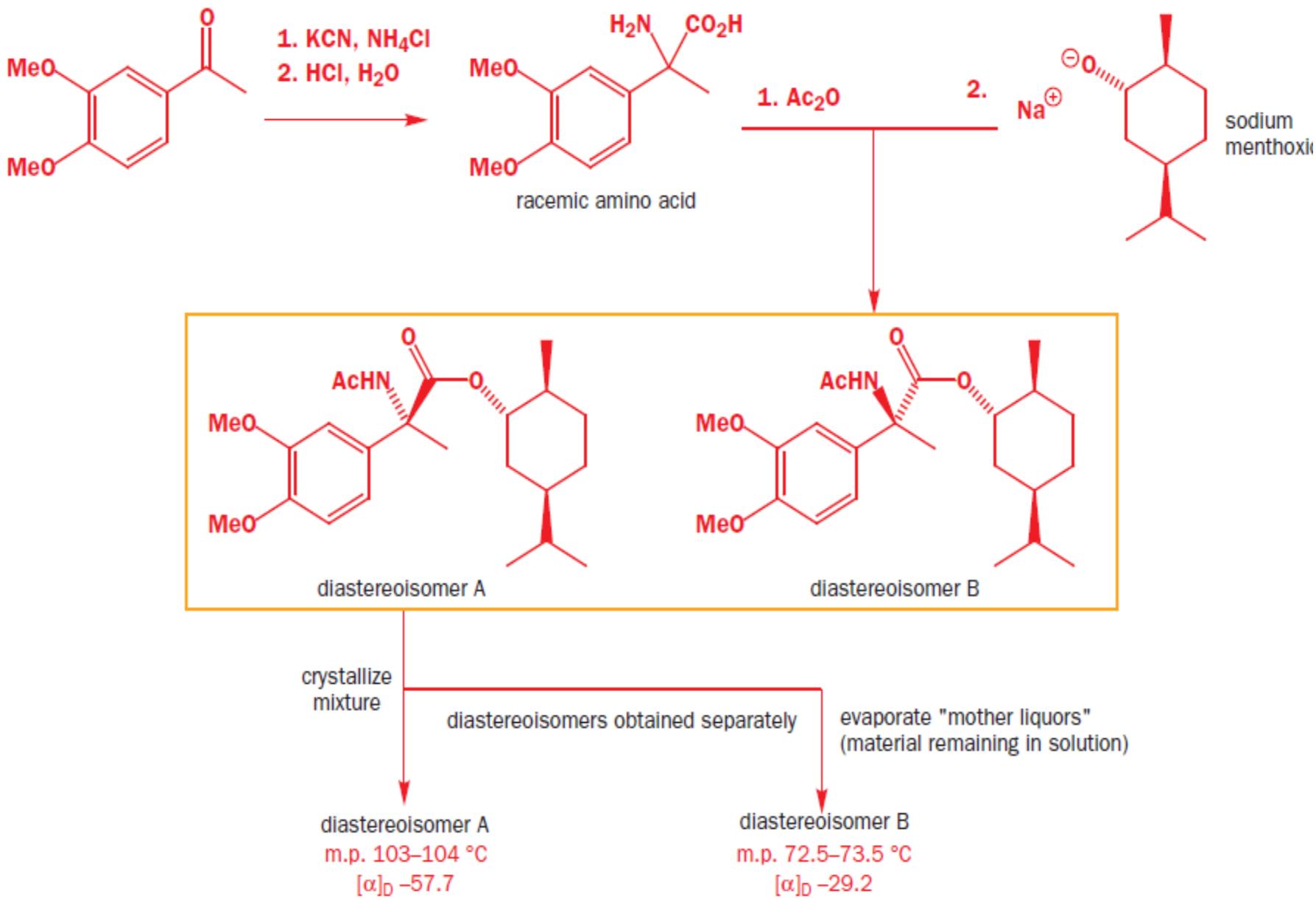
Resolution of Enantiomer: Separating enantiomers is called resolution

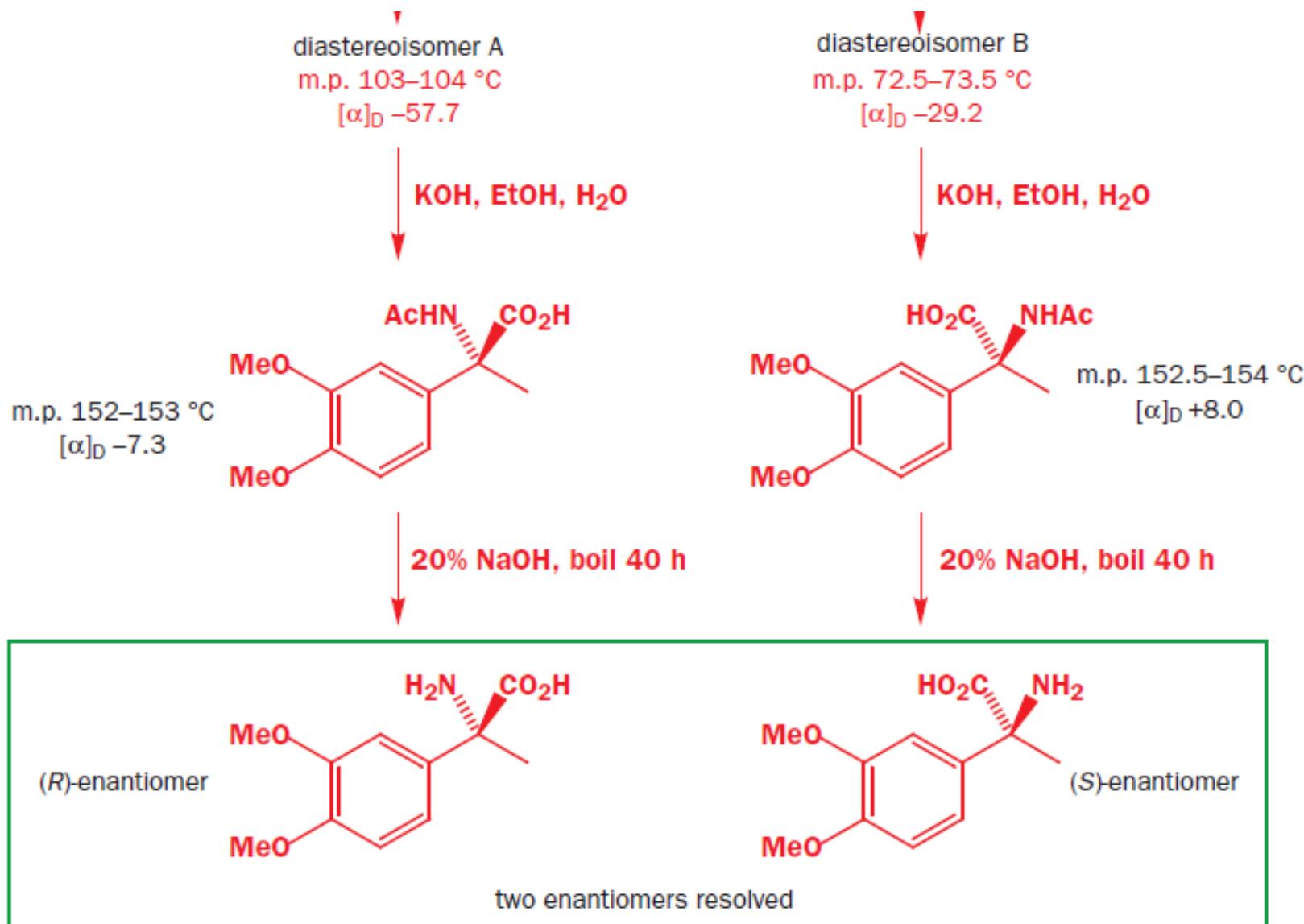


Example



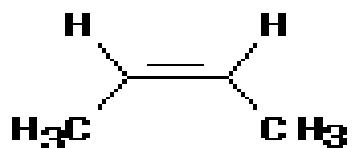
Example 2



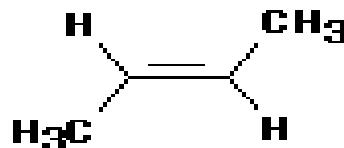


E/Z nomenclature

- IUPAC system for **naming** alkene isomers, called the **E-Z** system, is based on the same priority **rules**. The general strategy of the **E-Z** system is to analyze the two groups at each end of the double bond.
- Higher priority group at one end of the double bond and the higher priority group at the other end of the double bond are on the **same** side (**Z**, from German zusammen = together) or on **opposite** sides (**E**, from German entgegen = opposite) of the double bond.

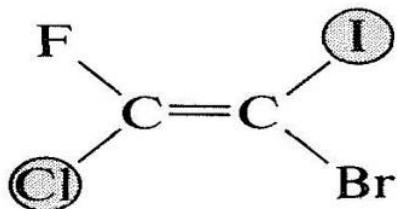


cis-2-butene
(Z)-2-butene

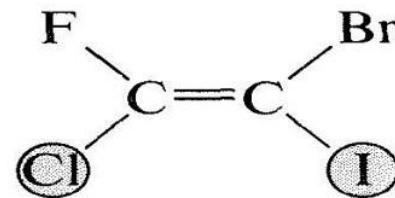


trans-2-butene
(E)-2-butene

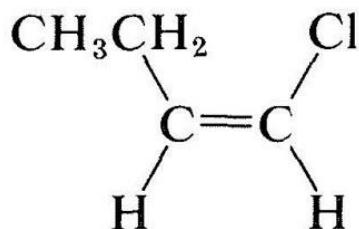
- Ex:



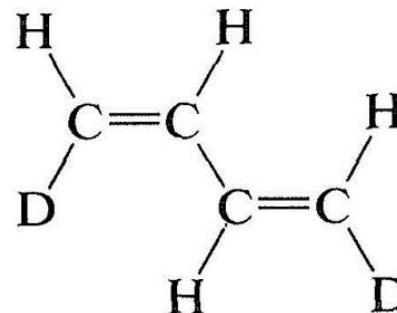
priority groups
on opposite sides
E configuration



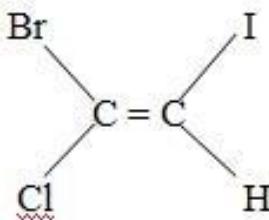
priority groups
on same side
Z configuration



(*Z*)-1-chloro-1-butene

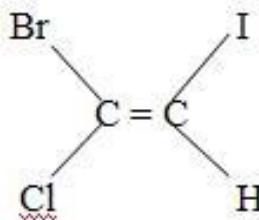


(*1Z,3E*)-1,3-butadiene-1,4-*d*₂



Z form

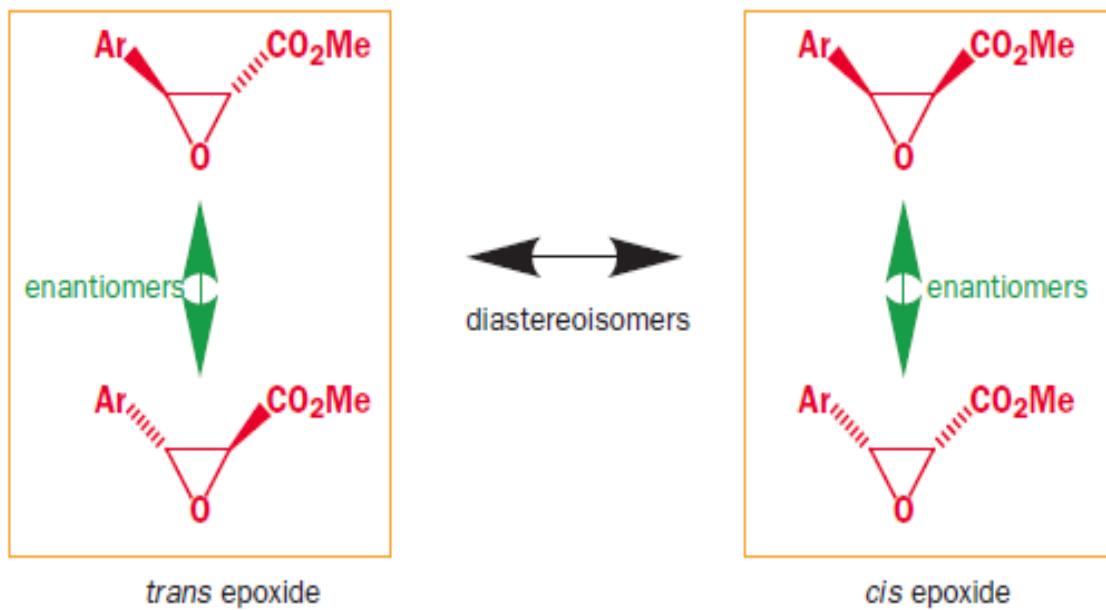
$\text{Br} > \text{Cl}$
 $\text{I} > \text{H}$



E- form

Diastereoisomers

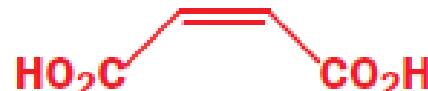
- **Diastereoisomers are stereoisomers that are not mirror images.**
Two diastereoisomers are different compound, and have different relative stereochemistry.
- Diastereoisomers may be achiral or chiral.
- Diastereoisomers can arise when structures have more than one stereogenic center.



butenedioic acids



fumaric acid

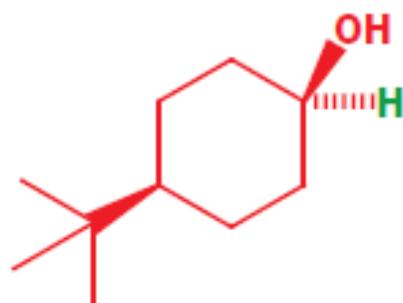


maleic acid

trans-butenedioic acid (fumaric acid)
m.p. 299–300 °C

cis-butenedioic acid (maleic acid)
m.p. 140–142 °C

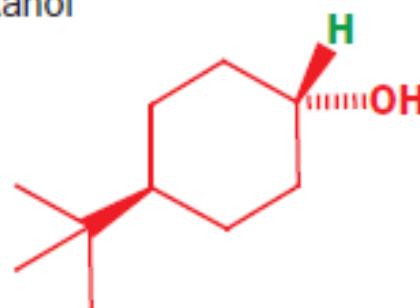
4-*t*-butylcyclohexanol



cis 4-*t*-butylcyclohexanol

mp 82–83 °C

¹H NMR: δ_H of green proton 4.02



trans 4-*t*-butylcyclohexanol

mp 80–81 °C

¹H NMR: δ_H of green proton 3.50

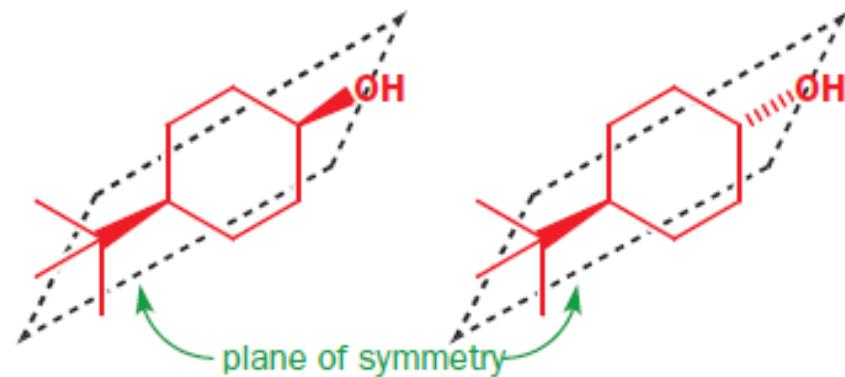
Diastereoisomers can be chiral or achiral

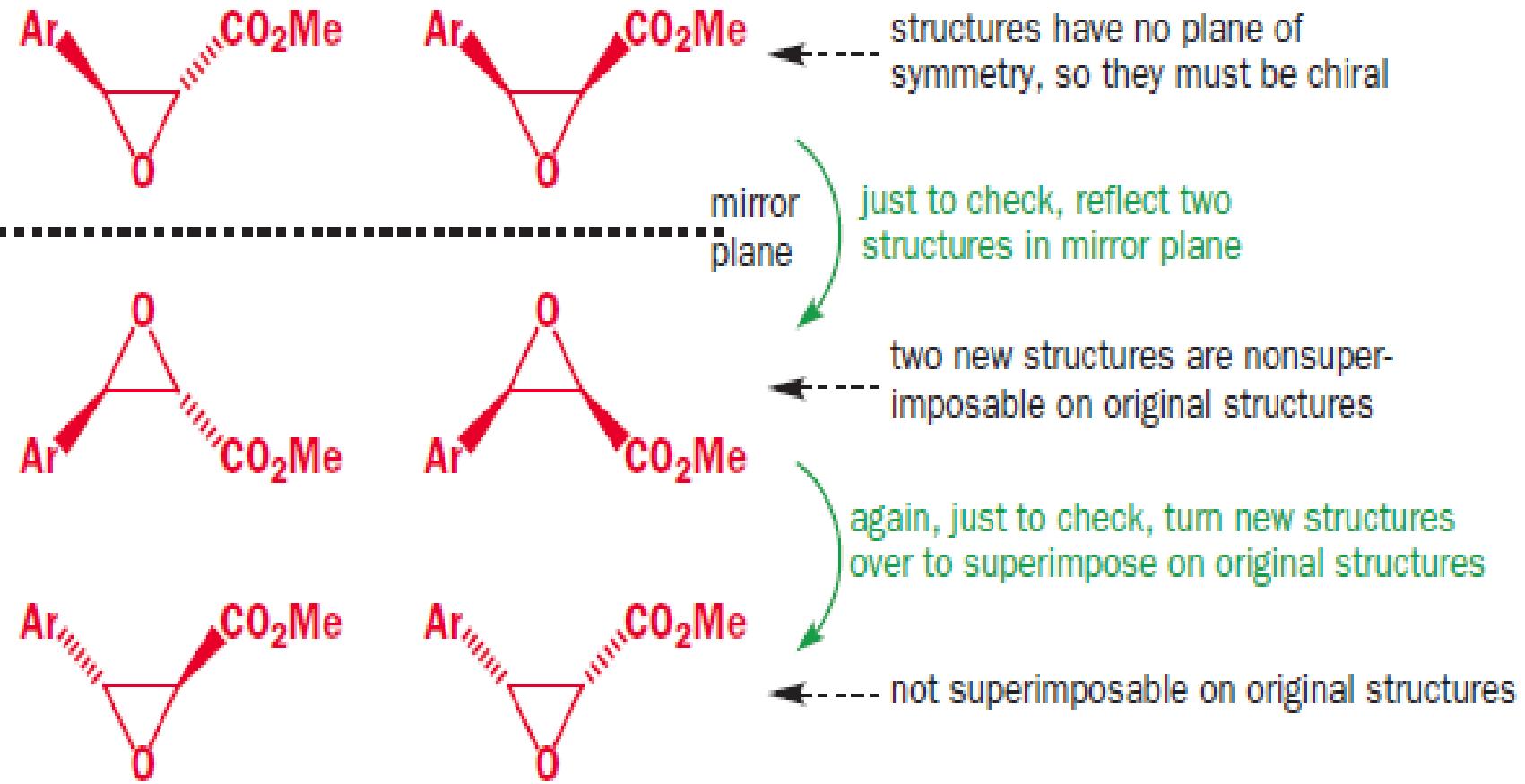


fumaric acid

maleic acid

plane of symmetry in plane of page





- The above pair of diastereoisomers are chiral because they don't have plane of symmetry.

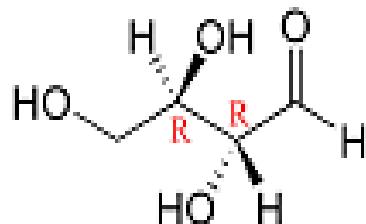
Converting enantiomers and diastereoisomers

- To go from one enantiomer to another both steriogenic centers are inverted.
- To go from one diastereoisomers to another only one of the two is inverted.

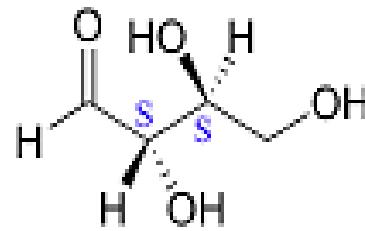


Examples

enantiomers

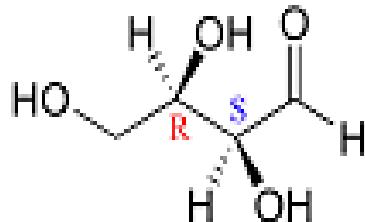


D-erythroose

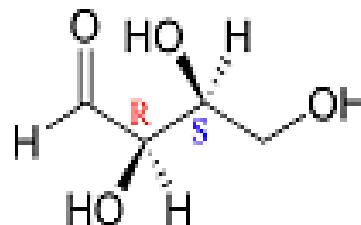


L-erythrose

diastereomers



D-threose

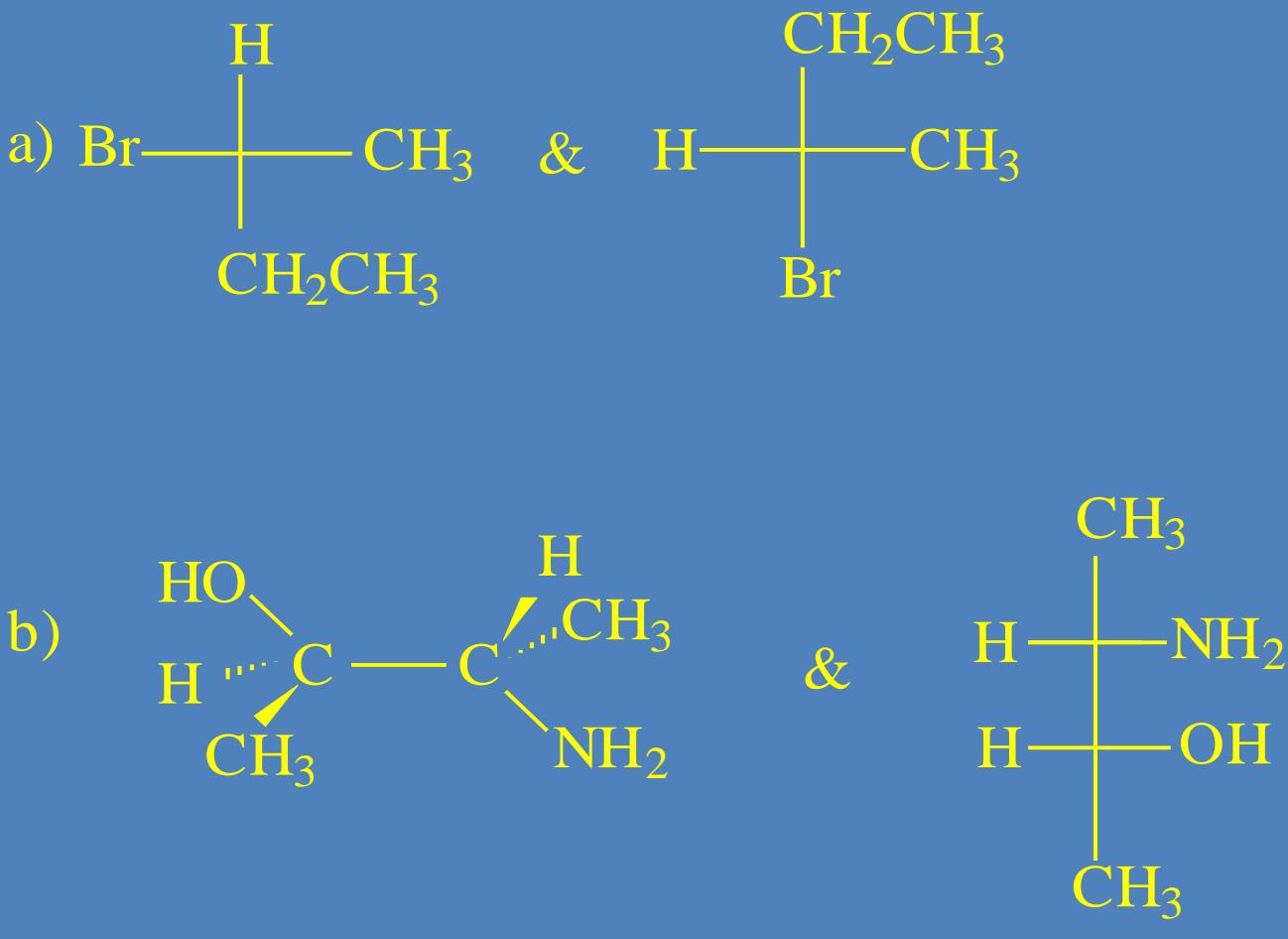


L-threose

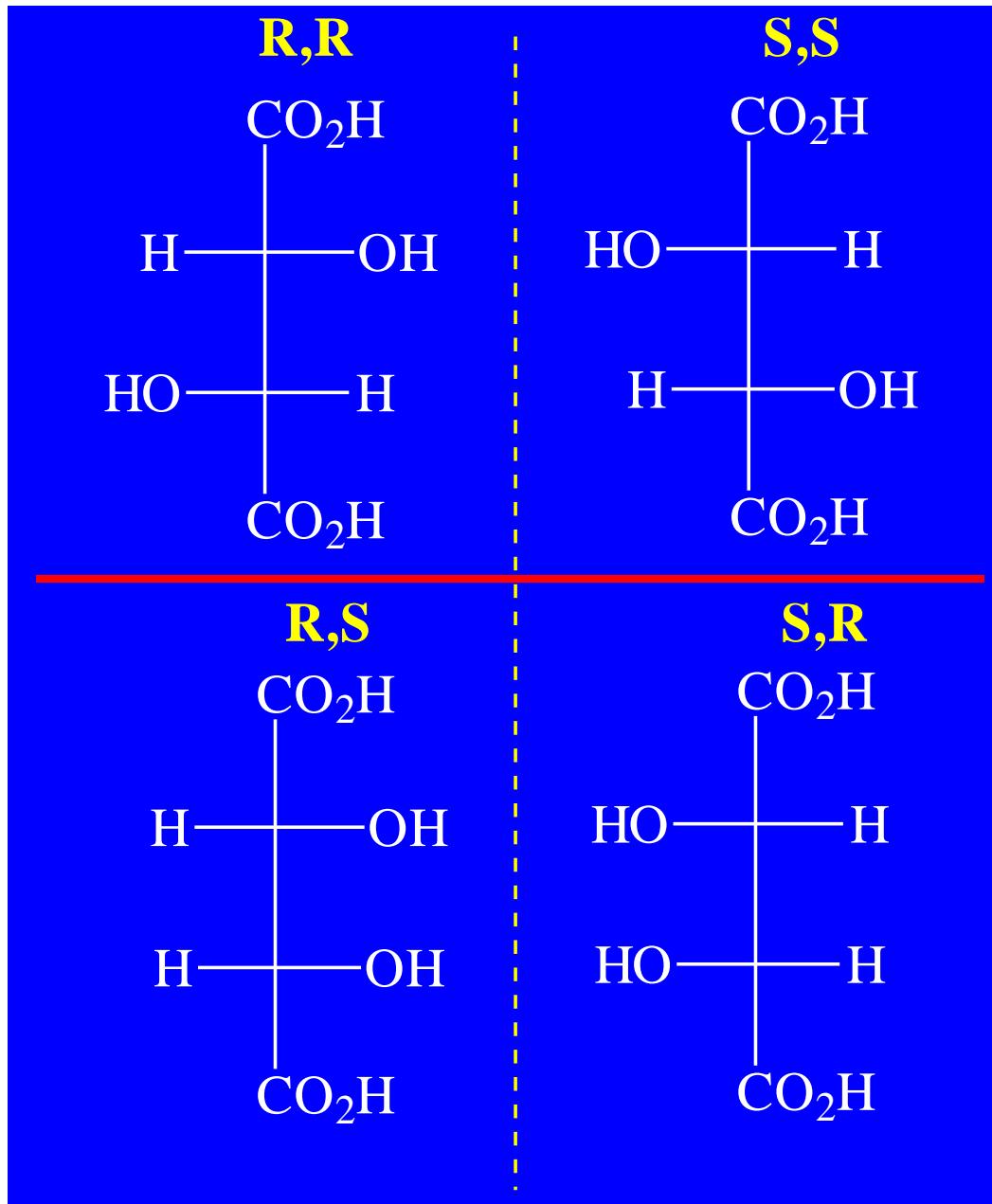
enantiomers

diastereomers

Identical, Enantiomers or Diastereomers?



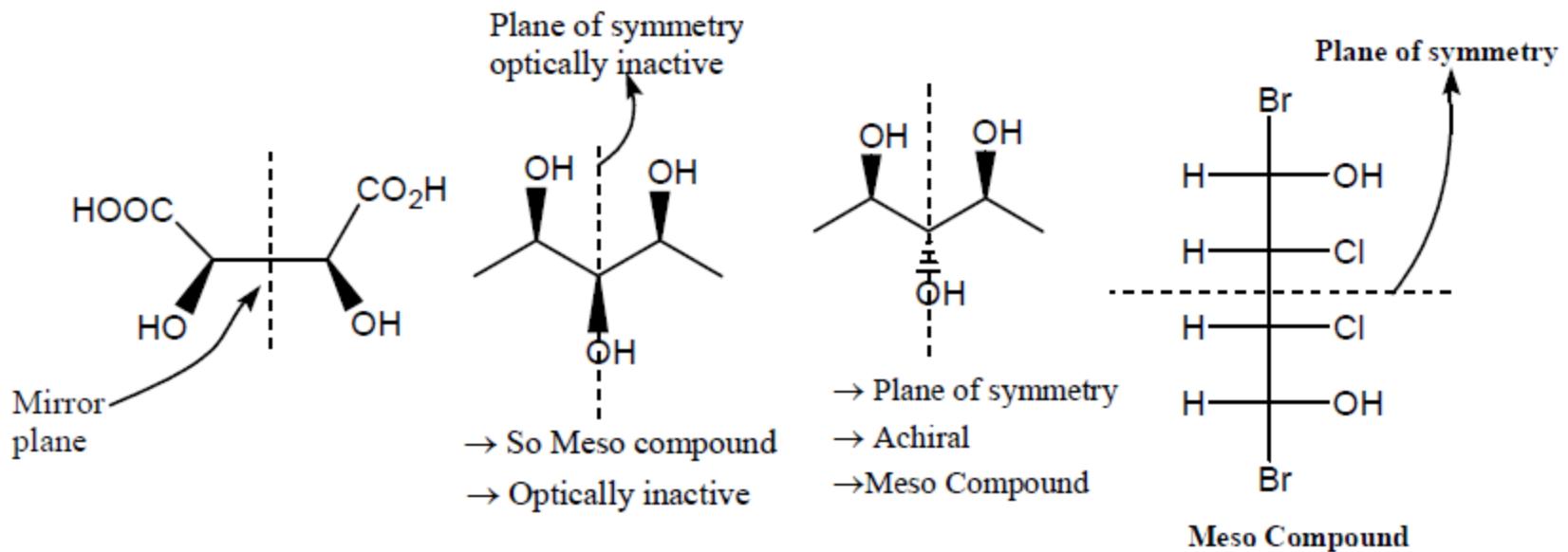
Tartaric Acids



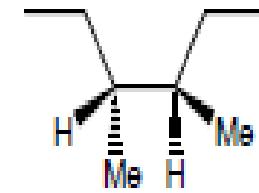
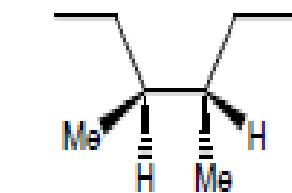
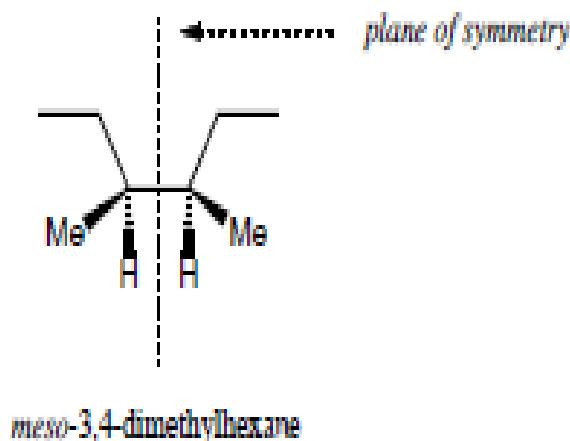
Meso compound

- Compounds that contain stereogenic center but achiral are called Meso compound.

For example:



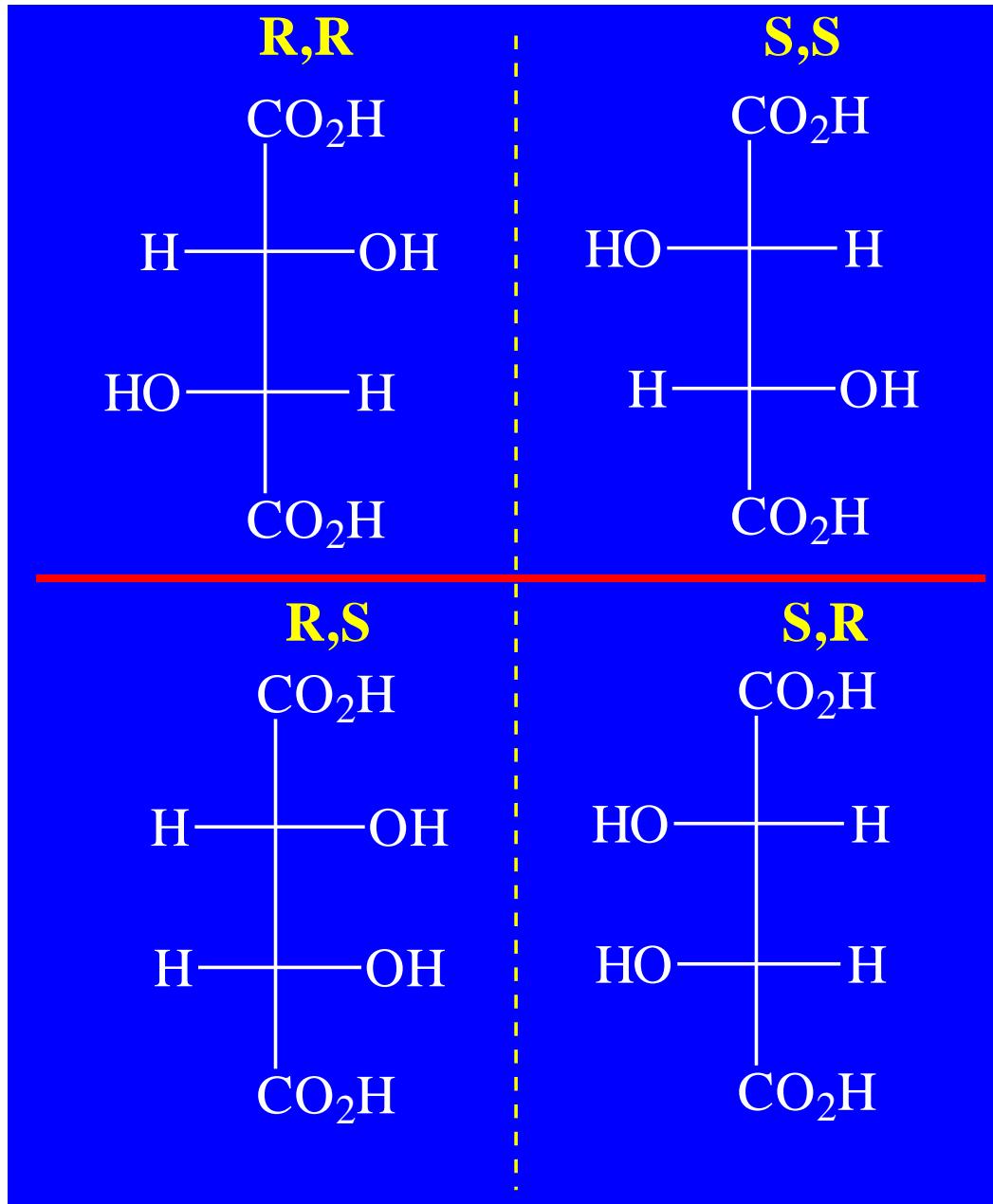
- The best way to identify a meso compound is to prove that it is superimposable with its mirror image. However, a quick test is to see if it contains a plane of symmetry:



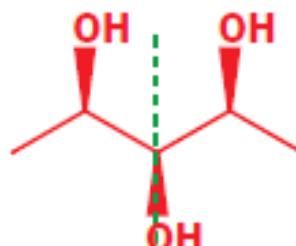
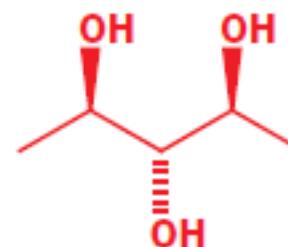
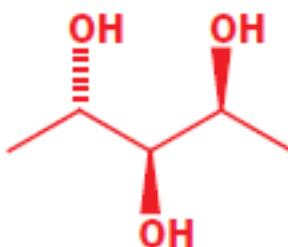
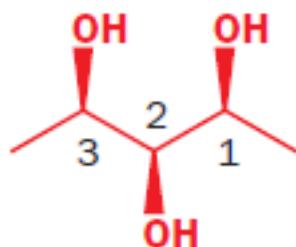
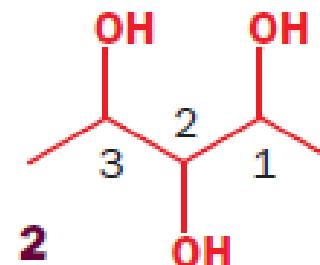
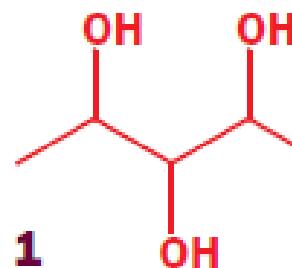
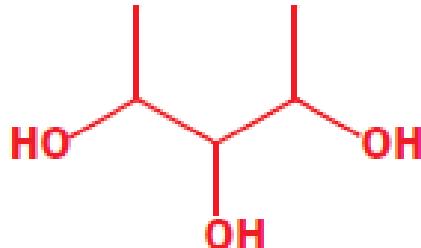
Compounds containing a plane of symmetry are achiral!

No plane of symmetry

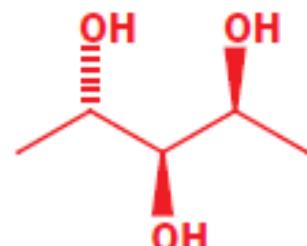
Tartaric Acids



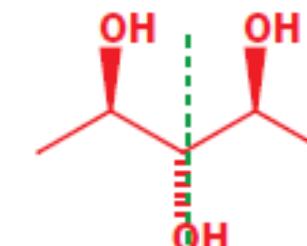
Investigating the stereochemistry of a compound



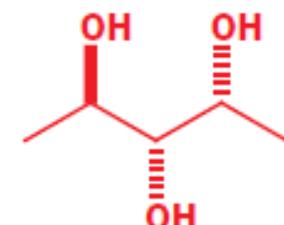
plane of symmetry
achiral (*meso*)



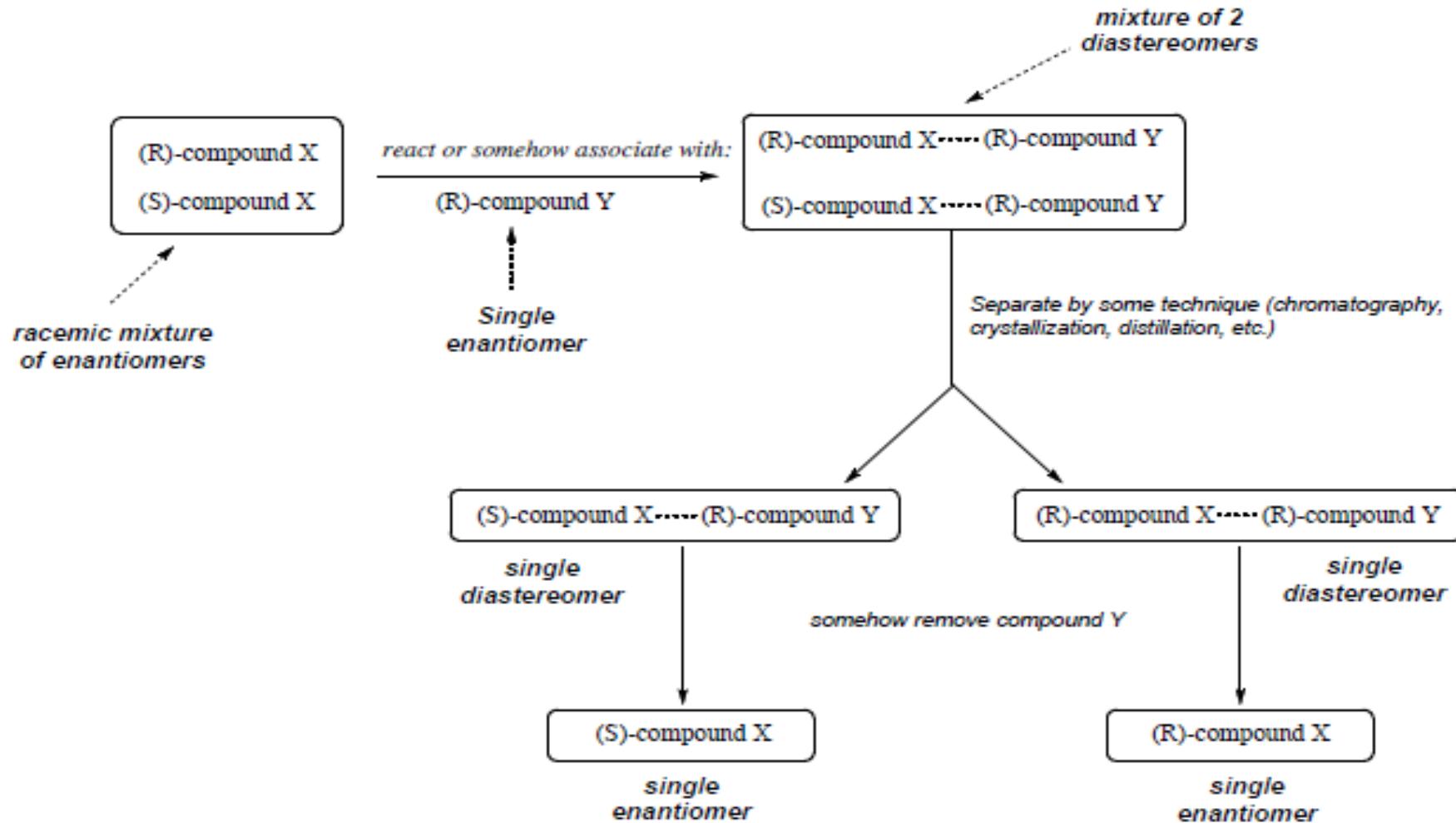
chiral



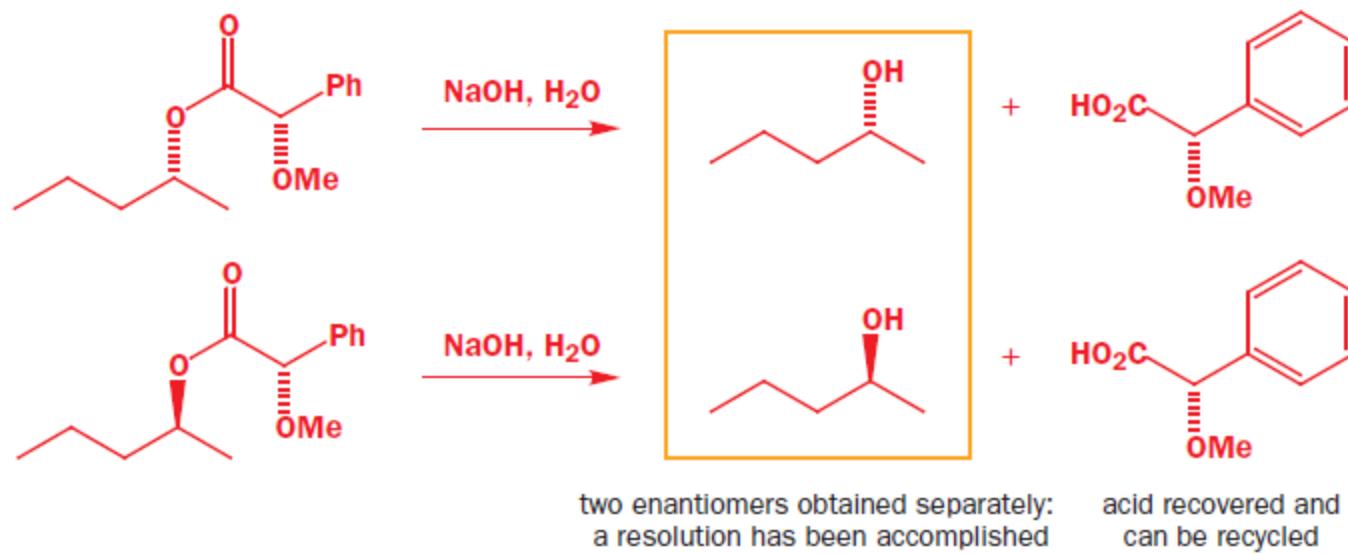
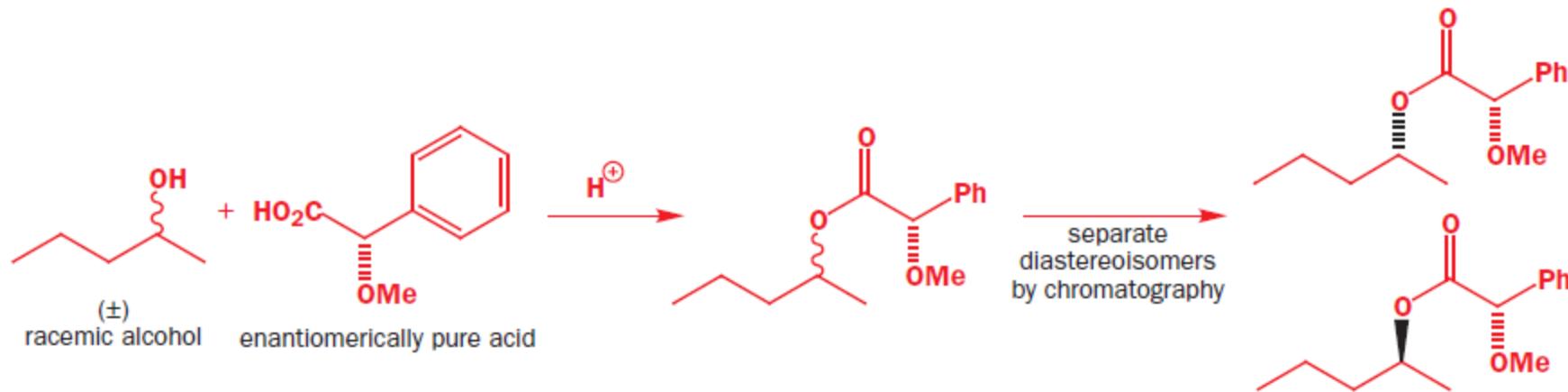
plane of symmetry
achiral (*meso*)



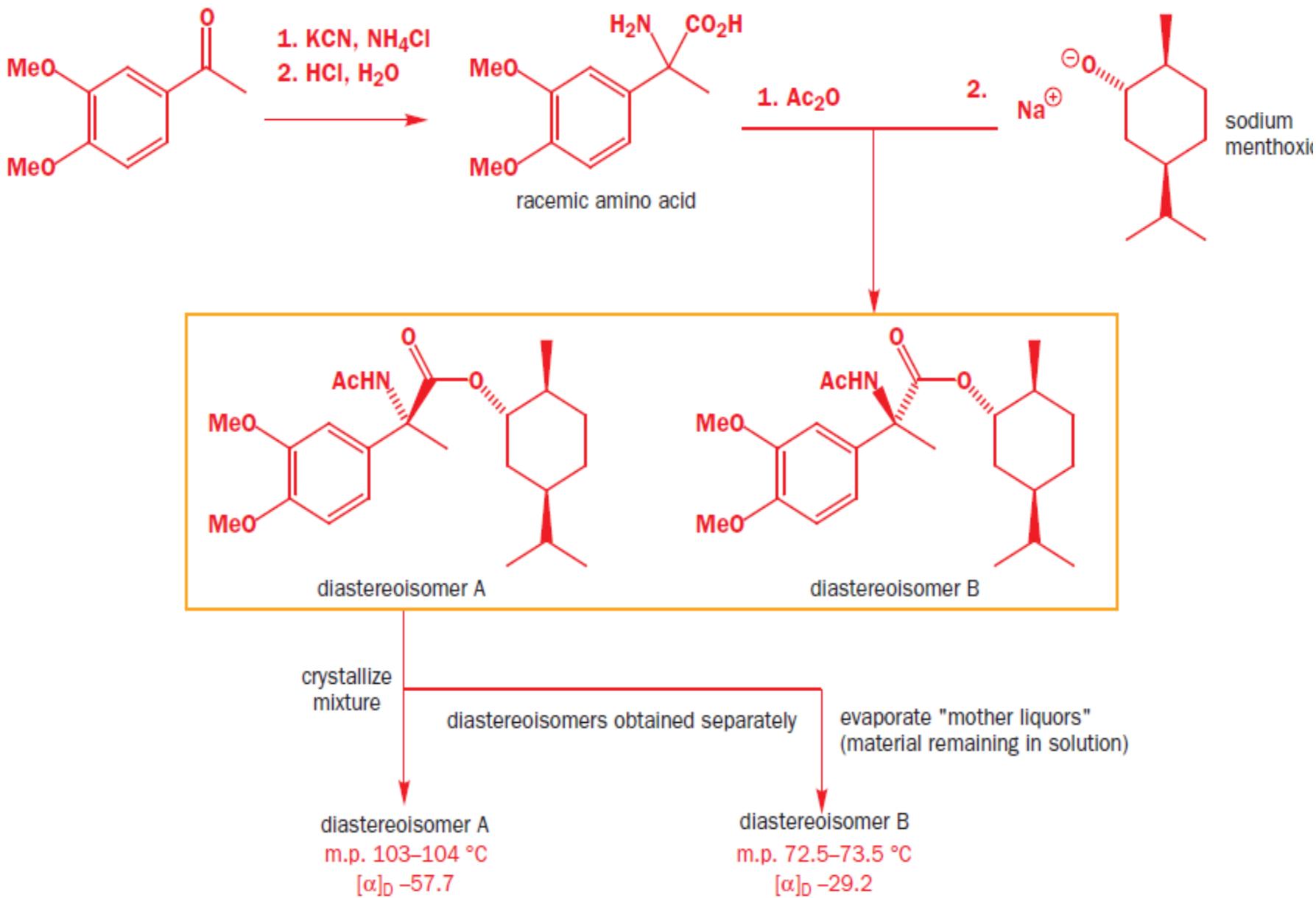
Resolution of Enantiomer: Separating enantiomers is called resolution

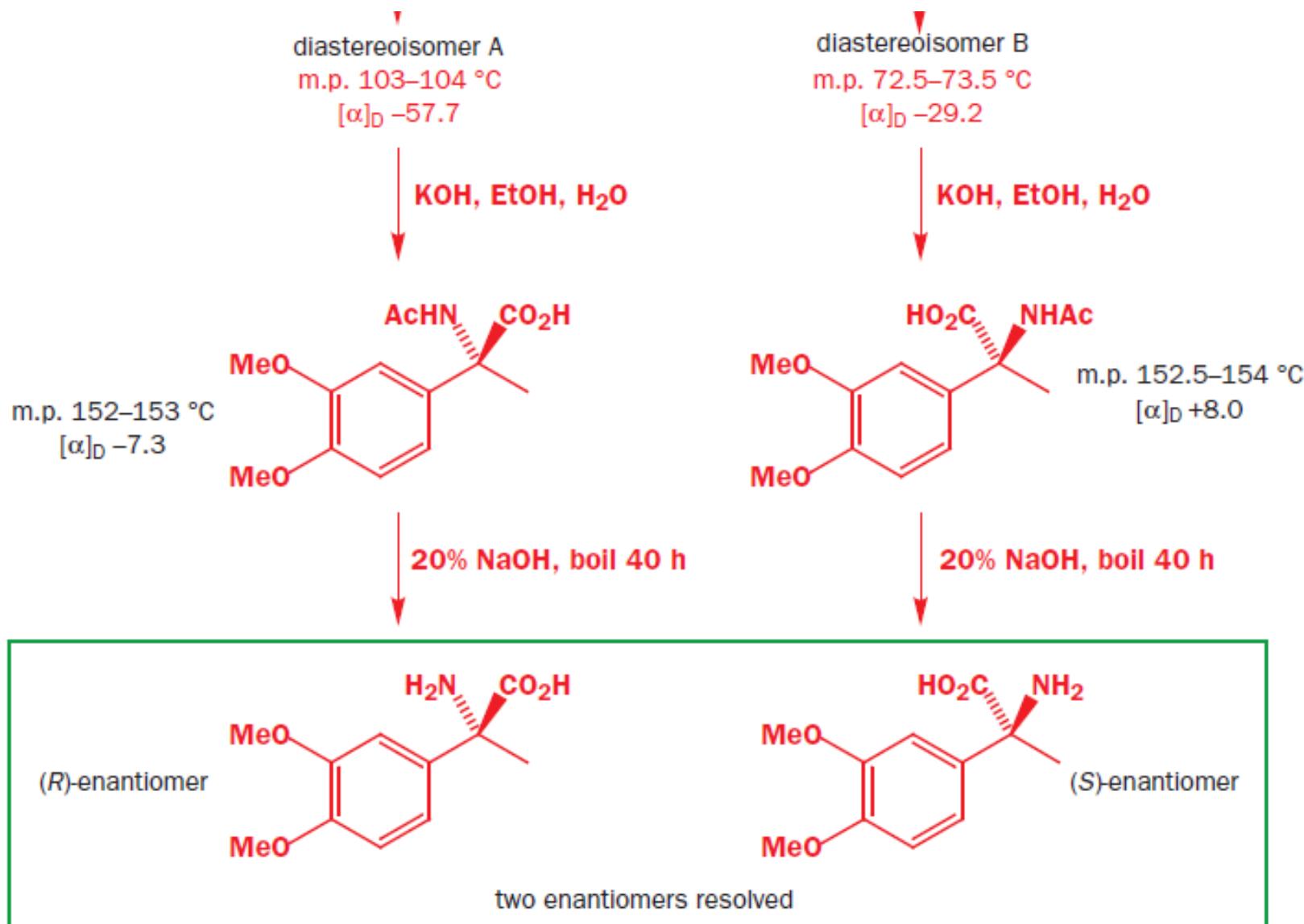


Example



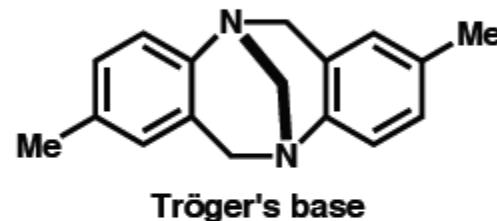
Example 2



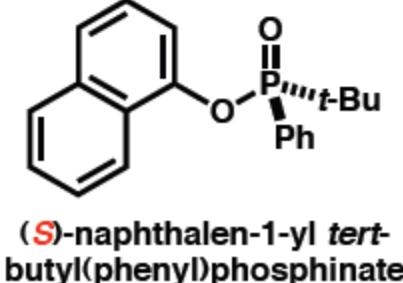
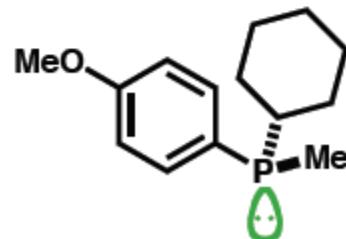
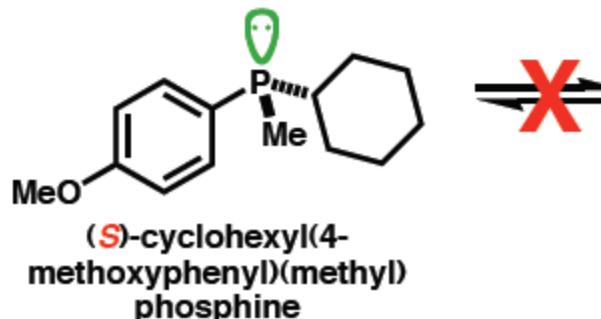


Central chirality at elements other than carbon

- Any tetrahedral or pyramidal atom with four (three) different substituents can be chiral
- Nitrogen / amines have the potential to be chiral...
- But rapid **pyramidal inversion** normally **prevents** isolation of either enantiomer
- If substituents are **constrained in a ring** then rigid structure prevents inversion

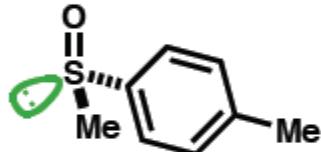


- Trigonal pyramidal phosphorus(III) is configurationally stable below 200°C
- Tetrahedral phosphorus (V) is configurationally stable

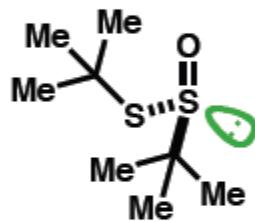


Central chirality at elements other than carbon II

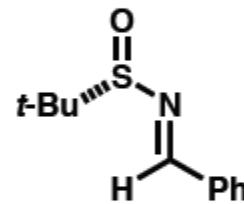
- Sulfoxides are tetrahedral; remember they have a lone pair!
- Configurationally stable at room temperature
- Certain anions (Cl^-) can cause racemisation (interconversion of the enantiomers)



(*R*)-1-methyl-4-(methylsulfinyl)benzene



(*R*)-S-tert-butyl 2-methylpropane-2-sulfinothioate



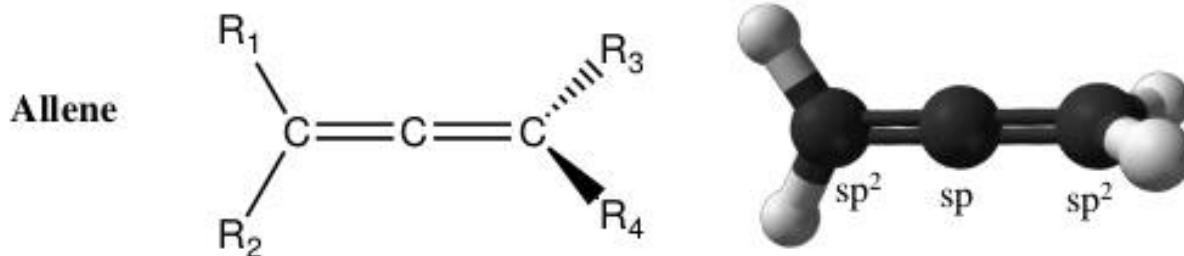
(*S*)-N-benzylidene-2-methylpropane-2-sulfinamide

- It should be stressed that the definition of a chiral compound is that it **cannot be superimposed upon its mirror image**
- A stereogenic centre (central chirality) is sufficient for the existence of chirality BUT **it is not a requirement**
- Furthermore, as we shall see, a compound can have a stereogenic centre BUT be **achiral**

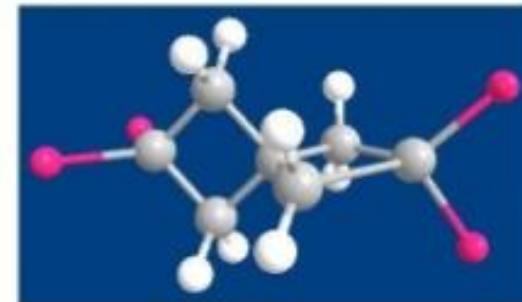
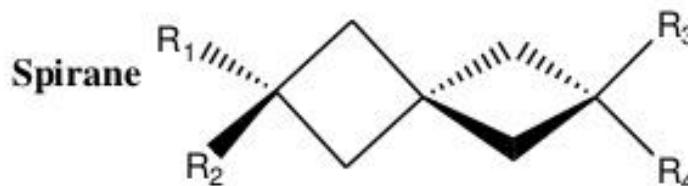
Chiral compounds with no stereogenic centres: Axial Chirality, Planar chirality and Helicity

AXIAL CHIRALITY: Nonplanar arrangement of four groups around an axis

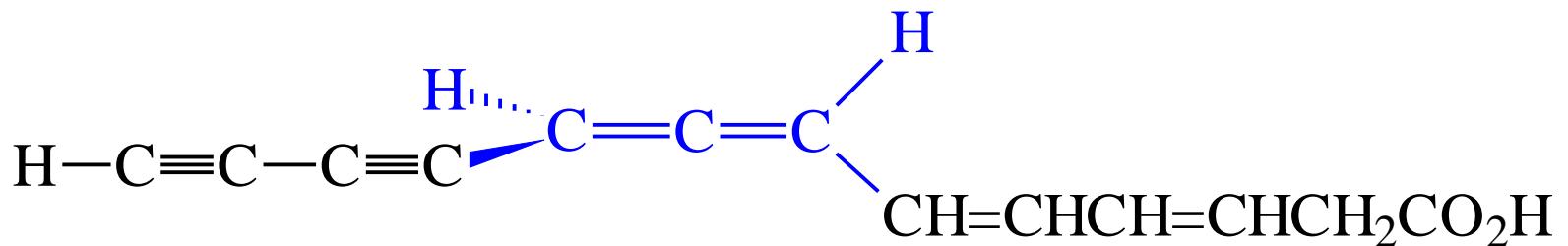
Molecules can be chiral even without stereocenters (we mentioned that stereocenters are not necessary). Axial Chirality and Planar Chirality.



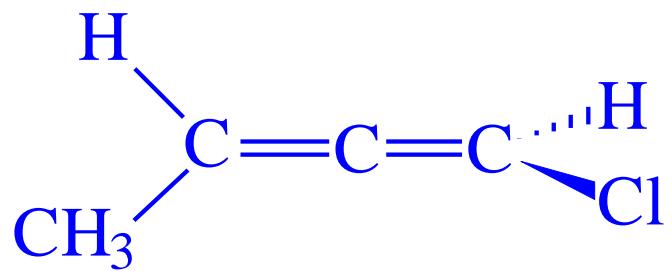
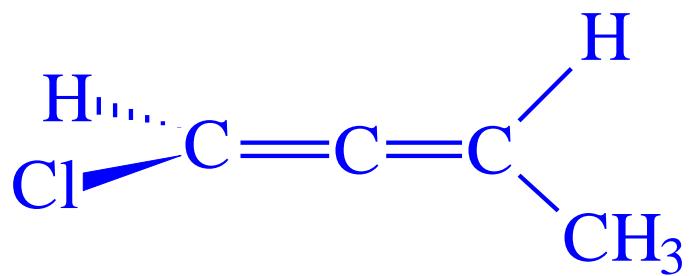
In specific thermodynamic conditions, these show activity of chiral molecule. But, in high temperature, high pressure, energetic barrier of movement around double-bond decreases and there is no chiral molecule activity shown.

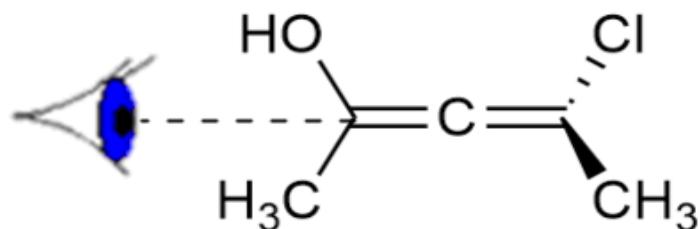


Mycomycin, an antibiotic

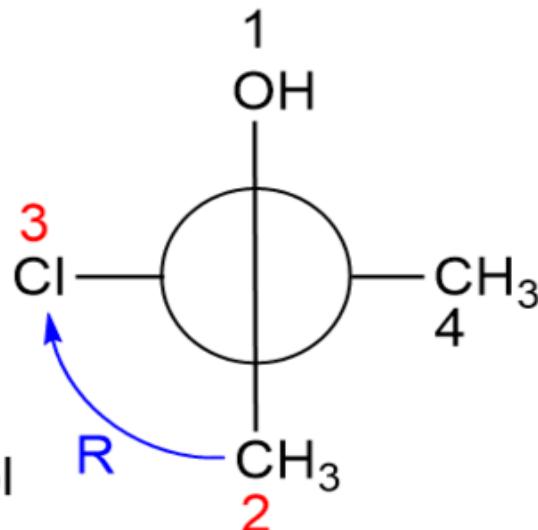


Nocardia acidophilus $[\alpha]^D = -130^\circ$

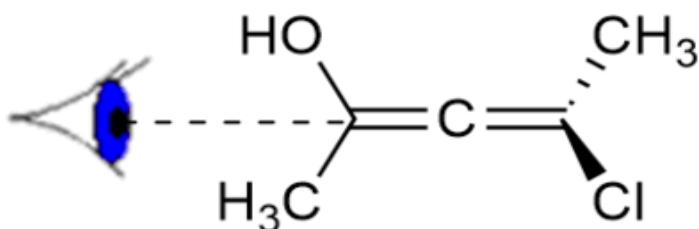




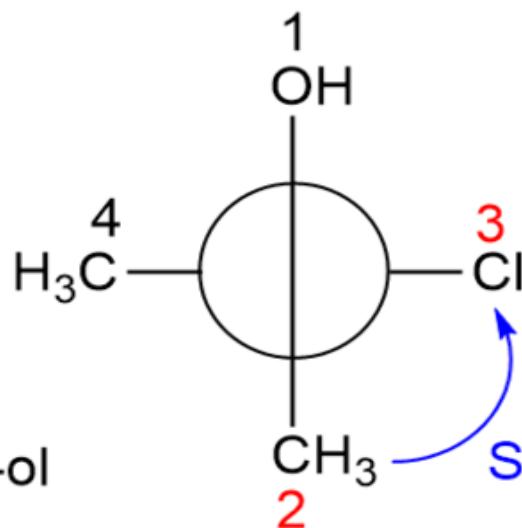
(*R*)-4-chloropenta-2,3-dien-2-ol



Clockwise = (*R*)



(*S*)-4-chloropenta-2,3-dien-2-ol

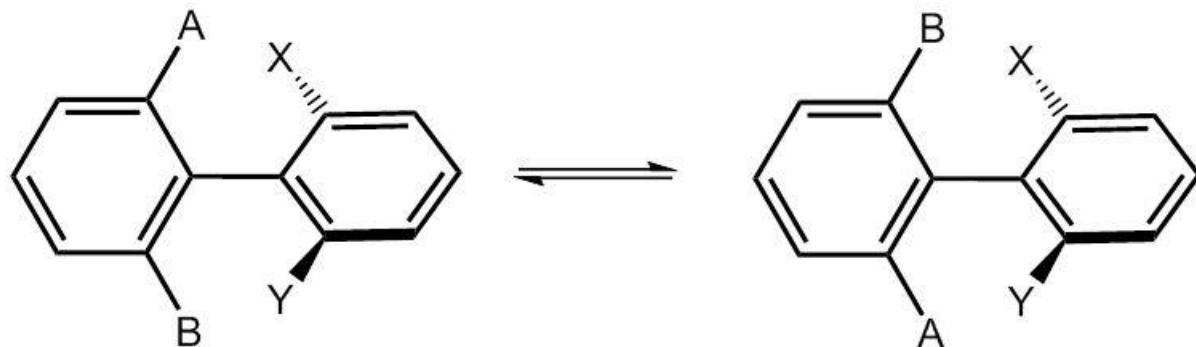


Anti-Clockwise = (*S*)

Atropisomers

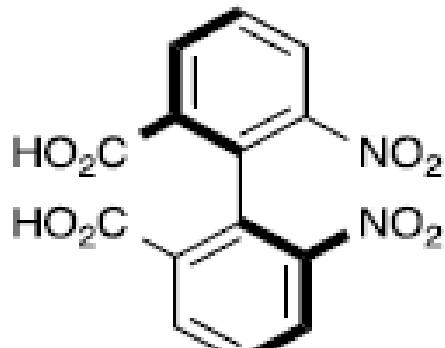
- Atropisomers are stereoisomers resulting from hindered rotation about single bonds where the steric strain barrier to rotation is high enough to allow for the isolation of the conformers (from Greek, *a* = not and *tropos* = turn).
- The name was introduced by Kuhn in 1933, but atropisomerism was first detected in 6,6'dinitro-2,2'-diphenic acid by Cristie in 1922.
- Atropisomers are detectable by NMR if half lives exceed 10-12 sec
- Atropisomers are isolable if the half-life is above 1000 sec.

In the appropriately substituted biphenyls,
rotation around the bond joining the rings is
restricted and the enantiomers can be isolated:

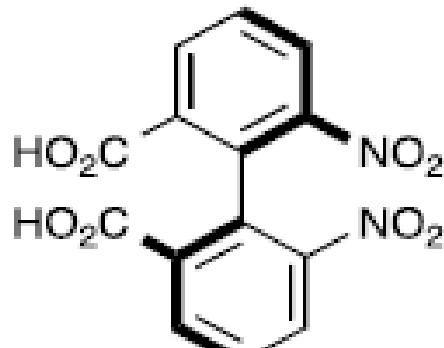


Conformational isomers that are stable, isolable
compounds are called **atropisomers**.

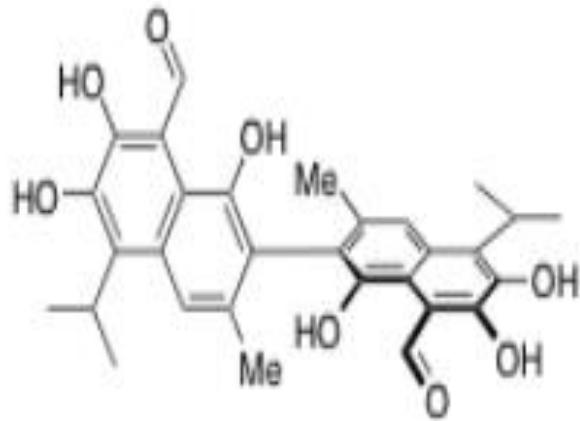
- Ex:-



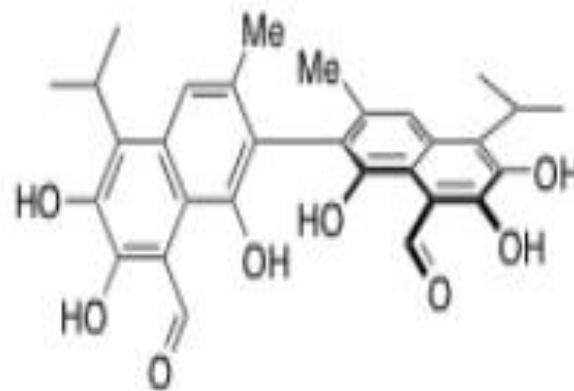
S



R

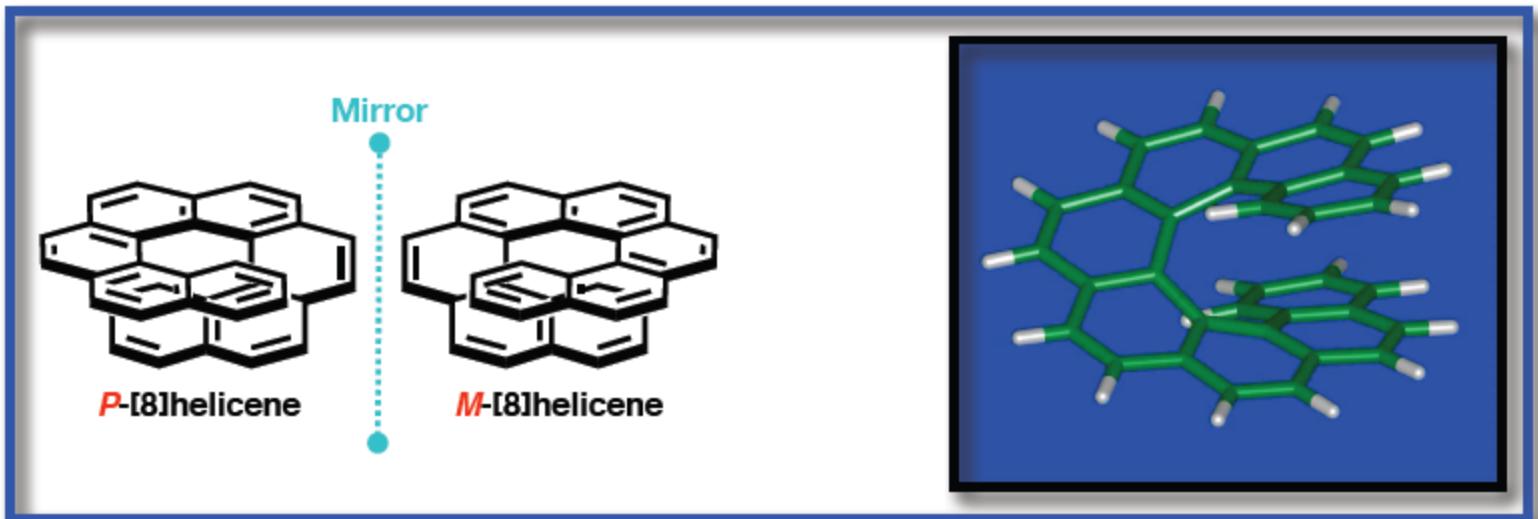


(*S*)-gossypol

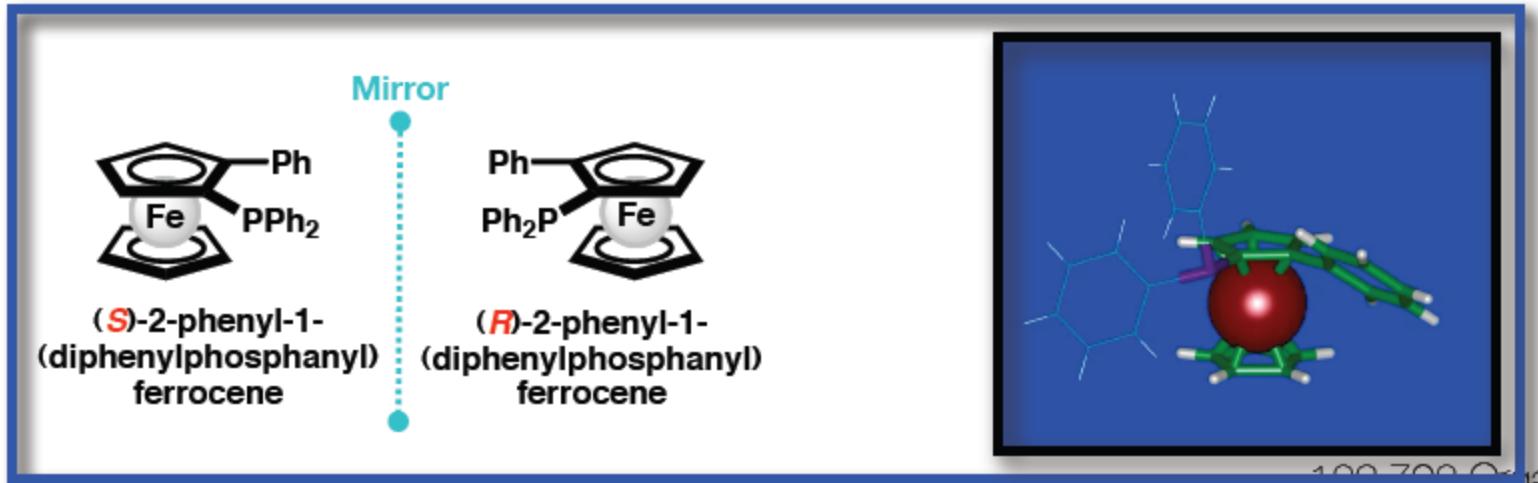


(*R*)-gossypol

- **Helical chirality** - molecules that twist (like a cork-screw)
- Right-handed helix is denoted *P* (clockwise as you travel away from viewer)



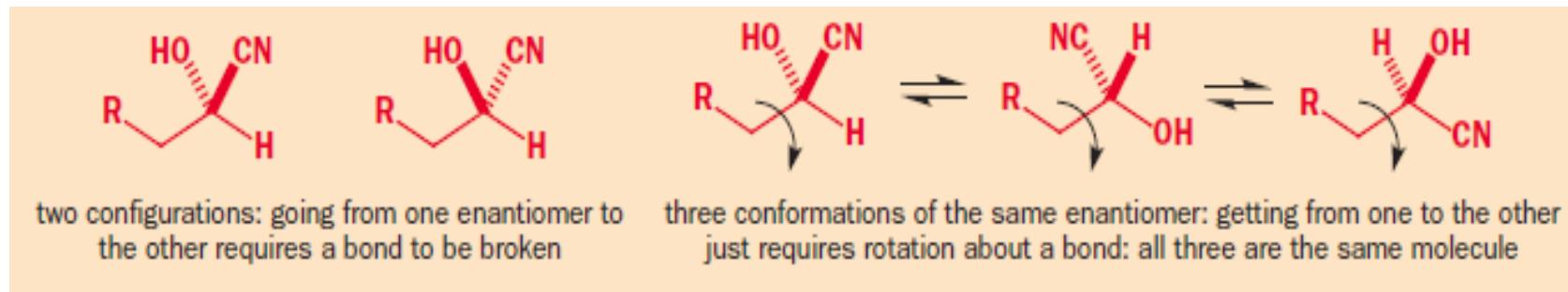
- **Planar chirality** - chirality resulting from the arrangement of out-of-plane groups with respect to a plane

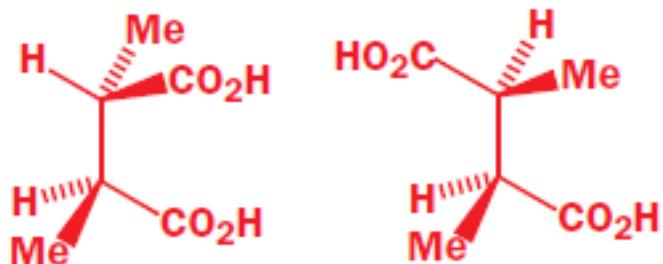


Conformational isomerism

Configuration and conformation

- Changing the *configuration* of molecule always means that bonds are broken
- A different *configuration* is a different molecule.
- Changing the conformation of molecule means rotating about bonds, but not breaking them.
- Conformation of molecule are readily interconvertible, and are all the same molecule.

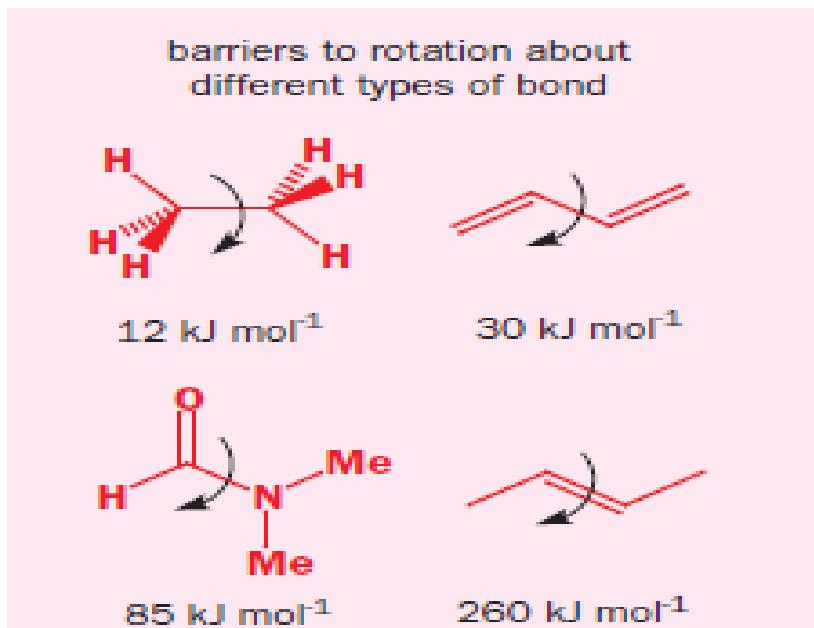




● Rotation or bond breaking?

- Structures that can be interconverted simply by rotation about single bonds are **conformations** of the same molecule
- Structures that can be interconverted only by breaking one or more bonds have different **configurations**, and are stereoisomers

Barriers to rotation



The energy barrier to the rotation about the C–N bond in an amide is usually about 80 kJ mol^{-1} , rate of about 0.1 s^{-1} at 20°C . Rotation about single bonds is much faster than this at room temperature, but there is nonetheless a barrier to rotation in ethane, for example, of about 12 kJ mol^{-1} .

Rates and barriers

It can be useful to remember some simple guidelines to the way in which energy barriers relate to rates of rotation. For example:

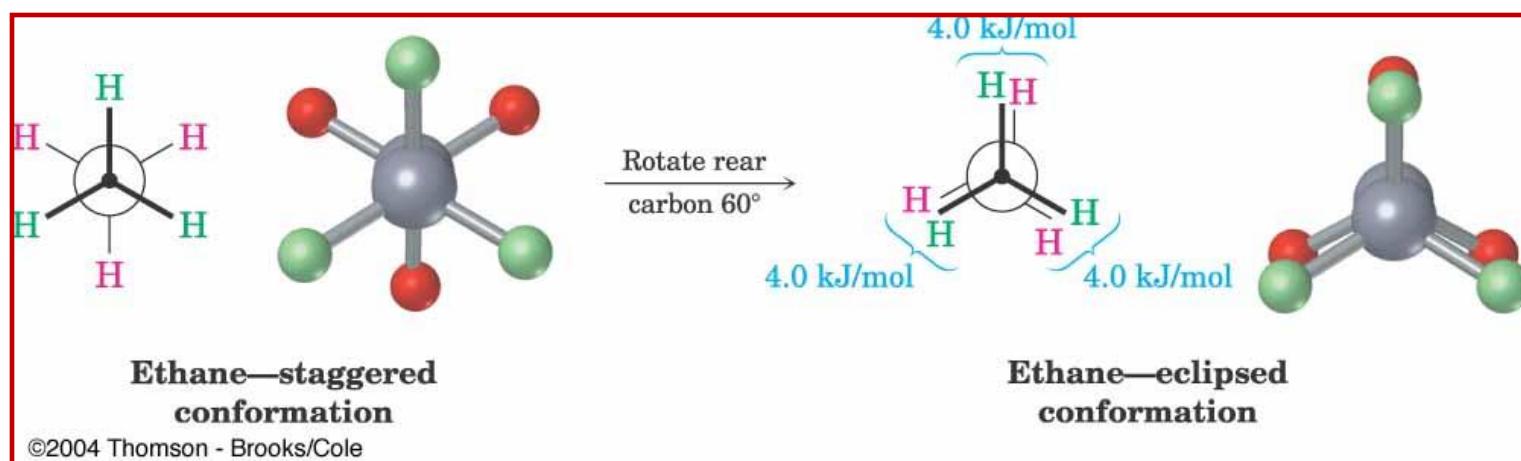
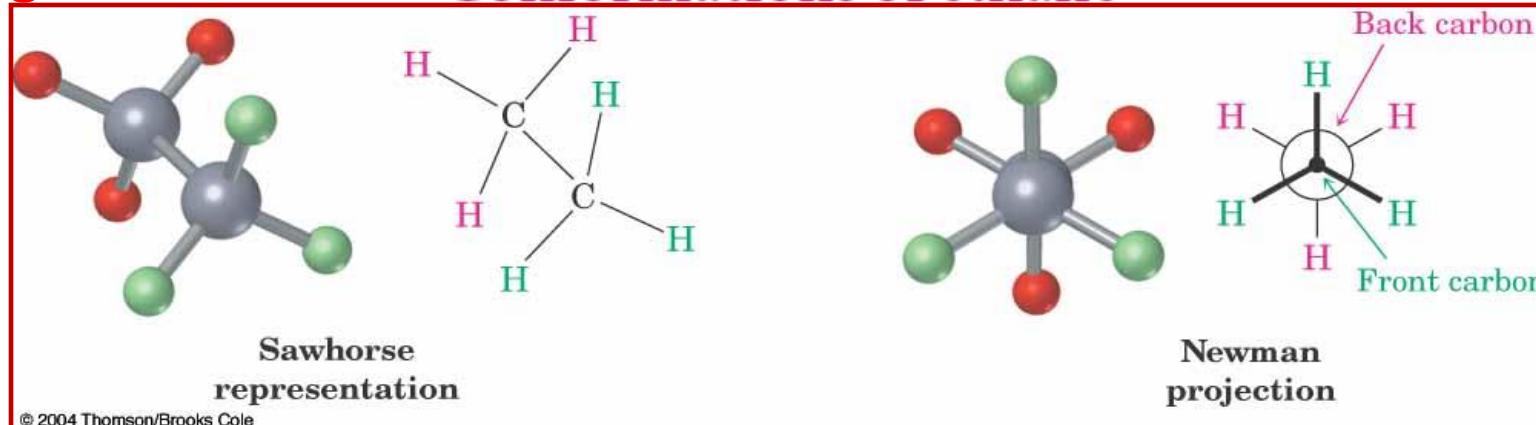
- A barrier of 73 kJ mol^{-1} allows one rotation every second at 25°C (that is, the rate is 1 s^{-1})
- Every 6 kJ mol^{-1} changes the rate at 25°C by about a factor of 10
- To see signals in an NMR spectrum for two different conformations, they must interconvert no faster than

(very roughly) 1000 s^{-1} —a barrier of about 55 kJ mol^{-1} at 25°C . This is why NMR shows two methyl signals for DMF, but only one set of signals for butadiene. See p. 000 for more on this

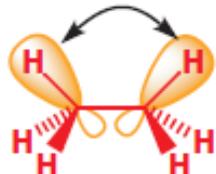
- For conformations to interconvert slowly enough for them to exist as different compounds, the barrier must be over 100 kJ mol^{-1} . The barrier to rotation about a C=C double bond is 260 kJ mol^{-1} —which is why we can separate *E* and *Z* isomers

Why should there be an energy barrier in the rotation about a single bond?

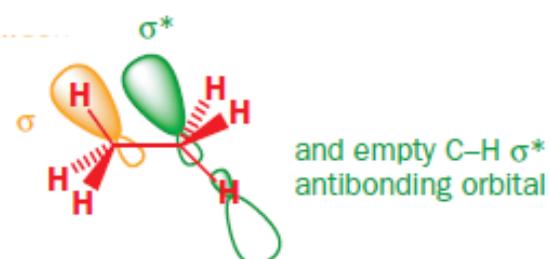
Conformations of ethane



eclipsed:
filled orbitals repel



staggered:
stabilizing interaction between
filled C-H σ bond...



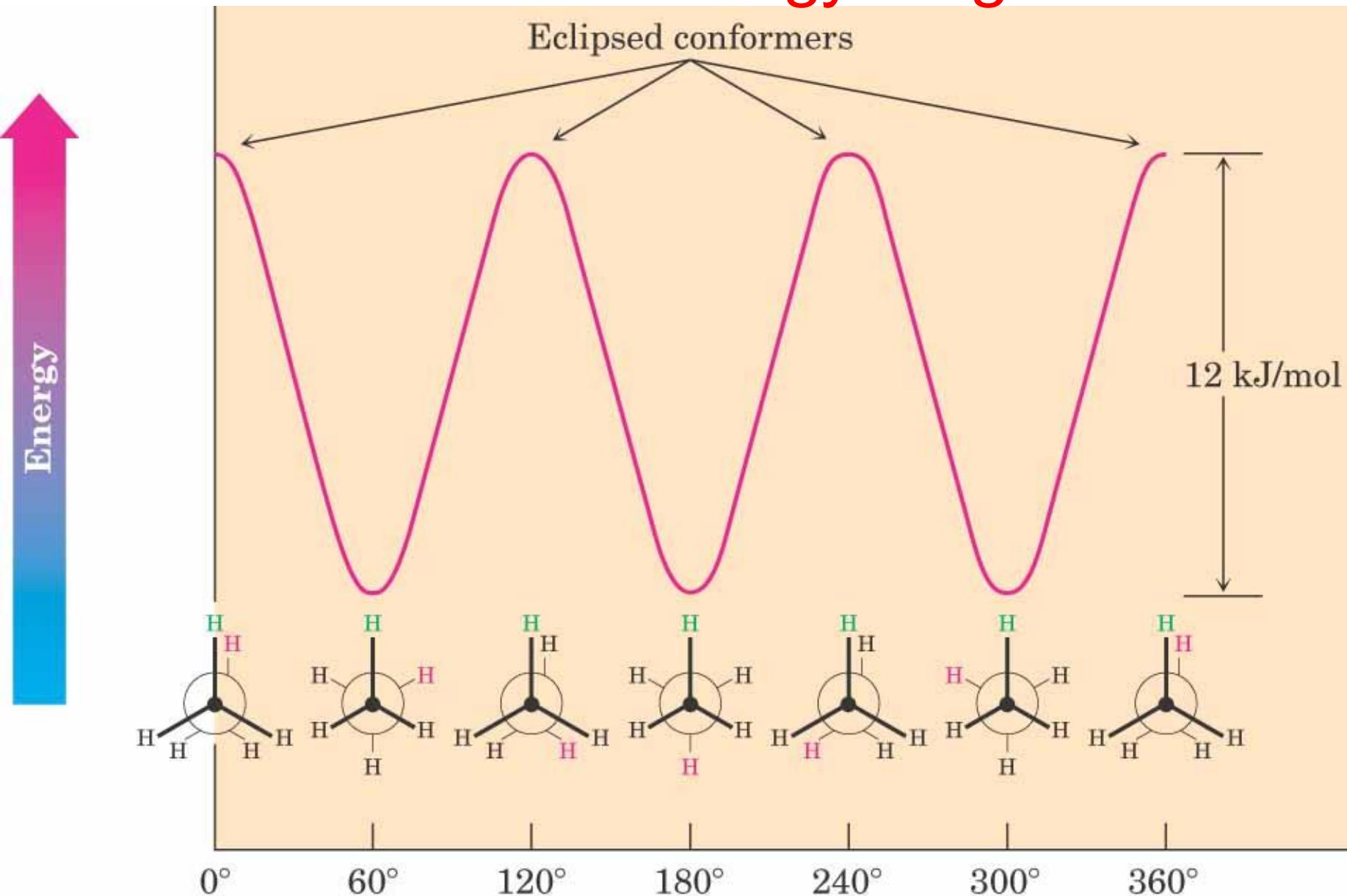
Definitions

- **Conformations** - Different spatial arrangements that a molecule can adopt due to rotation about sigma bonds.
- **Staggered** - A low energy conformation where the bonds on adjacent atoms bisect each other (60° dihedral angle), maximizing the separation.
- **Eclipsed** - A high energy conformation where the bonds on adjacent atoms are aligned with each other (0° dihedral angle).

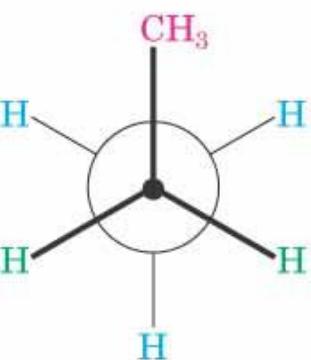
Types of strain

- **Steric Strain**- Destabilization due to the repulsion between the electron clouds of atoms or groups. Groups try to occupy some common space.
- **Torsional Strain**- Destabilization due to the repulsion between pairs of bonds caused by the electrostatic repulsion of the electrons in the bonds. Groups are eclipsed.
- **Angle Strain** - Destabilisation due to distortion of a bond angle from it's optimum value caused by the electrostatic repulsion of the electrons in the bonds. e.g. cyclopropane

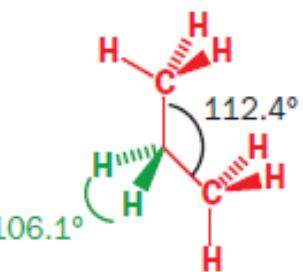
Potential Energy Diagram



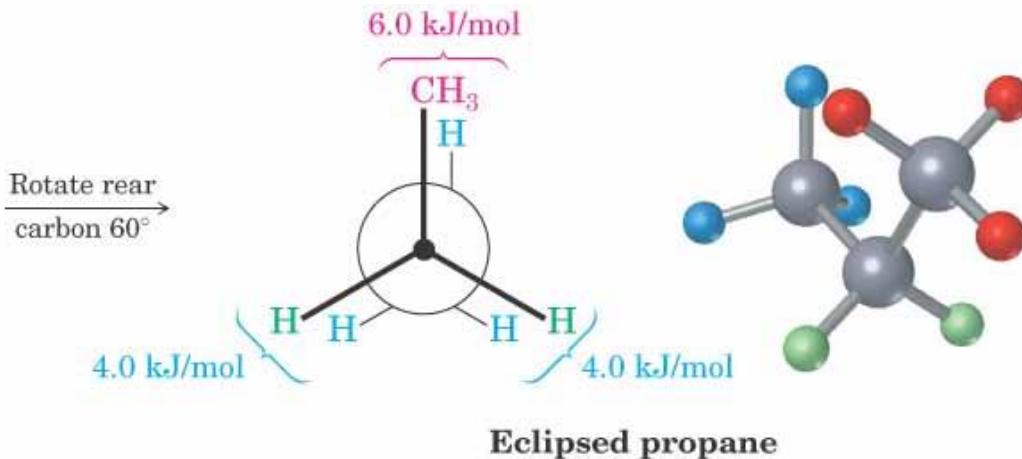
Conformations of propane



Staggered propane

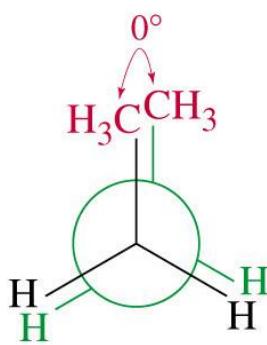
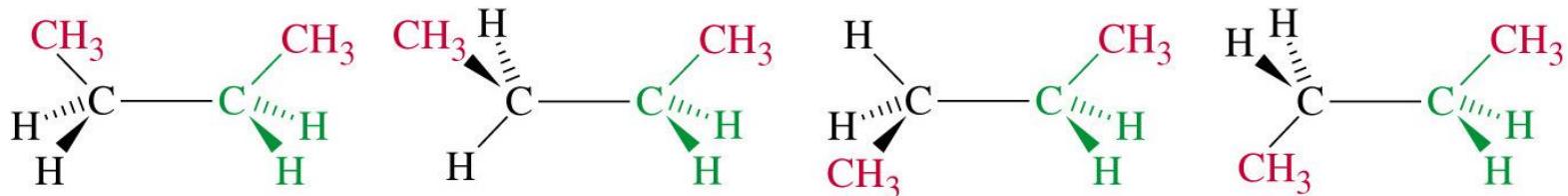


there is greater repulsion between two C-C bonds than between two C-H bonds

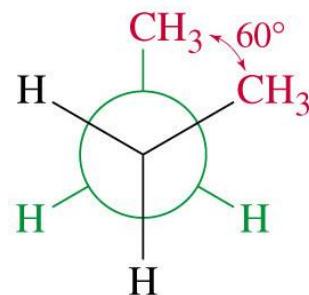


The rotational barrier is now slightly higher than for ethane: 14 kJ mol^{-1} as compared to 12 kJ mol^{-1} .

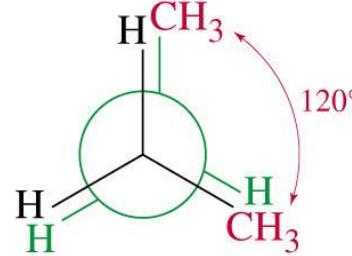
Butane Conformations (C_2-C_3)



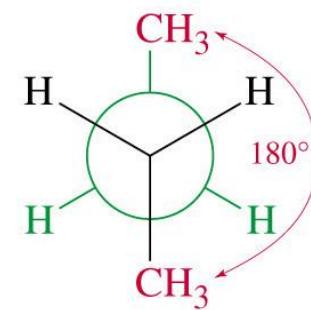
totally eclipsed (0°)



gauche (60°)



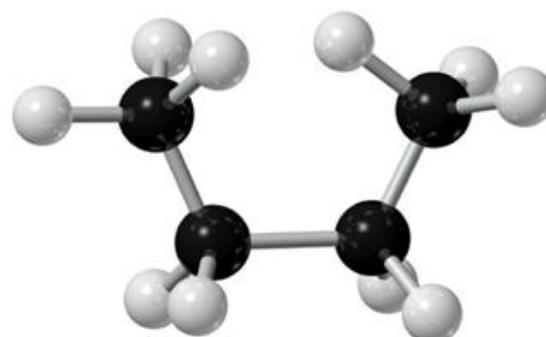
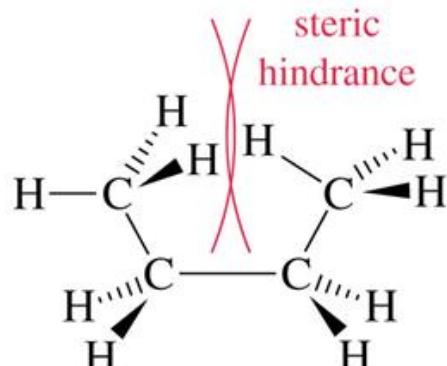
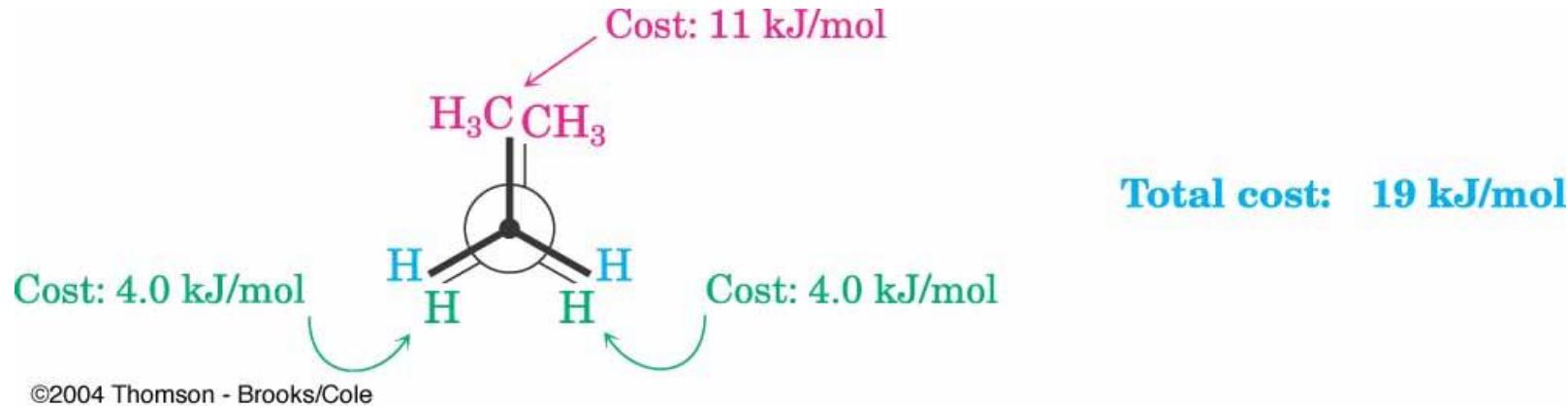
eclipsed (120°)



anti (180°)

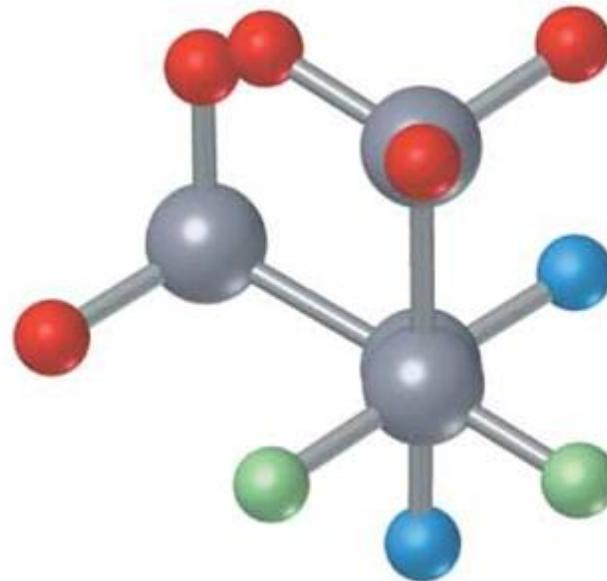
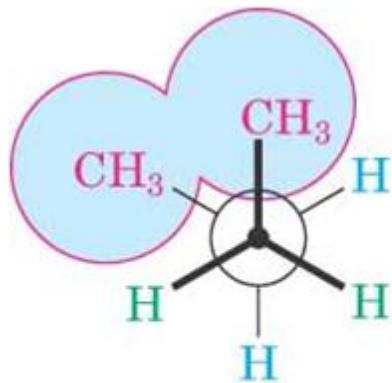
- **Anti** - Description given to two substituents attached to adjacent atoms when their bonds are at 180° with respect to each other.
- **Syn** - Description given to two substituents attached to adjacent atoms when their bonds are at 0° with respect to each other.
- **Gauche** - Description given to two substituents attached to adjacent atoms when their bonds are at 60° with respect to each other.

2 Different Eclipsed Conformations



Totally eclipsed conformation of butane

Gauche Interaction in Butane

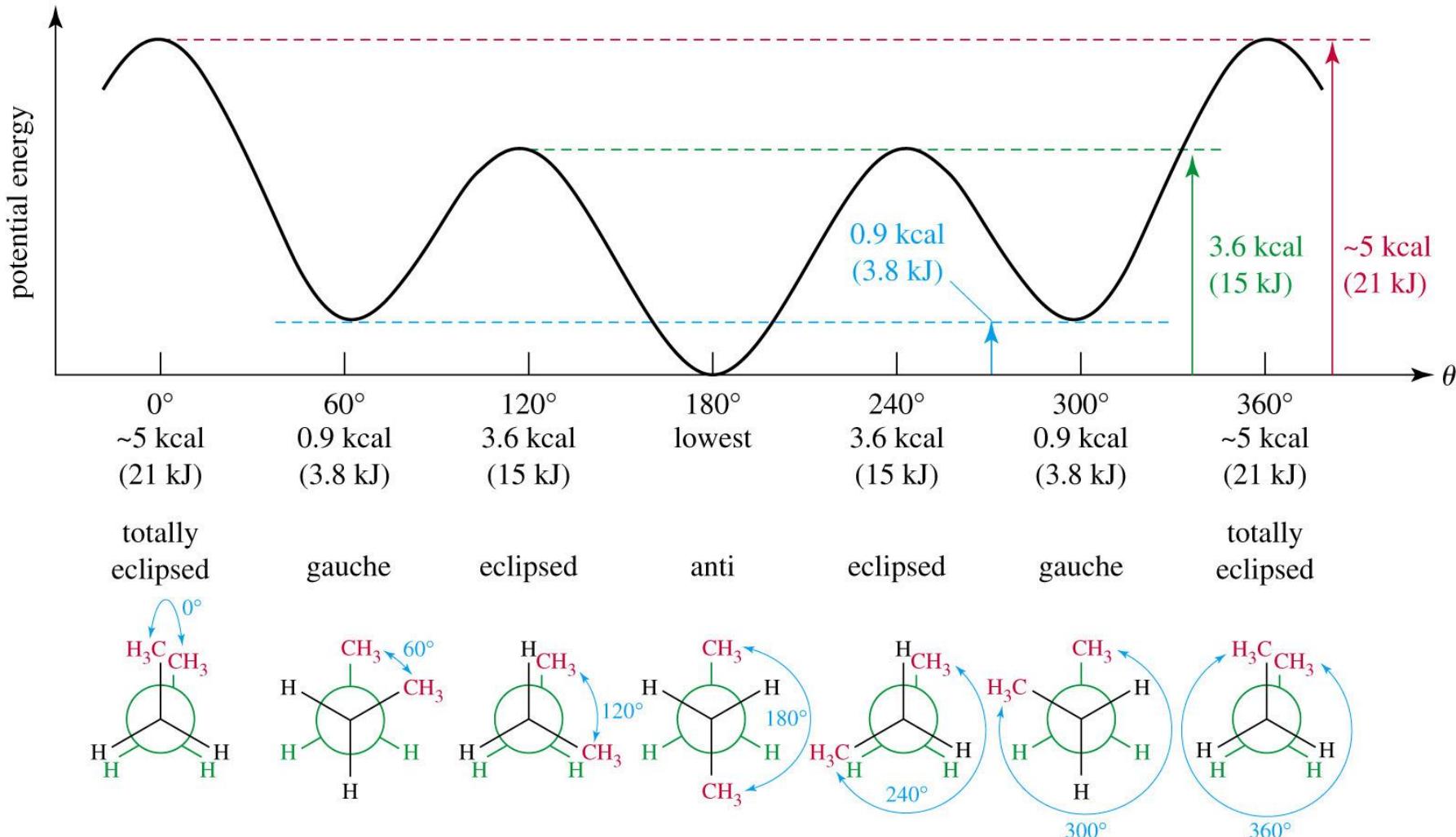


© 2004 Thomson/Brooks Cole

TABLE 4.1 Energy Costs for Interactions in Alkane Conformers

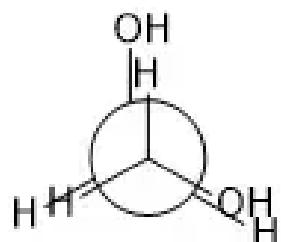
Interaction	Cause	Energy cost (kJ/mol)	Energy cost (kcal/mol)
$\text{H} \leftrightarrow \text{H}$ eclipsed	Torsional strain	4.0	1.0
$\text{H} \leftrightarrow \text{CH}_3$ eclipsed	Mostly torsional strain	6.0	1.4
$\text{CH}_3 \leftrightarrow \text{CH}_3$ eclipsed	Torsional plus steric strain	11	2.6
$\text{CH}_3 \leftrightarrow \text{CH}_3$ gauche	Steric strain	3.8	0.9

PE Diagram for Butane

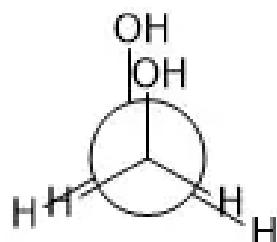


The rotation is very rapid indeed: the barrier of 20 kJ mol^{-1} corresponds to a rate at room temperature of $2 \times 10^9 \text{ s}^{-1}$. This is far too fast for the different conformers to be detected by NMR . the NMR spectrum of butane shows only one set of signals representing an average of the two conformations.

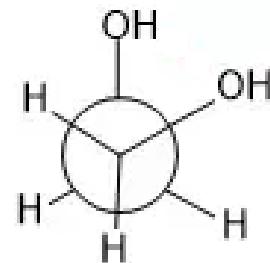
Conformations of ethylene glycol (1,2-ethanediol)



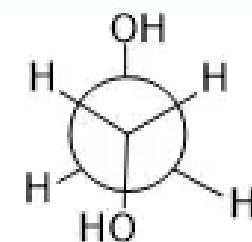
partially Eclipsed



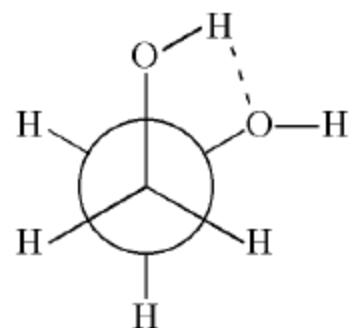
Eclipsed



Gauche



Anti



gauche $\text{CH}_2\text{OHCH}_2\text{OH}$

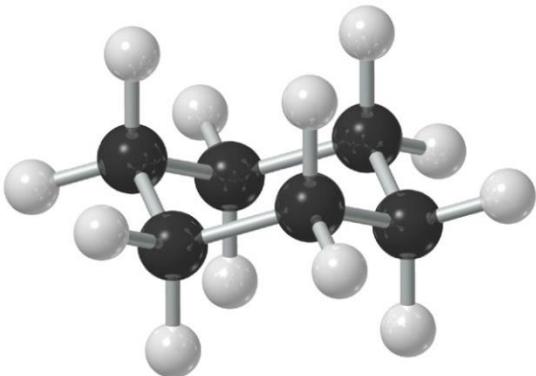
O-H···O (21 kJ/mol or 5.0 kcal/mol)

OH –OH gauche : Steric strain < 4
kJ/mol

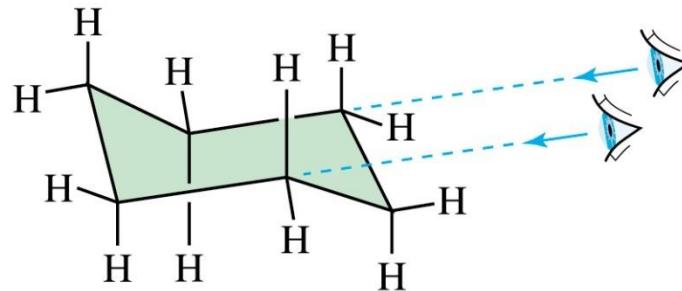
Conformation of cyclohexane

- The cyclohexane ring is very important because it is virtually strain free. This is one of the reasons why compounds containing six-membered rings are very common.
- There are two nonplanar conformations, called the **chair conformation** and the **boat conformation**, that are completely free of angle strain.

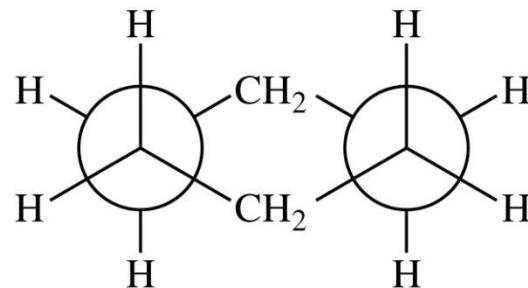
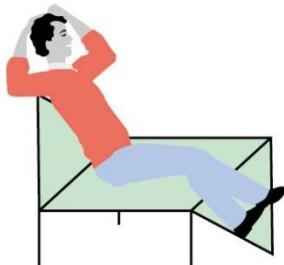
Chair Conformation



chair conformation

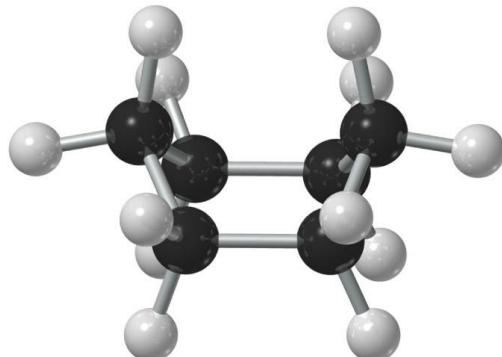


viewed along the “seat” bonds

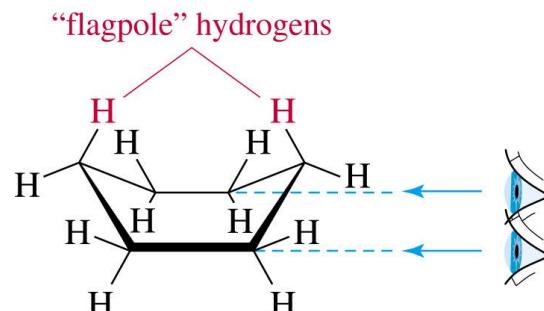


Newman projection

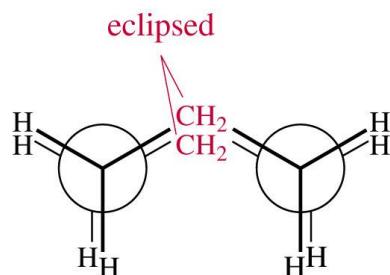
Boat Conformation



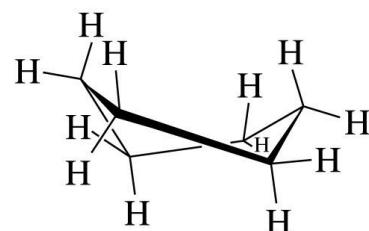
boat conformation



symmetrical boat



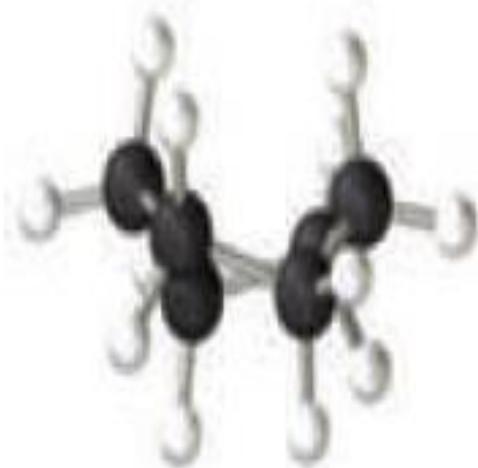
Newman projection



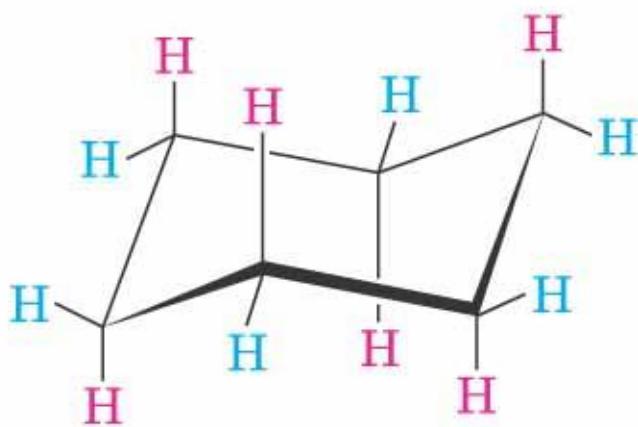
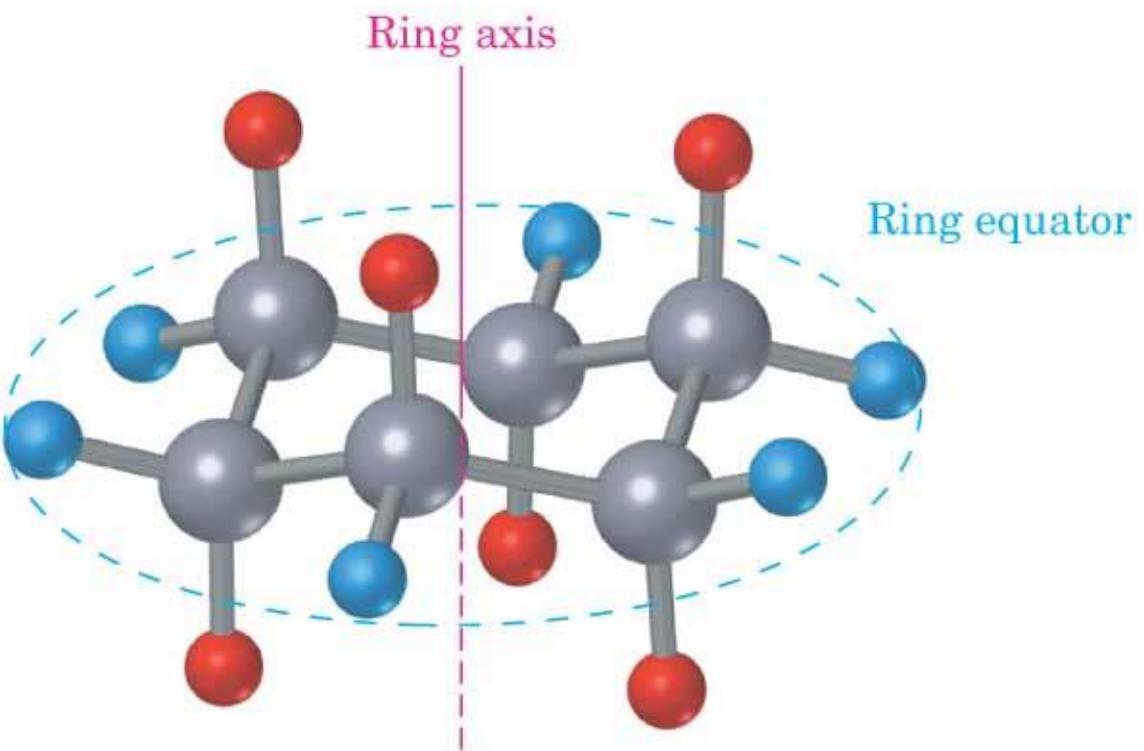
"twist" boat

The Newman projection shows that two bonds of the boat conformation are eclipsed. The torsional strain due to these eclipsing interactions and the steric strain due to the interaction of the flagpole hydrogens make the boat conformation higher in energy than the chair conformation. The boat conformation is flexible enough to twist somewhat to slightly decrease its overall strain energy.

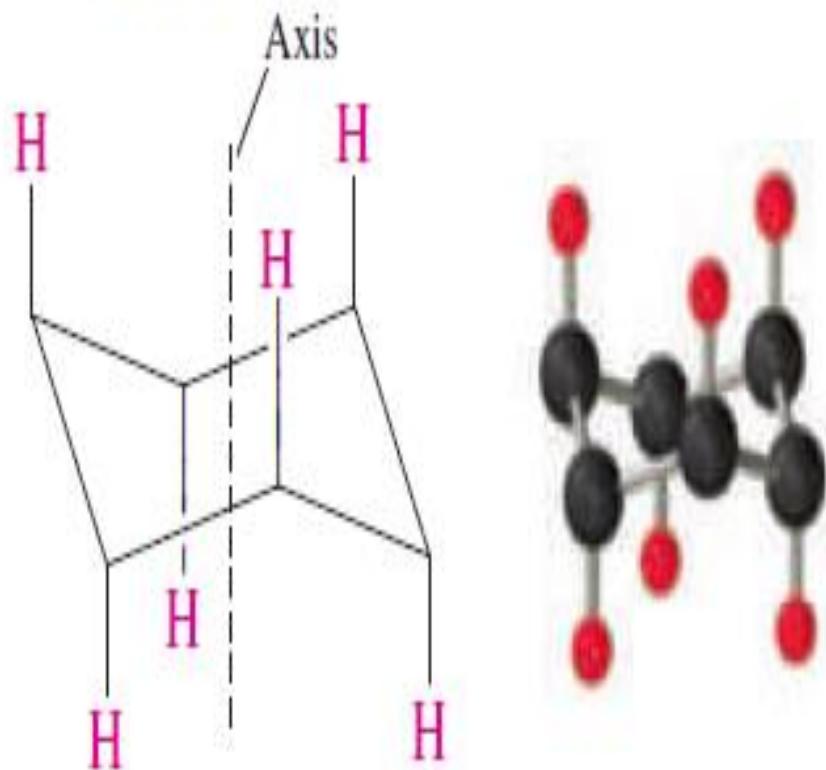
G Twist Boat Conformation



In the twist boat conformation the “bow” and the “stern” of the boat have been twisted slightly. Although this decreases the flagpole interaction and relieves some of the torsional strain, angle strain is introduced. Overall, the twist boat conformation is a little more stable than the boat conformation but not nearly as stable as the chair conformation.

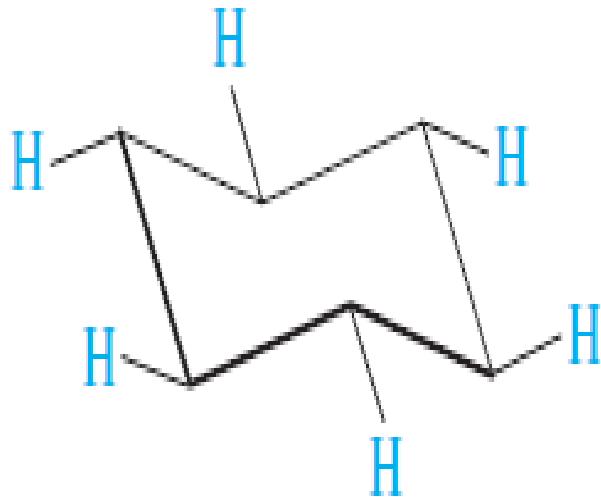


C Axial Hydrogens

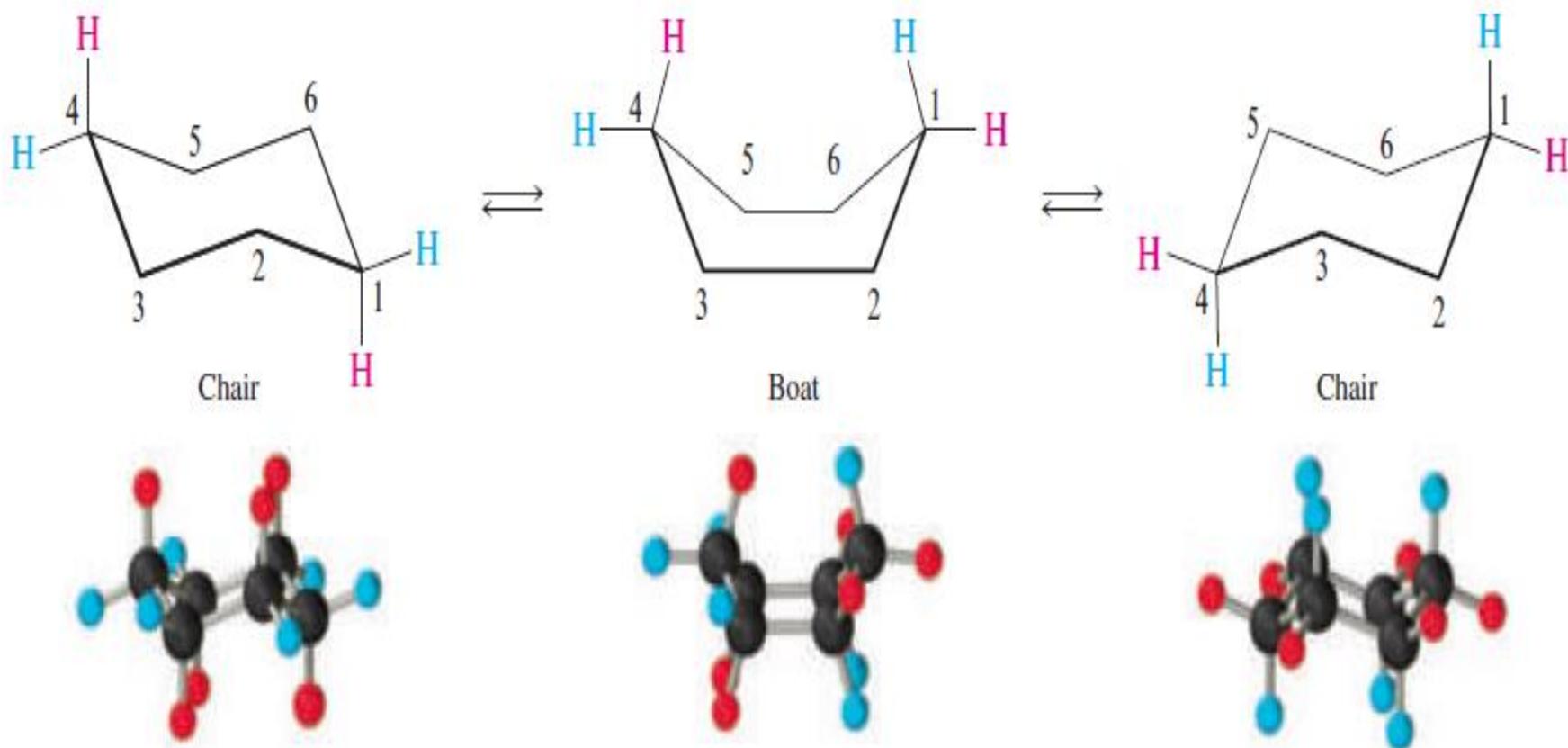


In the chair conformation cyclohexane has two different types of hydrogens. The bonds to one type are parallel to the axis of the ring. These are called **axial hydrogens**. The axial bonds alternate up and down around the ring.

① Equatorial Hydrogens

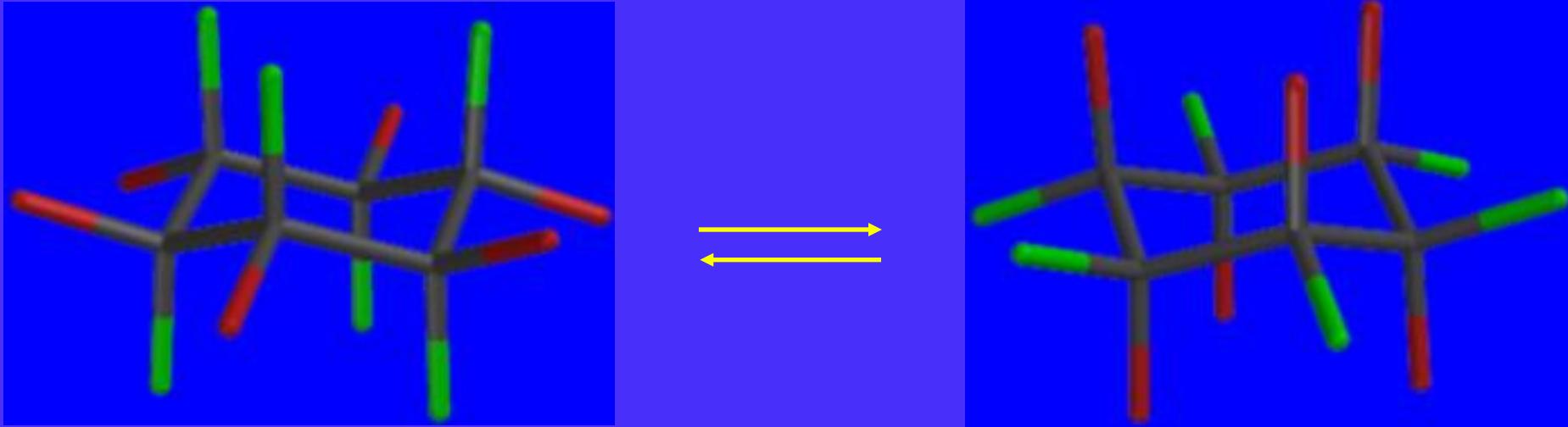


The other hydrogens are directed outward from the ring. They are called **equatorial hydrogens** because they lie around the "equator" of the ring. Now go back to structure ①, in which both types of hydrogens are shown, and identify the **axial hydrogens (red)** and the **equatorial hydrogens (blue)**. Also examine the view of the axial and equatorial hydrogens provided by the Newman projection.

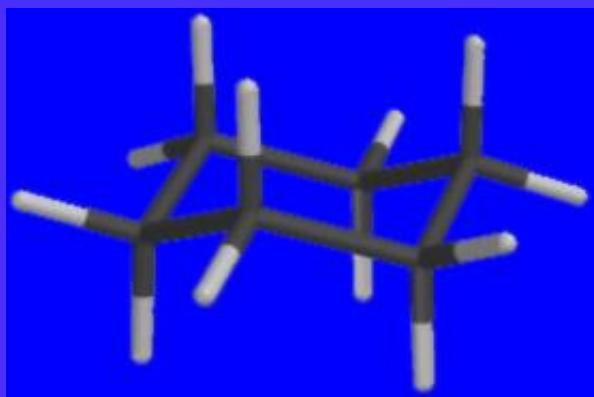


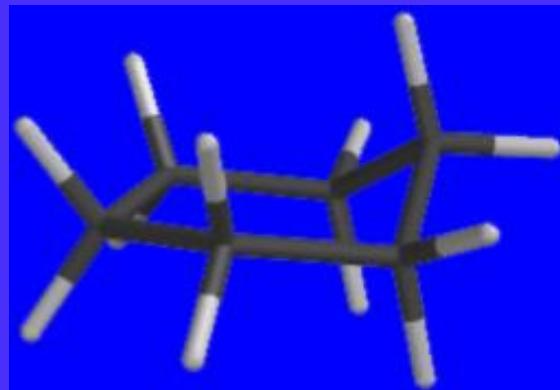
*Conformational Inversion
(Ring-Flipping) in
Cyclohexane*

Conformational Inversion

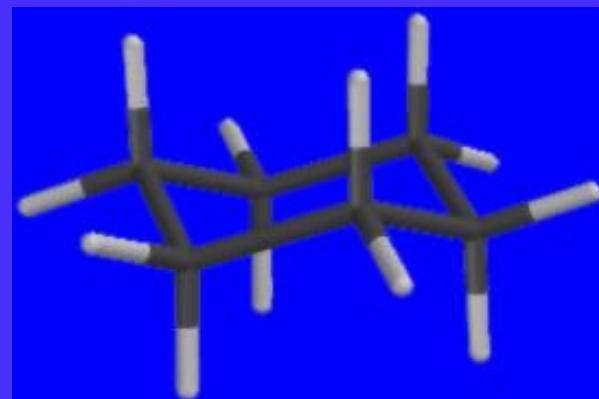
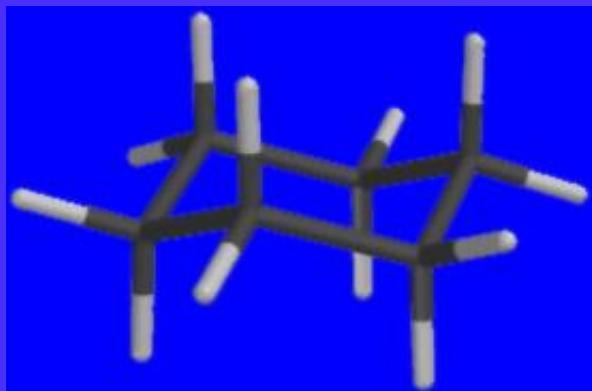


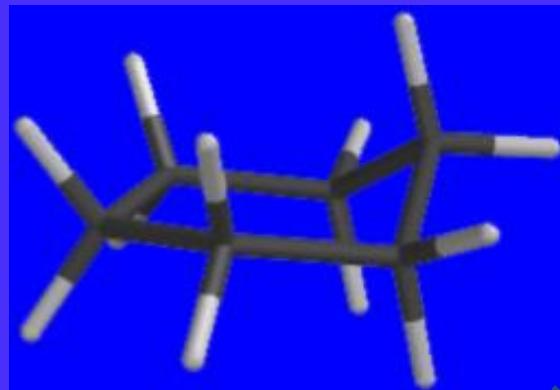
- chair-chair interconversion (ring-flipping)
- rapid process (activation energy = 45 kJ/mol)
- *all axial bonds become equatorial and vice versa*



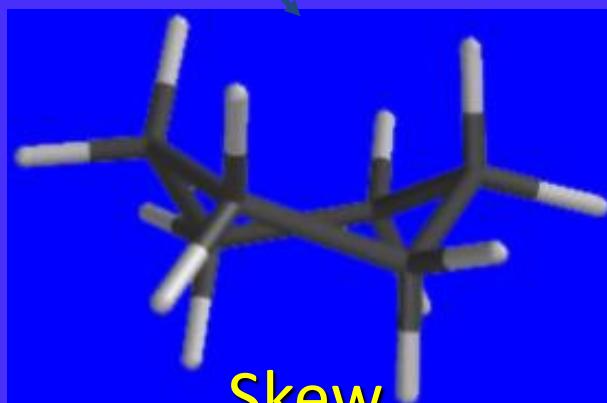


Half-chair

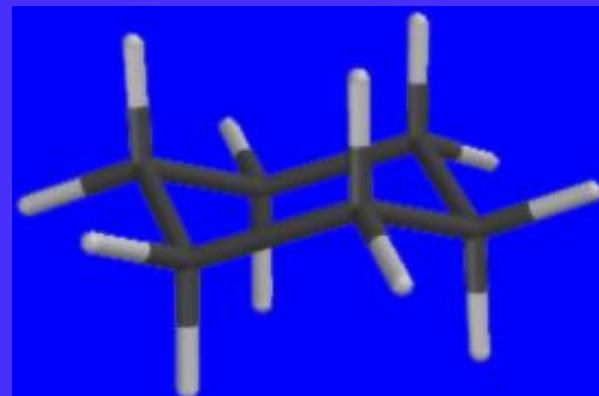
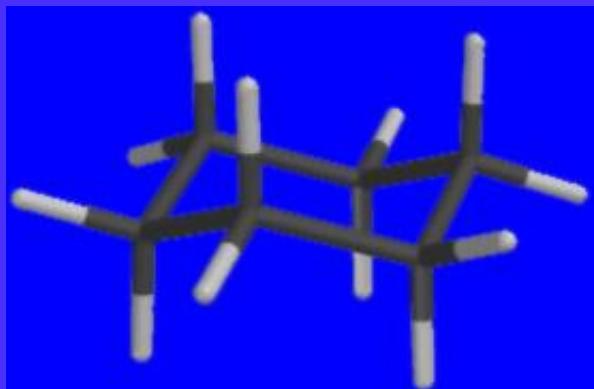


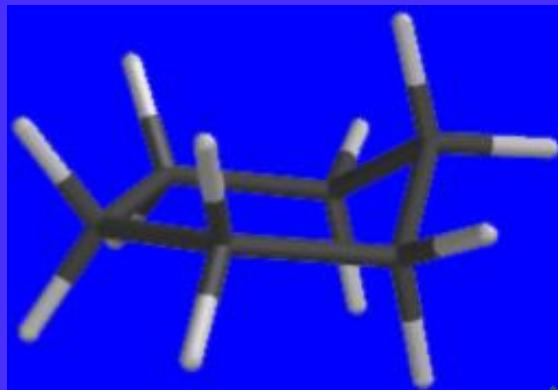


Half-chair

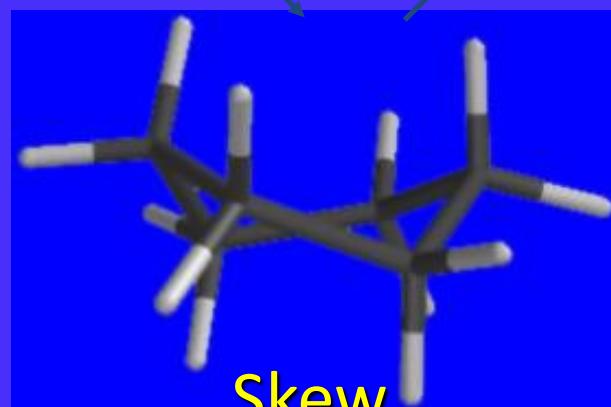


Skew
boat

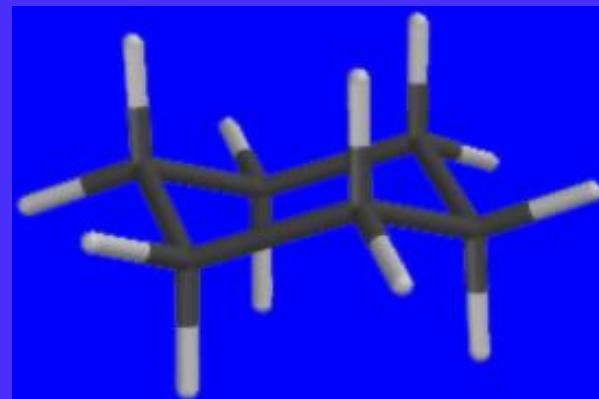
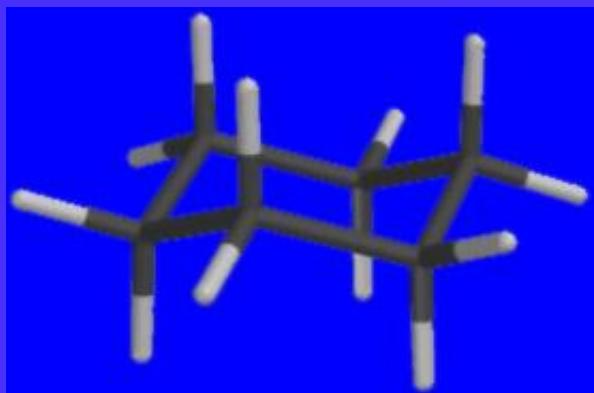


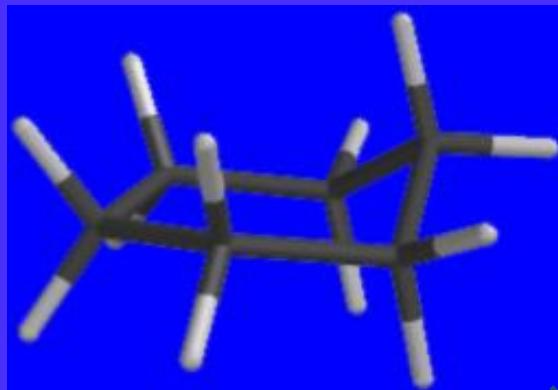


Half-chair

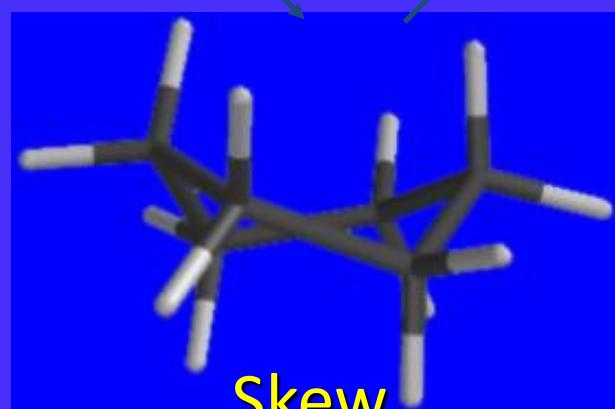


Skew
boat

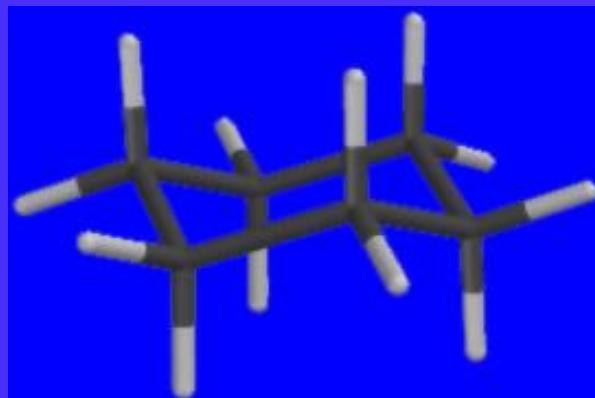
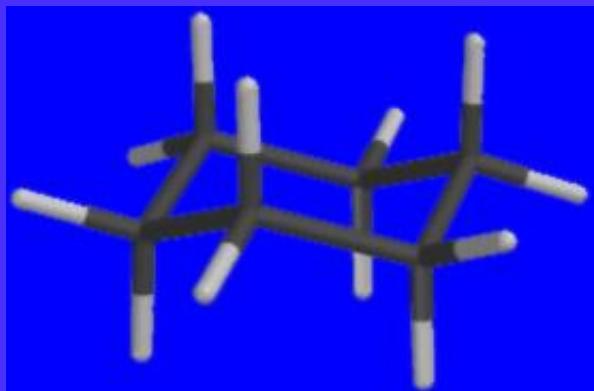


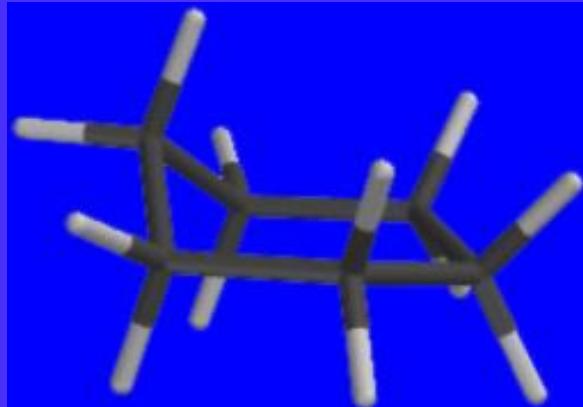
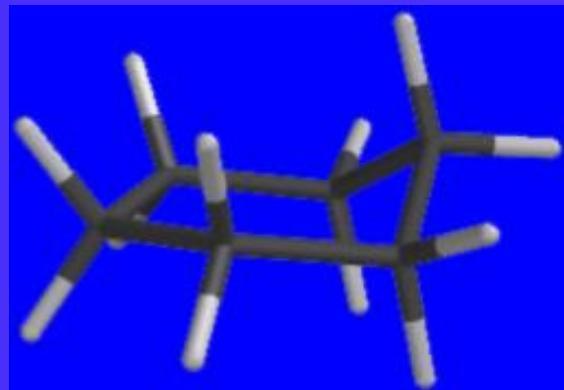


Half-chair



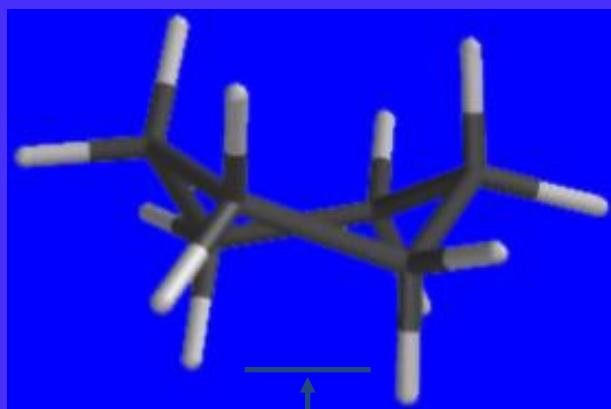
Skew
boat



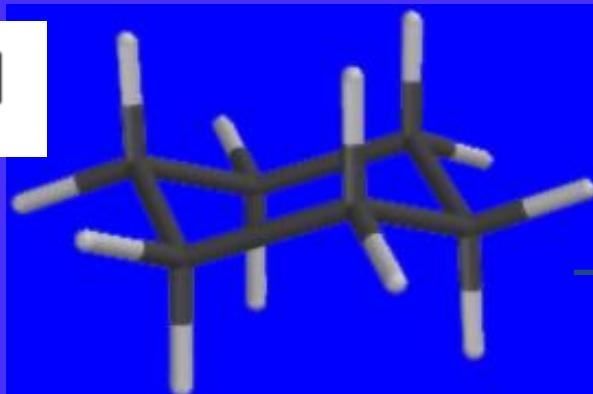
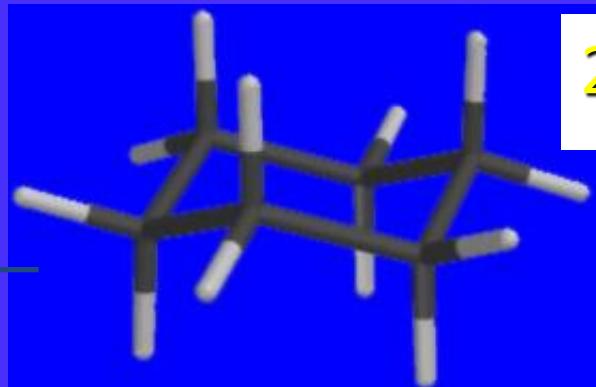


45 kJ/mol

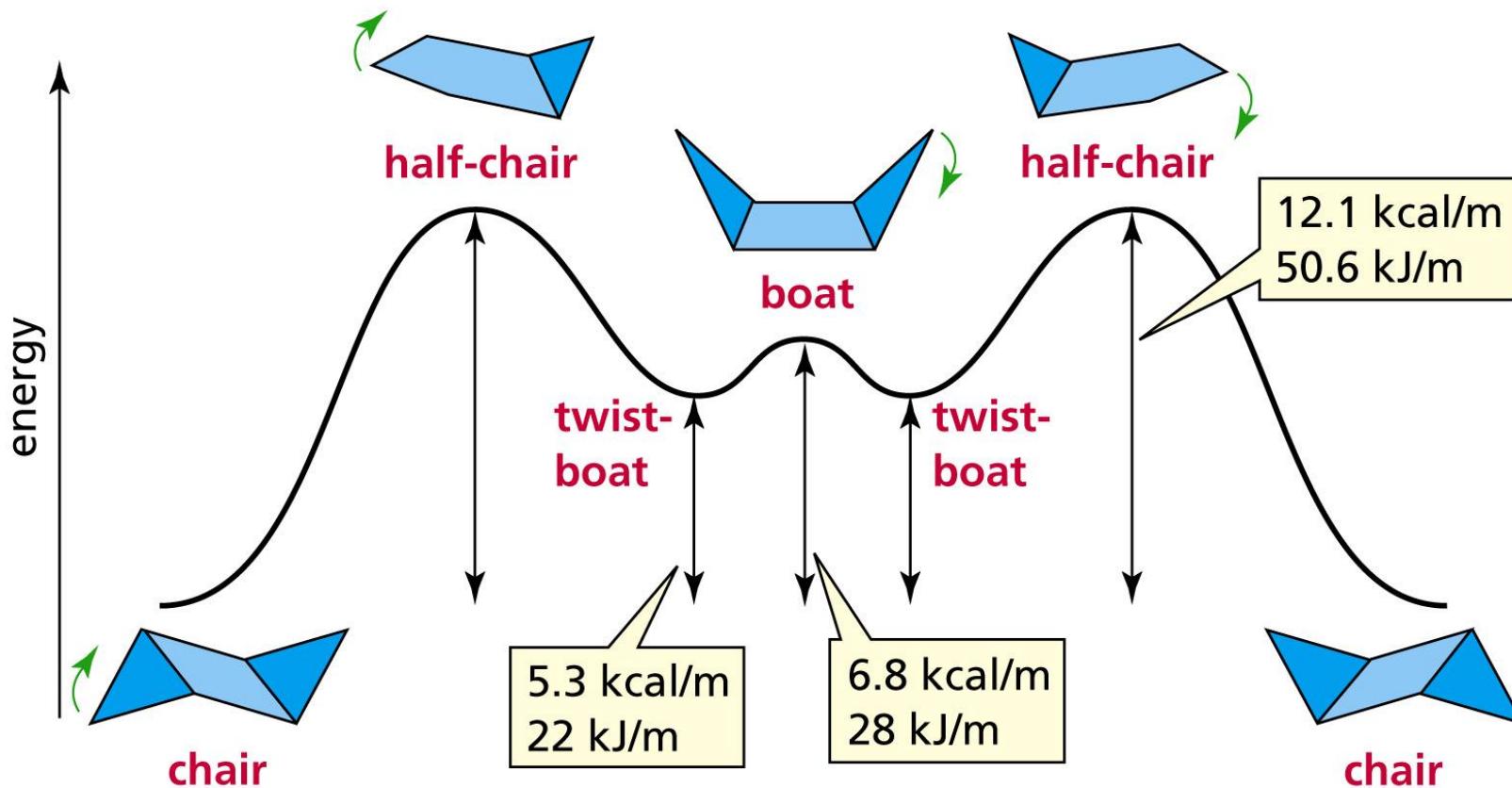
45 kJ/mol



23 kJ/mol



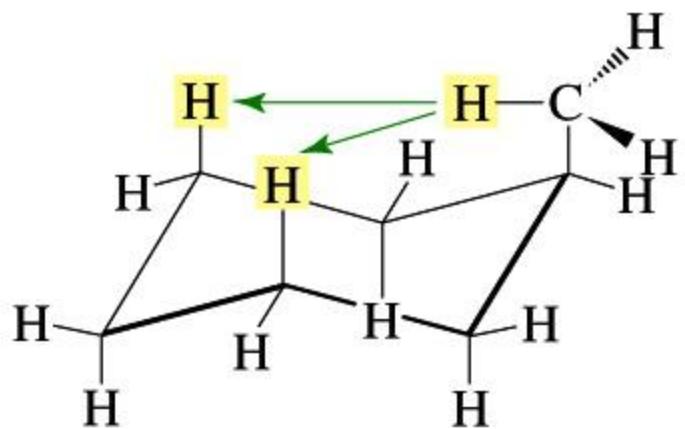
The Conformations of Cyclohexane and Their Energies



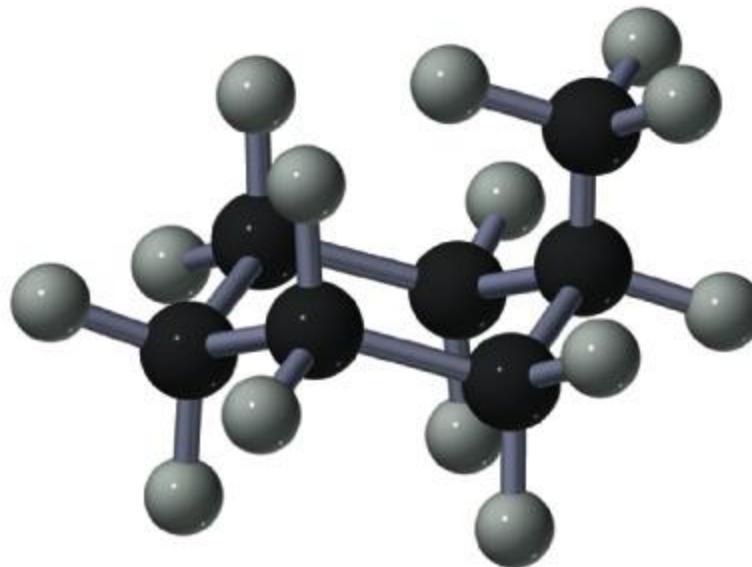
Conformational Analysis of Monosubstituted Cyclohexanes

- most stable conformation is chair
- substituent is more stable when equatorial

Steric Strain of 1,3-Diaxial Interaction in Methylcyclohexane

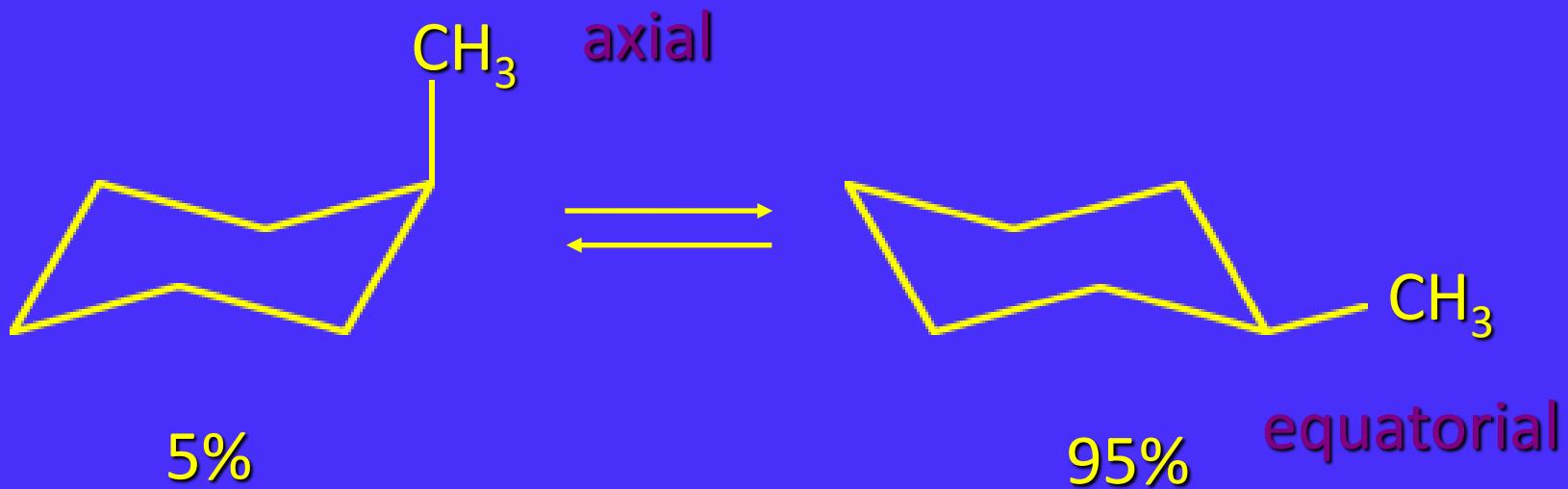


1,3-diaxial interactions



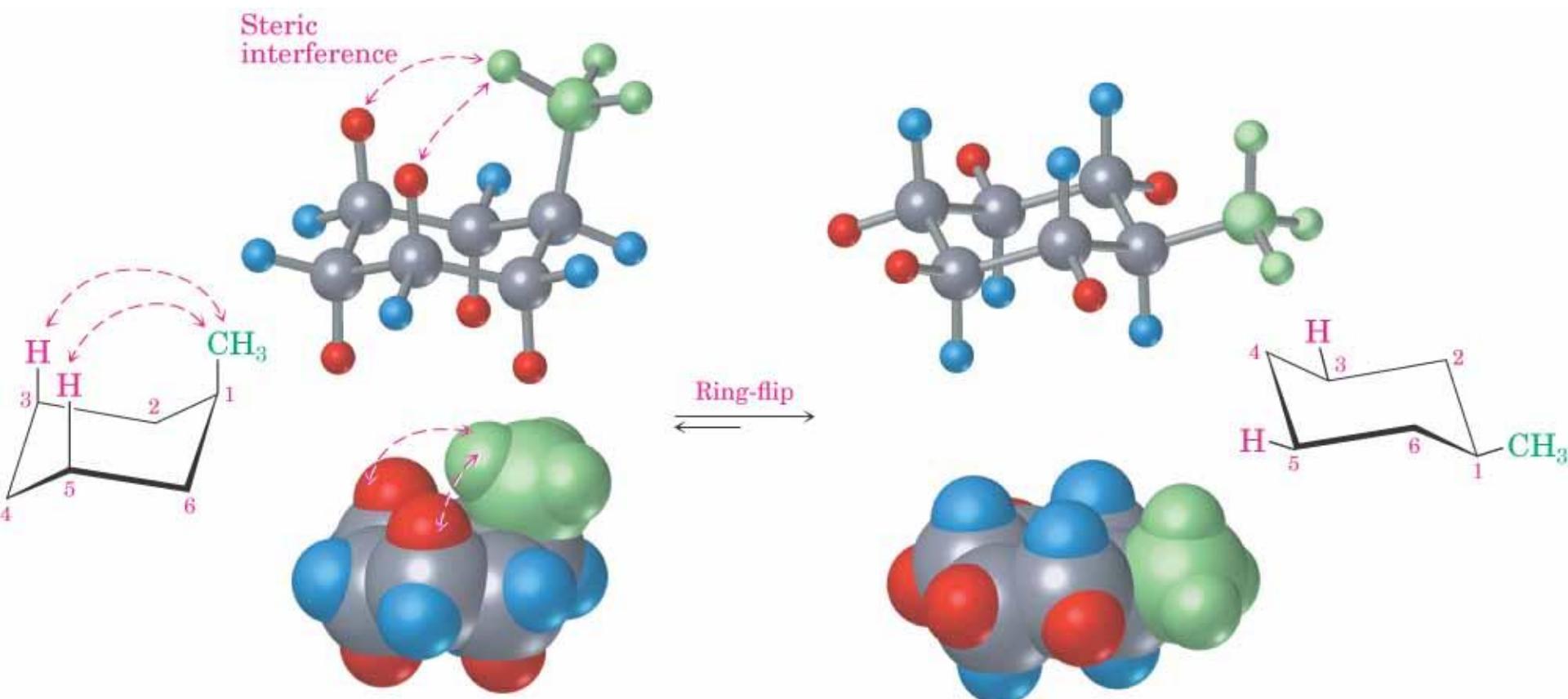
ball-and-stick model

Methylcyclohexane

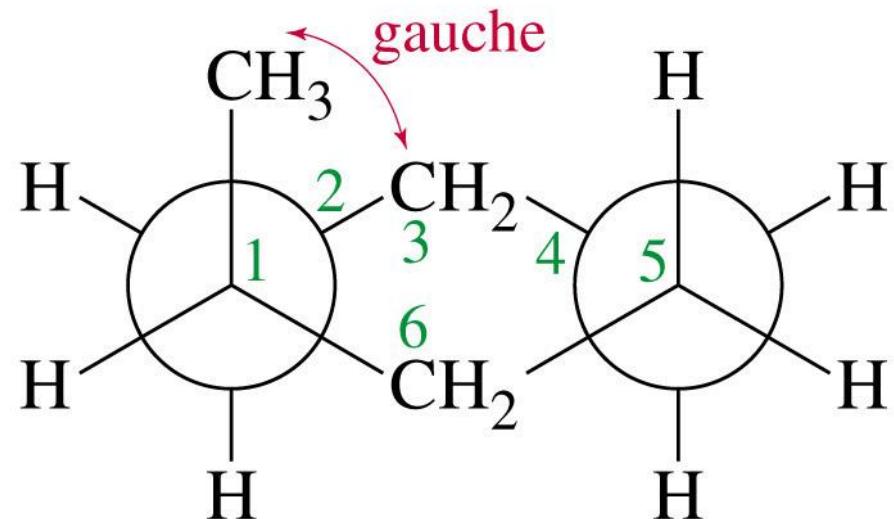
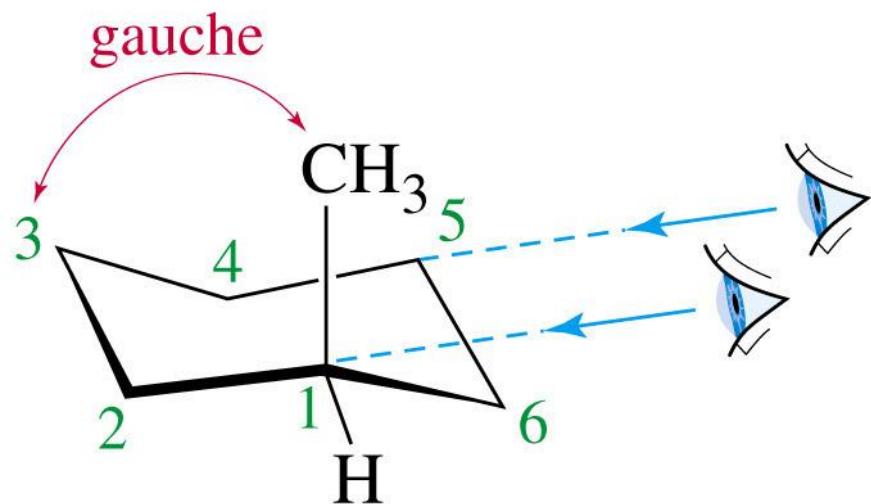


- Chair chair interconversion occurs, but at any instant 95% of the molecules have their methyl group equatorial.
- An axial methyl group is more crowded than an equatorial one.

Equatorial Conformation is Preferred

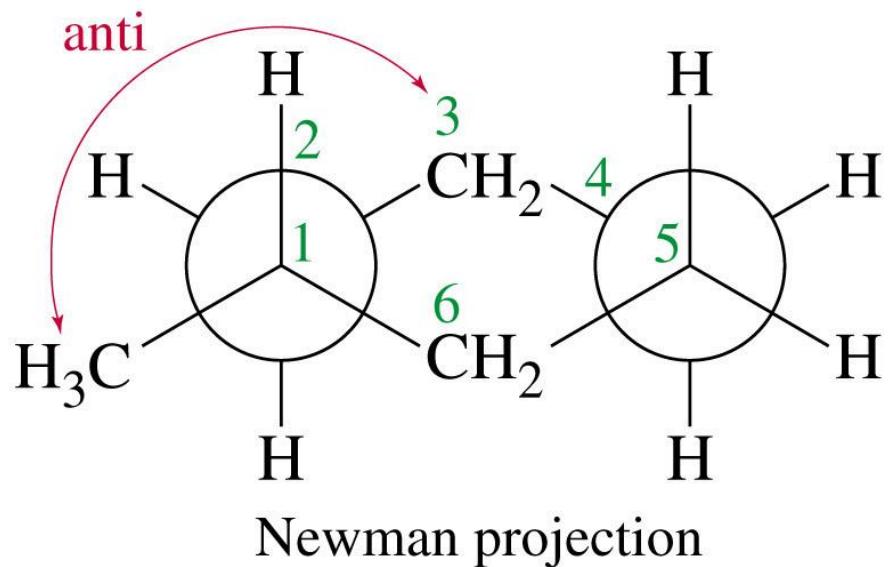
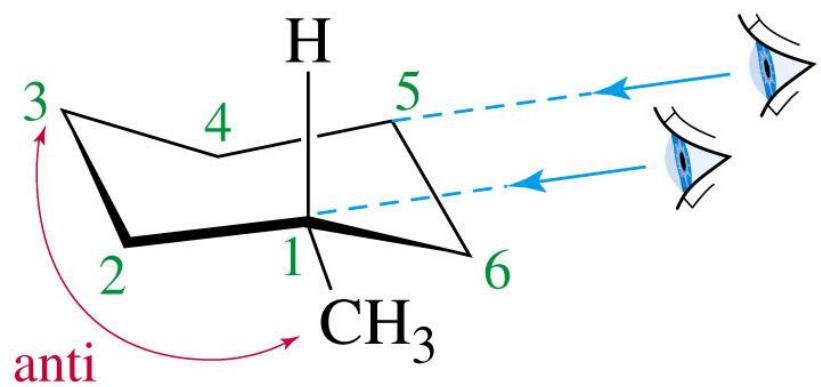


Axial Methyl group is Gauche to C₃ in the ring

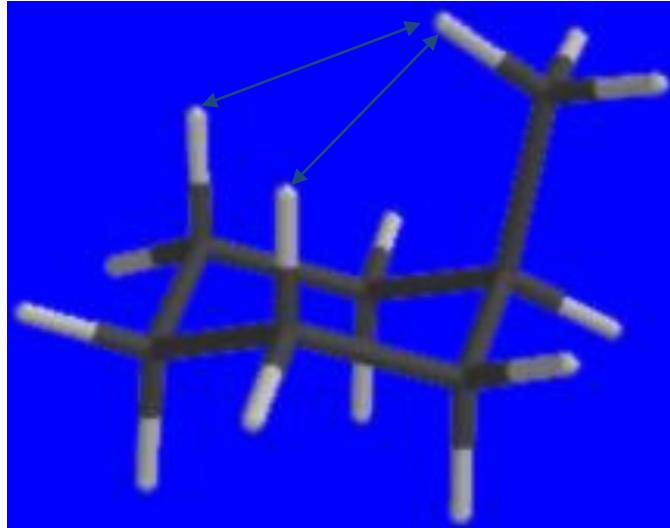


Newman projection
(a)

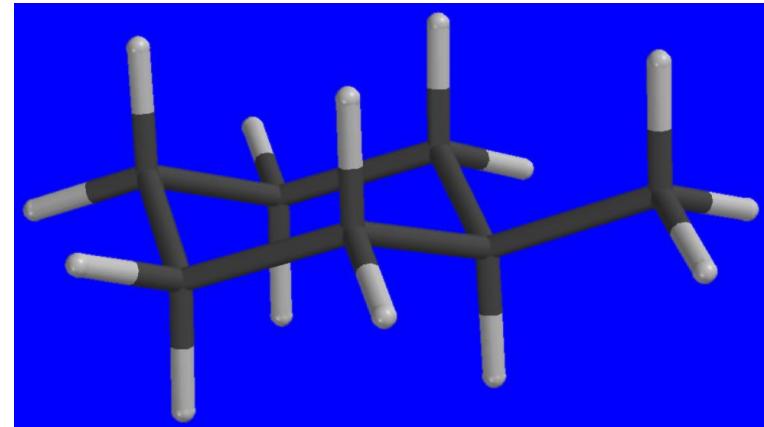
Equatorial Methyl Group is Anti to C₃ in the ring



Methylcyclohexane



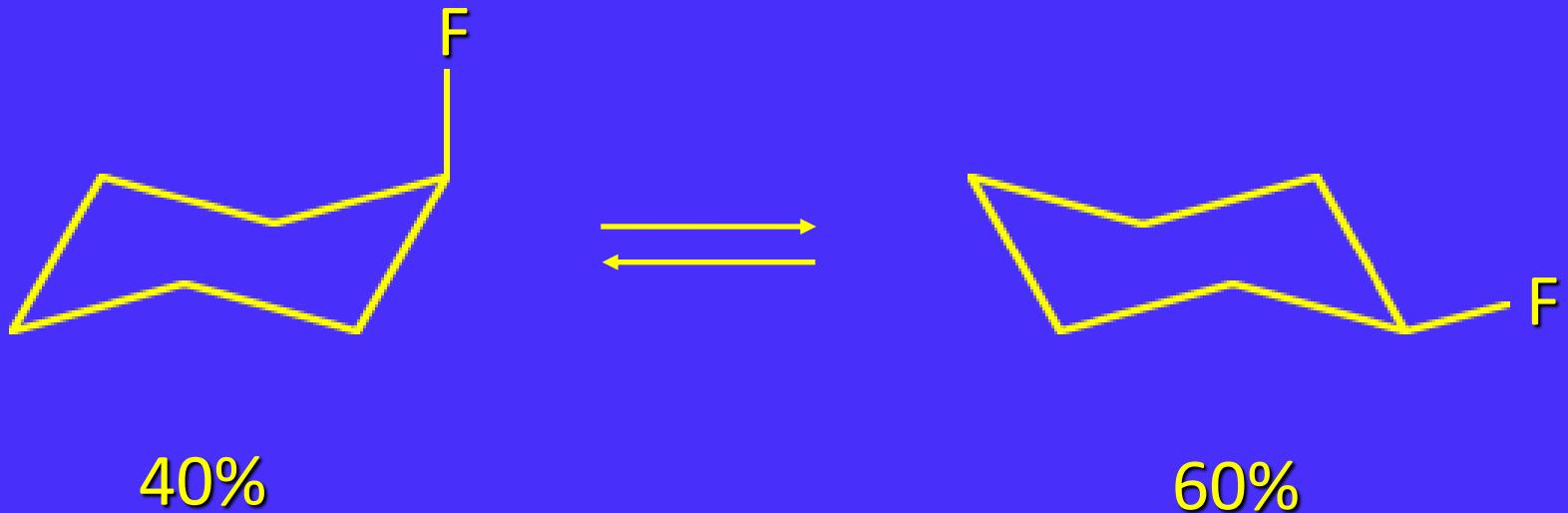
5%



95%

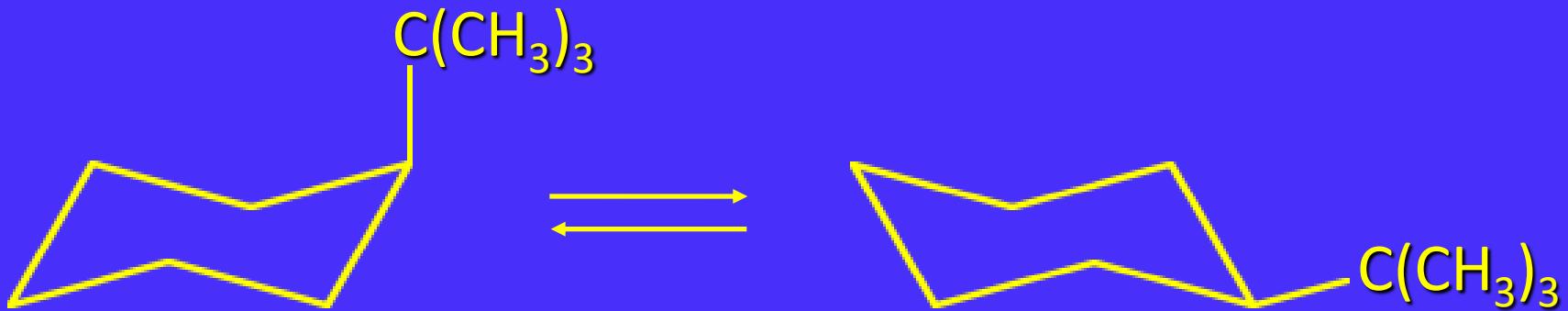
- Hydrogen atoms closer than 2.4 Angstroms will cause steric strain.
- This is called a "1,3-diaxial repulsion" a type of van der Waals strain or Steric strain.

Fluorocyclohexane



- Crowding is less pronounced with a "small" substituent such as fluorine.
- Size of substituent is related to its branching.

tert-Butylcyclohexane



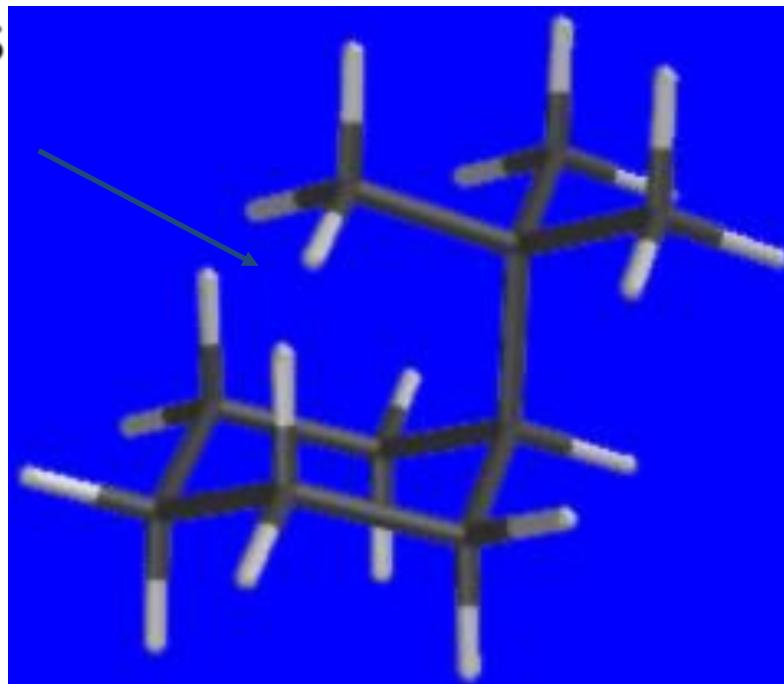
Less than 0.01%

Greater than 99.99%

- Crowding is more pronounced with a "bulky" substituent such as *tert*-butyl.
- *tert*-Butyl is highly branched.

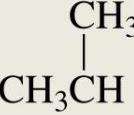
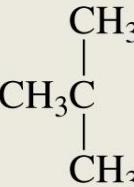
tert-Butylcyclohexane

van der Waals
strain due to
1,3-diaxial
repulsions



- The larger the substituent on a cyclohexane ring, the more the equatorial substituted conformer will be favored

Table 2.10 Equilibrium Constants for Several Monosubstituted Cyclohexanes at 25 °C

Substituent	Axial	$\xrightleftharpoons{K_{eq}}$	Equatorial	Substituent	Axial	$\xrightleftharpoons{K_{eq}}$	Equatorial
H		1		CN		1.4	
CH ₃		18		F		1.5	
CH ₃ CH ₂		21		Cl		2.4	
		35		Br		2.2	
		4800		I		2.2	
				HO		5.4	

$$K_{eq} = [\text{equatorial conformer}] / [\text{axial conformer}]$$

- The larger the substituent on a cyclohexane ring, the more the equatorial substituted conformer will be favored

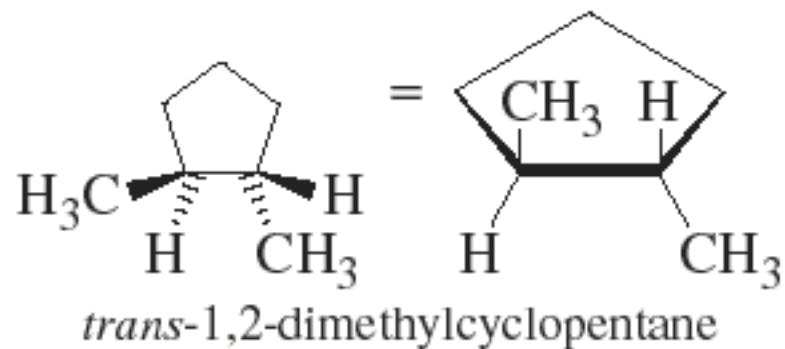
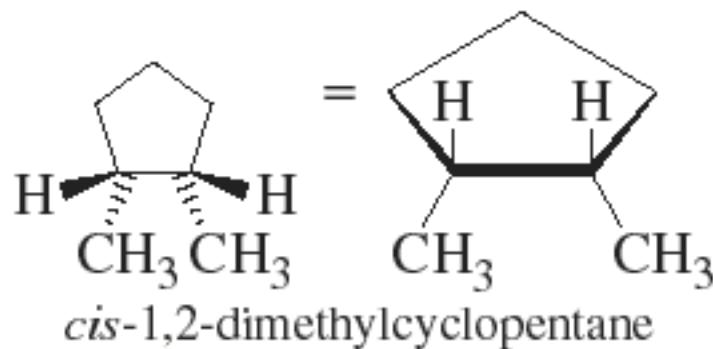
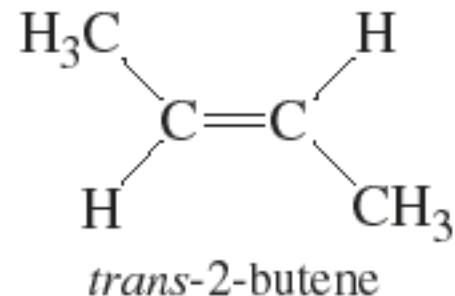
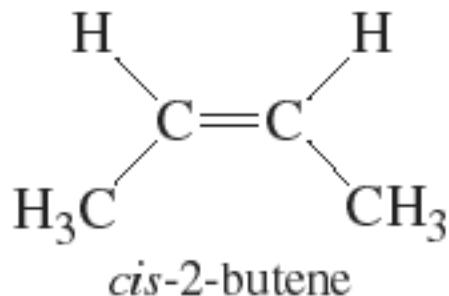
SUBSTITUENT	STERIC HINDRANCE FROM 1,3-DIAXIAL INTERACTIONS (KJ/MOL)	AXIAL-EQUATORIAL RATIO (AT EQUILIBRIUM)
—Cl	2.0	70 : 30
—OH	4.2	83 : 17
—CH ₃	7.6	95 : 5
—CH ₂ CH ₃	8.0	96 : 4
—CH(CH ₃) ₂	9.2	97 : 3
—C(CH ₃) ₃	22.8	9999 : 1

$$K_{\text{eq}} = [\text{equatorial conformer}] / [\text{axial conformer}]$$

Disubstituted Cyclohexanes
Cis-trans Isomerism

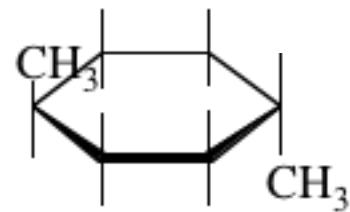
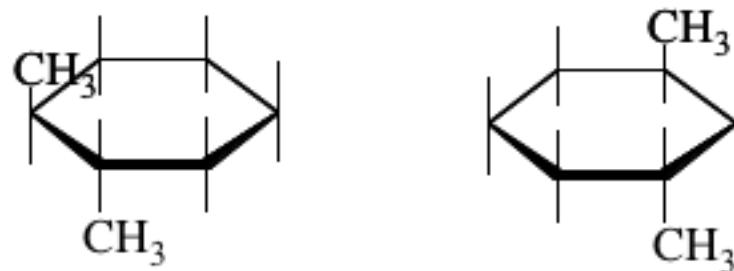
Cyclic Alkanes Stereochemistry

Cis - Trans Isomers



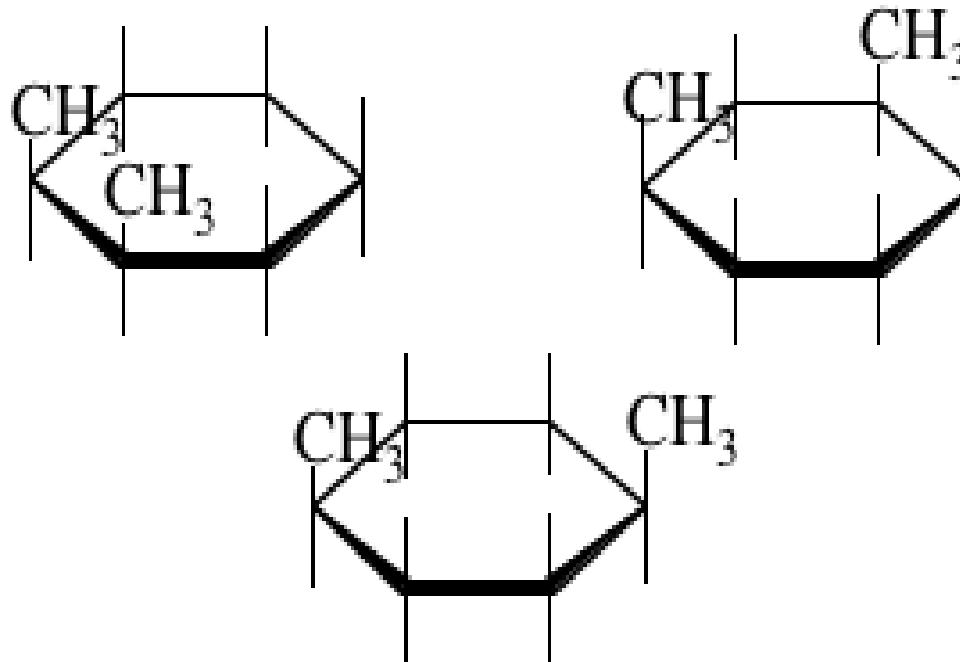
Cyclohexane Stereochemistry

Trans isomers



Cyclohexane Stereochemistry

Drawings: Cis isomers & the need for perspective



Are the methyl groups axial or equatorial?

What is the actual conformational shape of the cyclohexane ring?

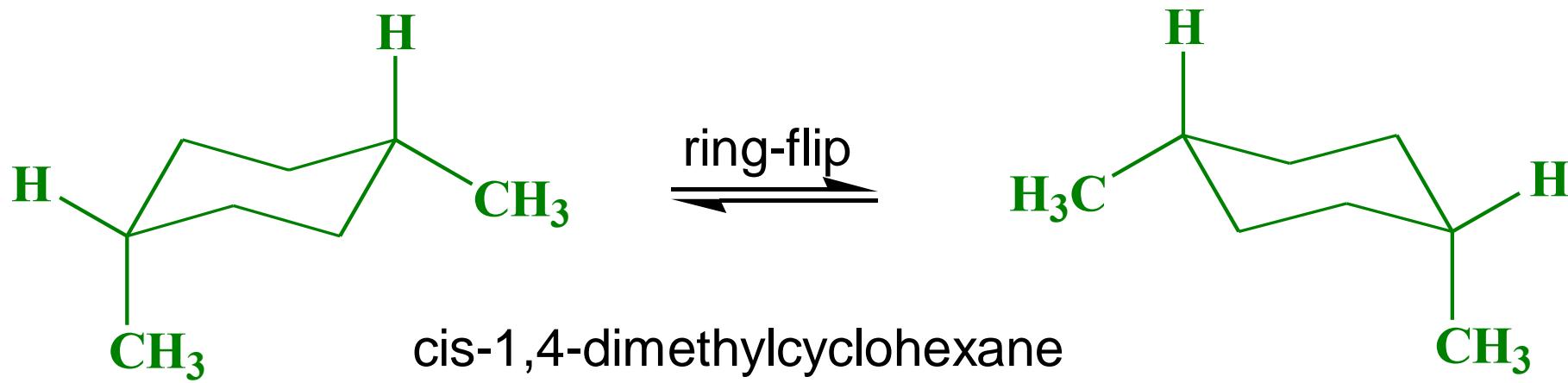
Cyclohexane Stereochemistry

Cis -Trans Isomers

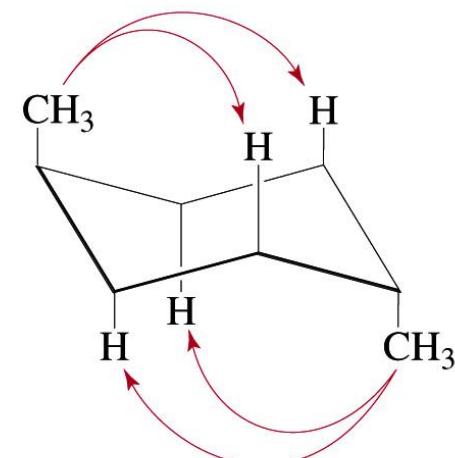
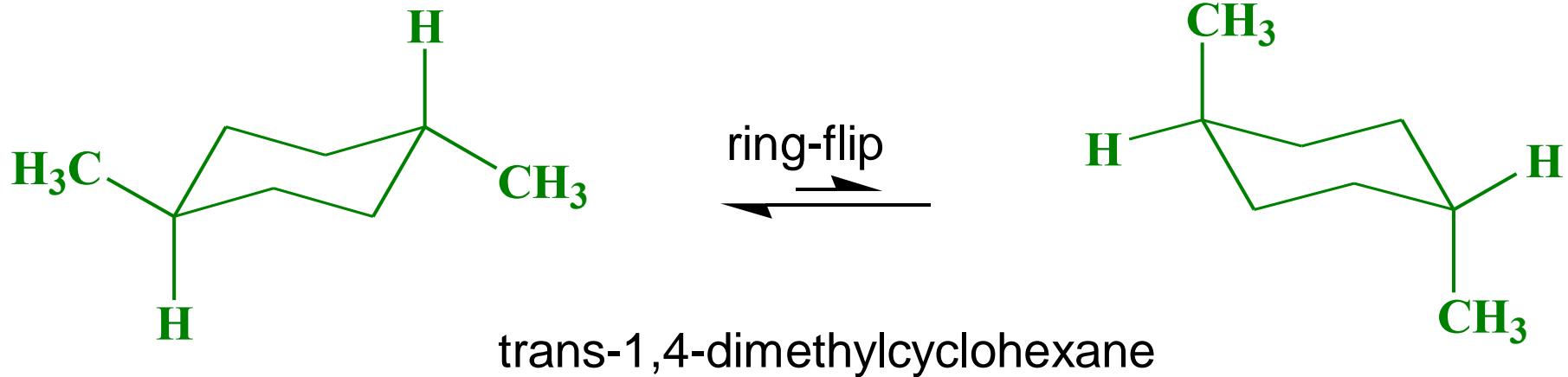
<i>Position</i>	<i>cis</i>	<i>trans</i>
1,2	e,a or a,e	e,e or a,a
1,3	e,e or a,a	a,e or e,a
1,4	e,a or a,e	e,e or a,a

Complete the Table: a = axial; e = equatorial

The Chair Conformers of *cis*-1,4-Dimethylcyclohexane

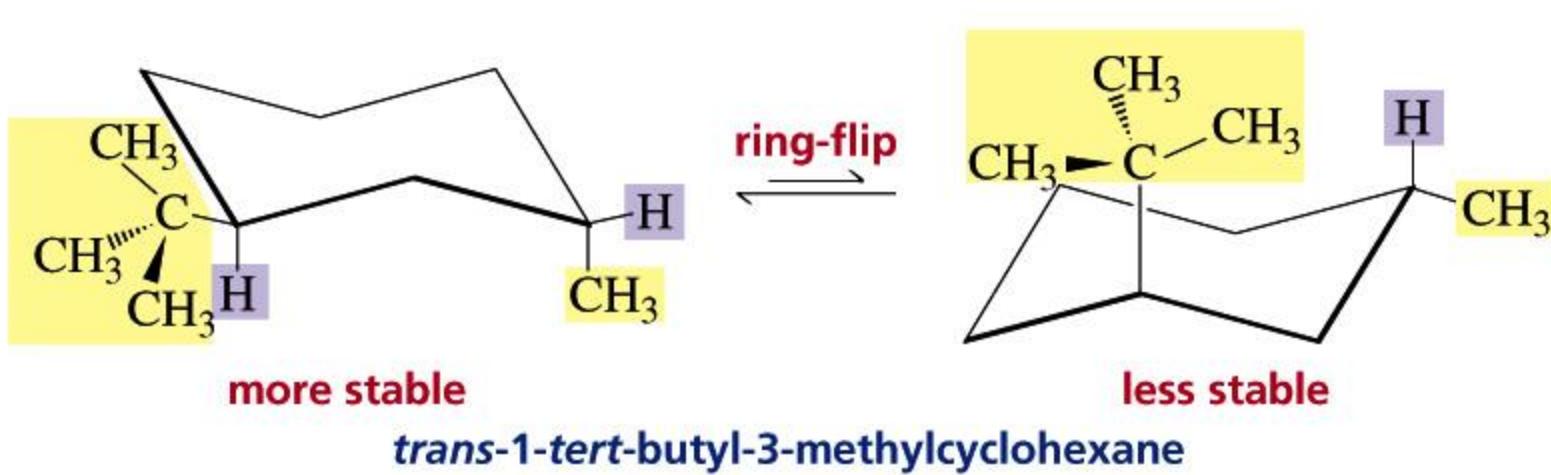


The Chair Conformers of *trans*-1,4-Dimethylcyclohexane

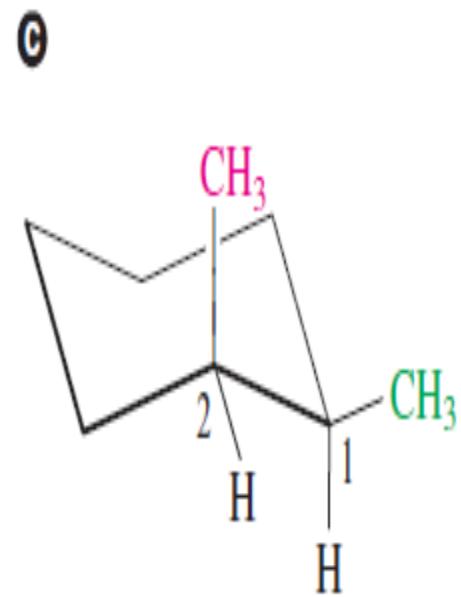
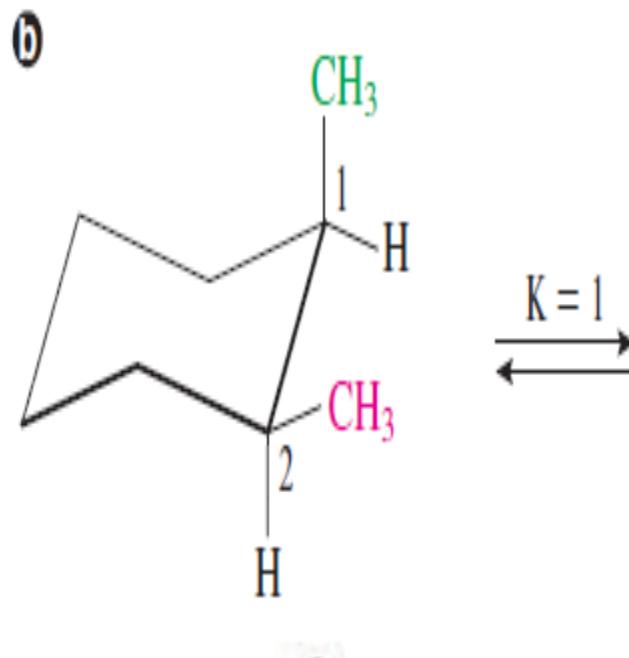
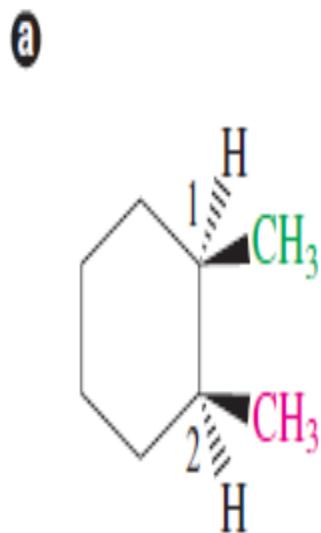


This chair conformer has four 1,3-diaxial interactions.

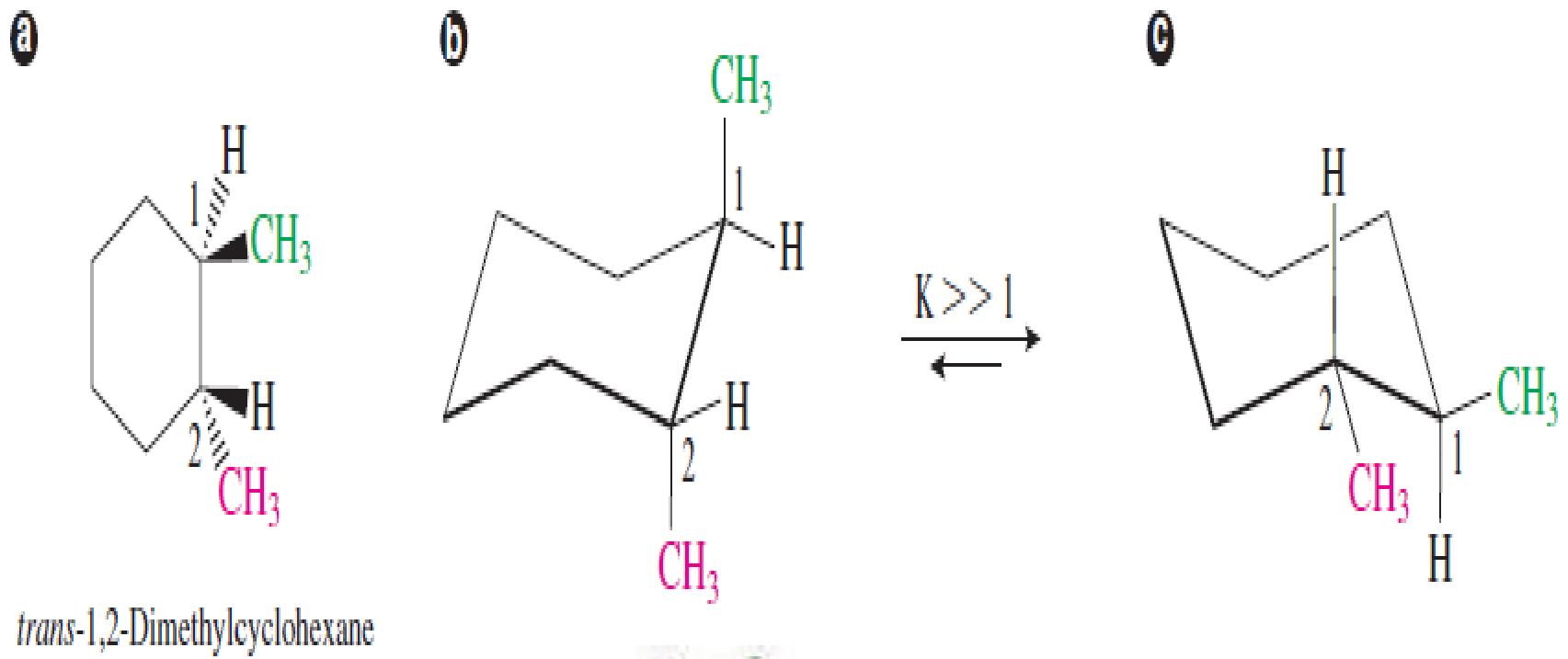
1-tert-Butyl-3-Methylcyclohexane

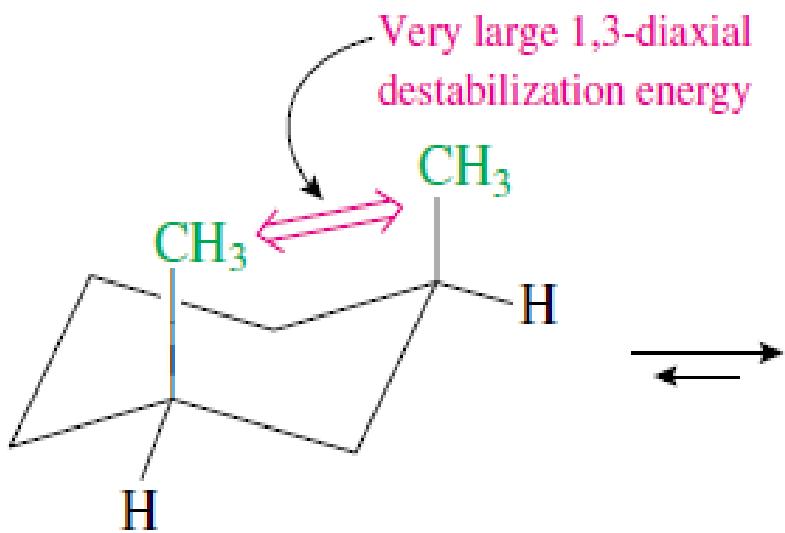


- Conformation of Cis-1,2 dimethyl cyclohexane

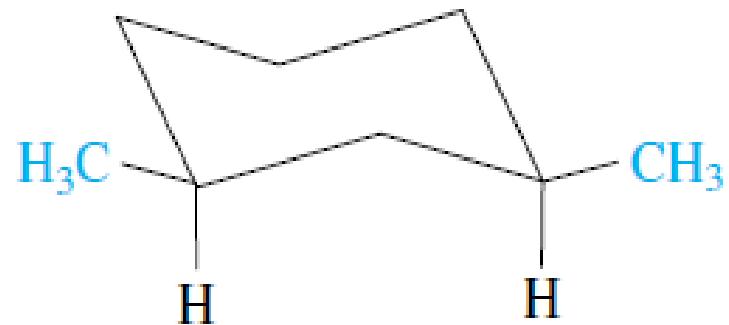


- Conformation of trans-1,2 dimethyl cyclohexane





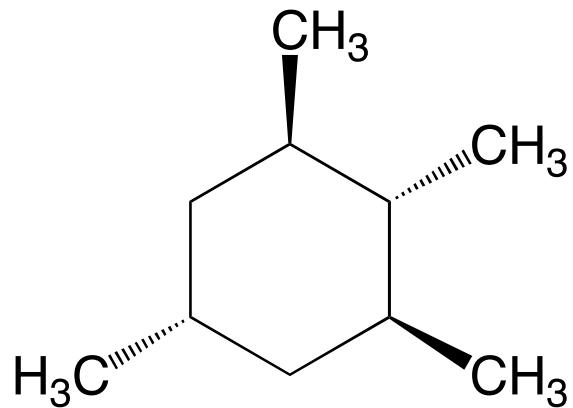
Both methyl groups
are **axial**.



Both methyl groups
are **equatorial**.

Question

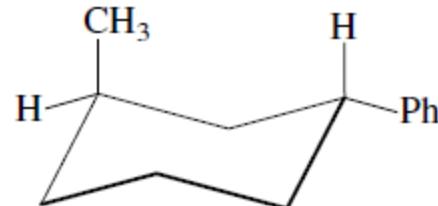
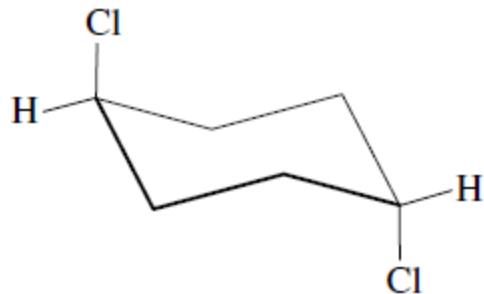
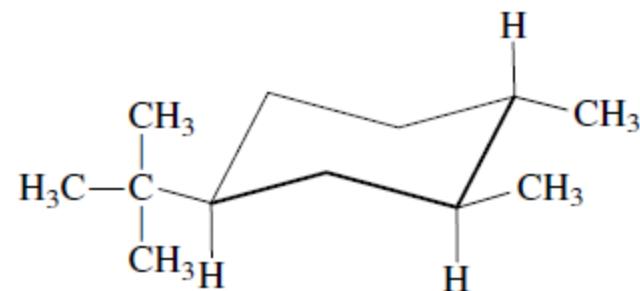
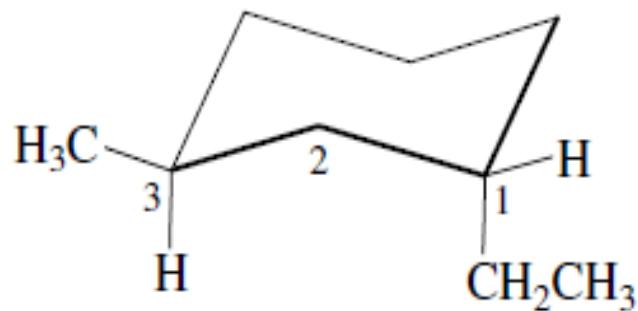
Consider the molecule below. What is the maximum number of methyl groups that can be in the equatorial position at the same time?



- A. 0
- B. 1
- C. 2
- D. 3
- E. 4

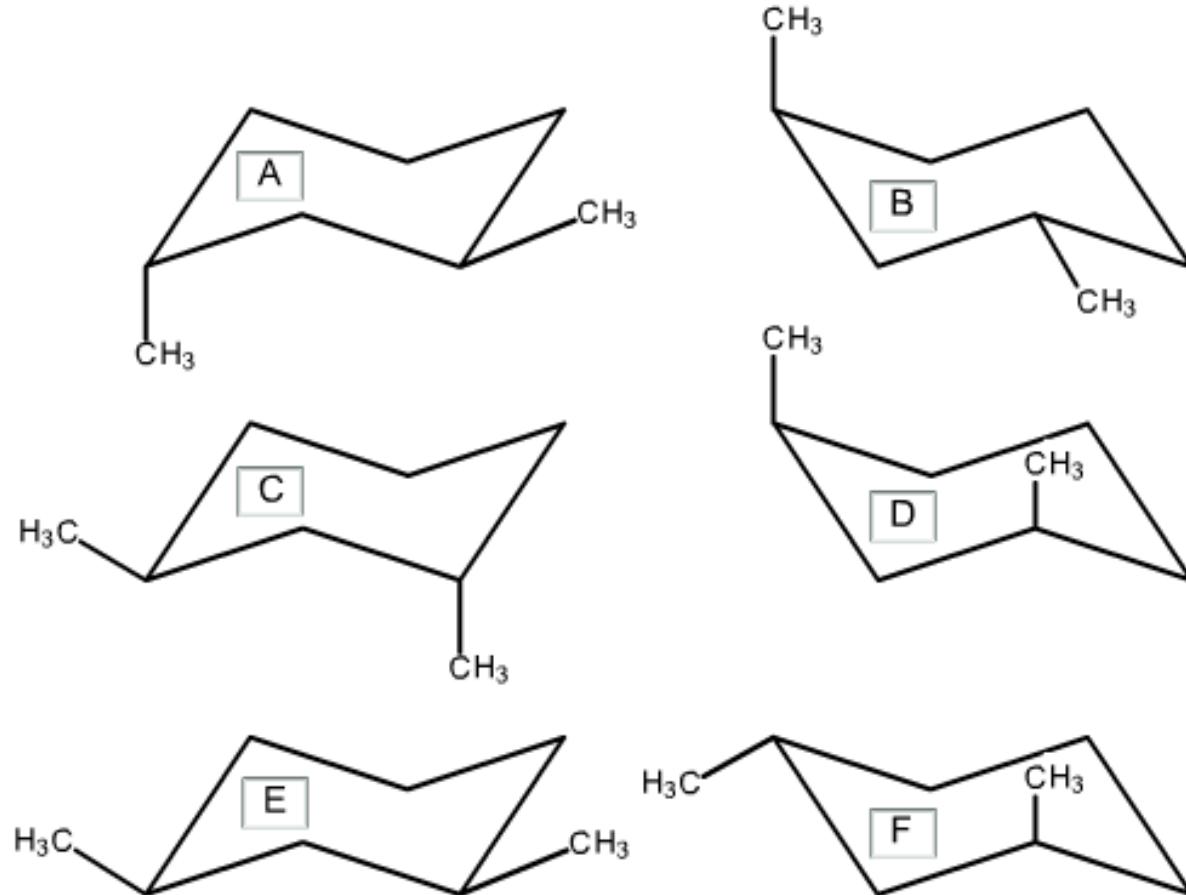
Questions

- Are the substituents cis or trans in the following conformation of one of the stereoisomers of 1-ethyl-3-methylcyclohexane? Is the ethyl group axial or equatorial? Is the methyl group axial or equatorial? Which is more stable, the conformation shown or the conformation resulting from a ring-flip? Which is more stable, the compound shown or its stereoisomer?

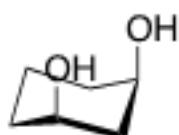
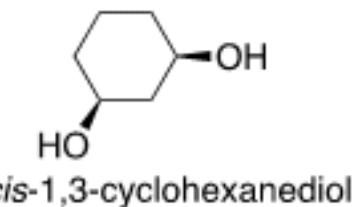


For *cis*-1,3-dimethylcyclohexane, which two chair conformations are in equilibrium?

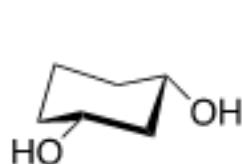
- A
- B
- C
- D
- E
- F



Select the most stable conformer of cis-1,3-cyclohexanediol



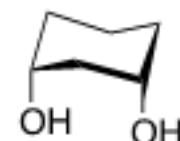
I



II



III



IV

STEREOSELECTIVE AND STEREOSPECIFIC REACTIONS:

A stereoselective process is one in which one stereoisomer predominates over another when two or more may be formed.

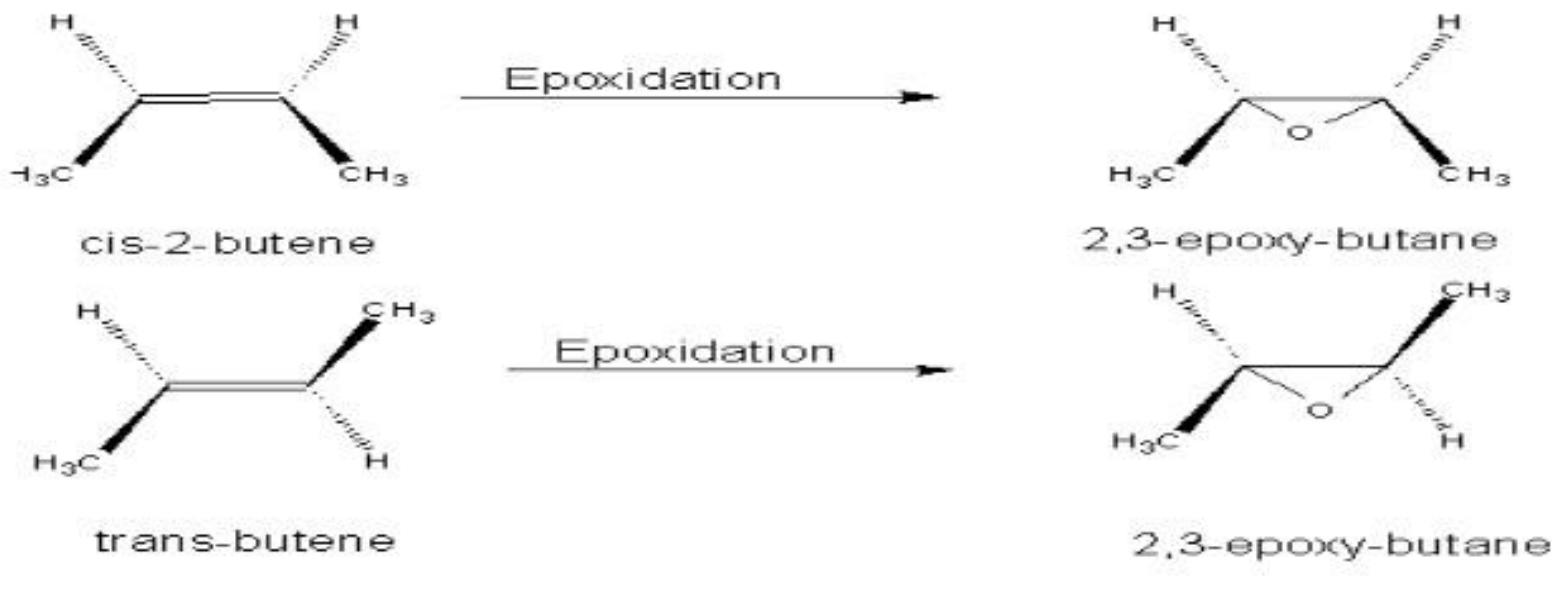
If the products are enantiomers, the reaction is **enantioselective**; if they are diastereoisomers, the reaction is **diastereoselective**.

Stereoselective reaction is a reaction which give us two stereoisomer, one of them is major (either due to the formation of a more stable product or through a more favourable reaction path with lesser activation energy).

Stereospecific reaction on the other hand is a reaction only allows formation of one stereoisomer. In this, the stereochemistry of the reactant completely determines the stereochemistry of the product without any other option.

Stereospecific Reaction

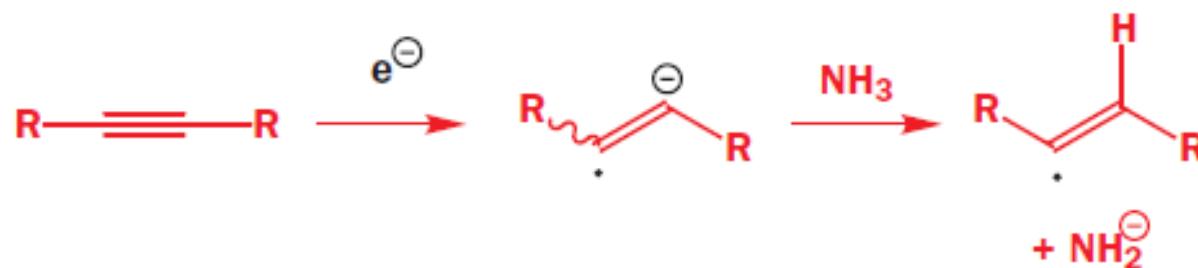
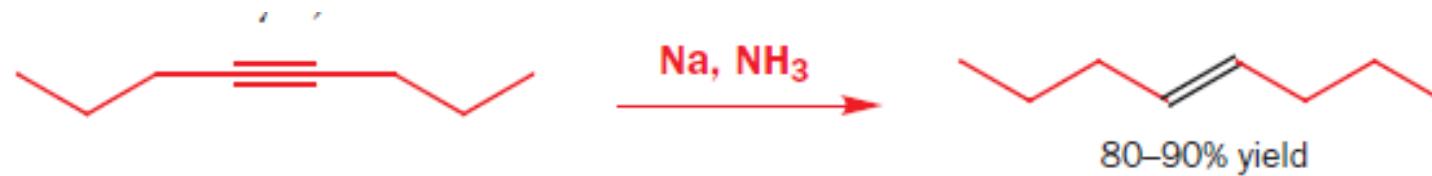
- Two stereochemically different reactants gives different stereoisomeric products in unequal amounts
- Reactants can exist as stereoisomers
- Different stereoisomers produces different stereoisomers in different ratio



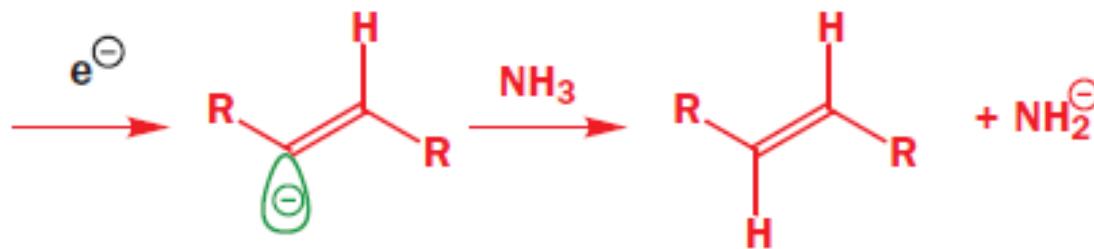
Stereospecific Reaction

- **Stereoselectivity** is the property of a chemical reaction in which a single reactant forms an unequal mixture of stereoisomers during a non-stereospecific creation of a new stereocenter or during a non-stereospecific transformation of a pre-existing one.
- The selectivity arises from differences in steric effects and electronic effects in the mechanistic pathways leading to the different products.
- Stereoselectivity can vary in degree but it can never be total since the activation energy difference between the two pathways is finite.

Stereoselective reaction:- is one in which the reactant is not necessarily chiral (as in the case of an alkyne) but in which the reaction produces predominantly or exclusively one stereoisomeric form of the product.



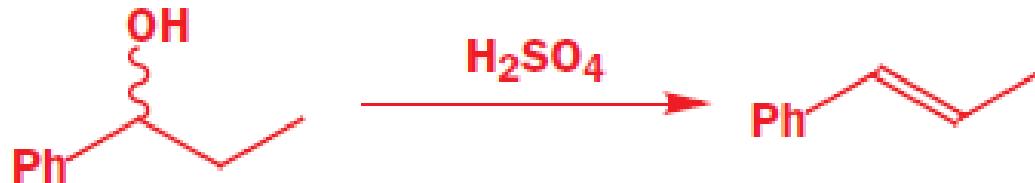
negative charge in sp² orbital



anion chooses to be *E*

Stereochemistry of E1 and E2 Reactions

E1 reactions are Stereoselective and Regiospecific : they form predominantly the more stable alkene. (and more substituted alkene: Saytzeff elimination).

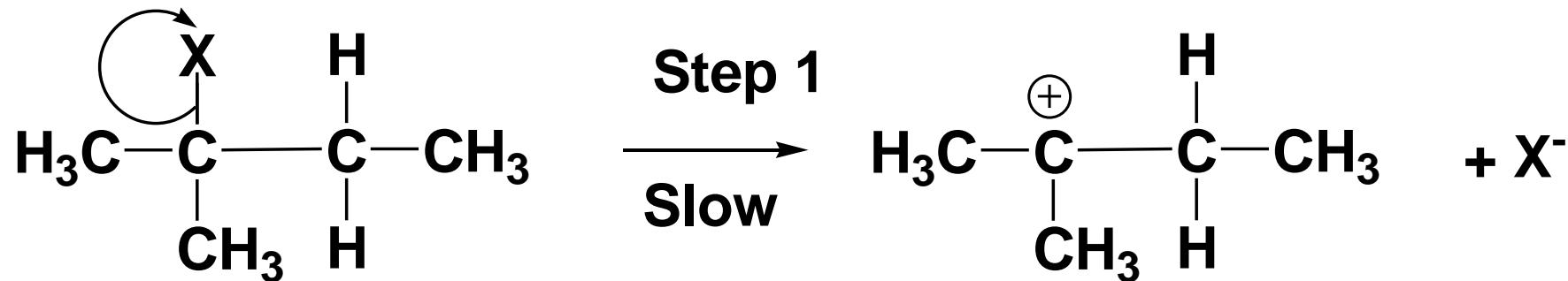


E2 reactions are both stereospecific , stereoselective and regiospecific: Gives 100% anti elimination product as well as form predominantly the more stable alkene.

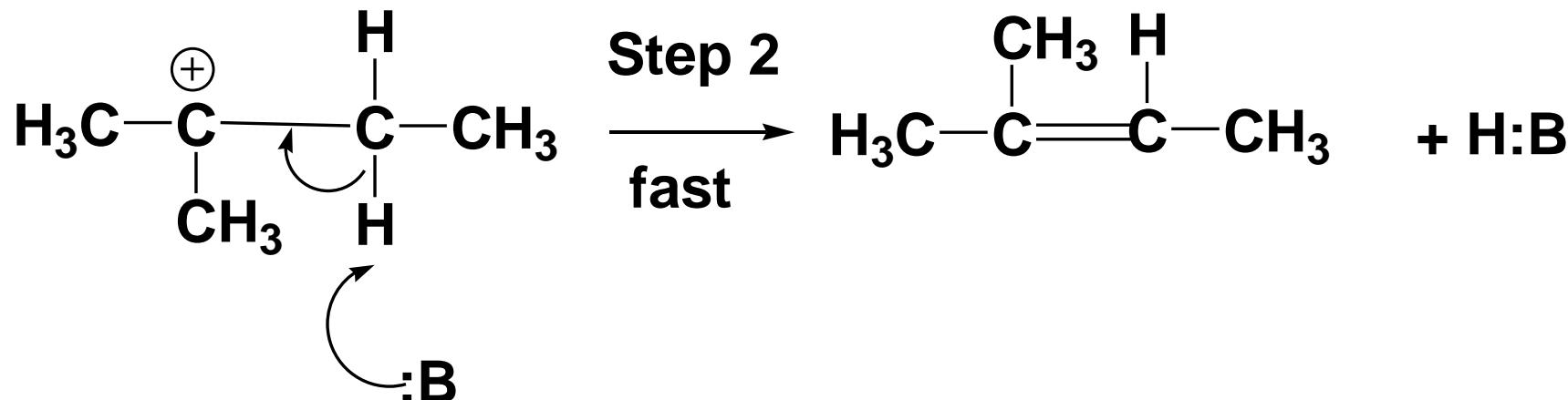
E1 Reaction Mechanism

Two step mechanism (similar to S_N1)

Step 1: substrate undergoes slow heterolysis to form halide ion and a carbocation intermediate

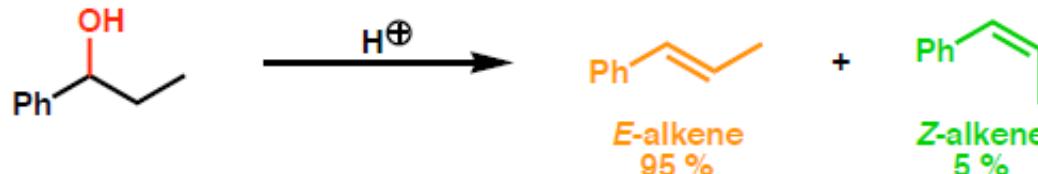


Step 2: the carbocation rapidly loses a proton to the base and forms the alkene

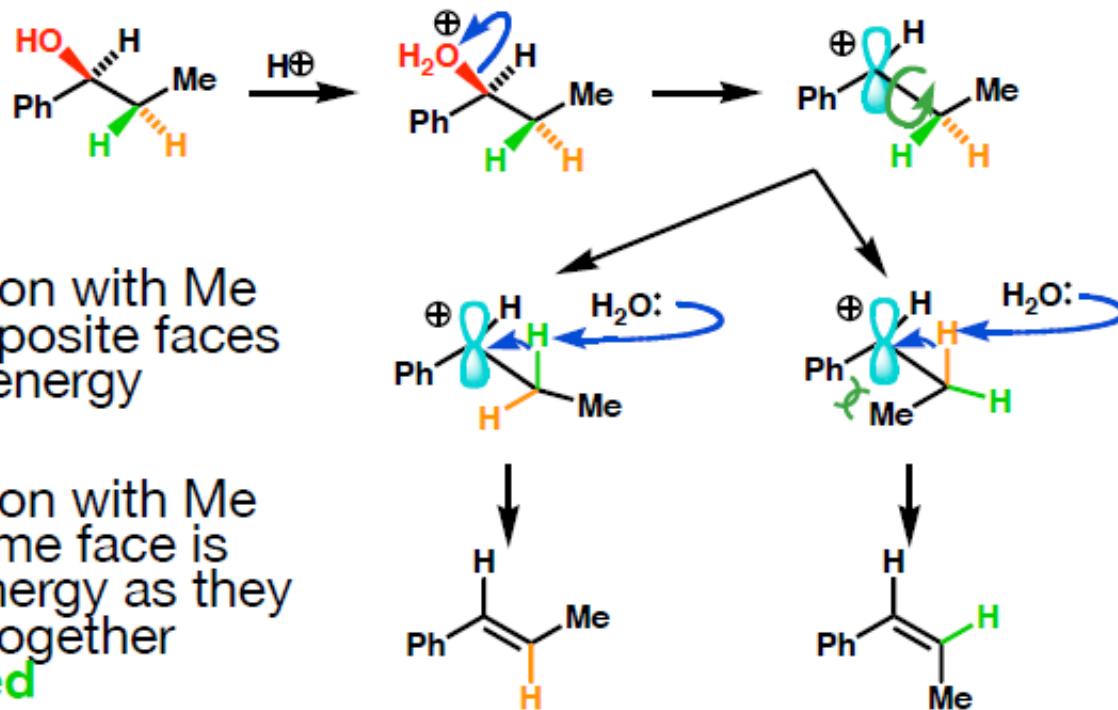


Stereoselectivity in E1 (*E* or *Z*)

- Potential for two products, *E* or *Z* alkene
- E* normally favoured as substituents far apart



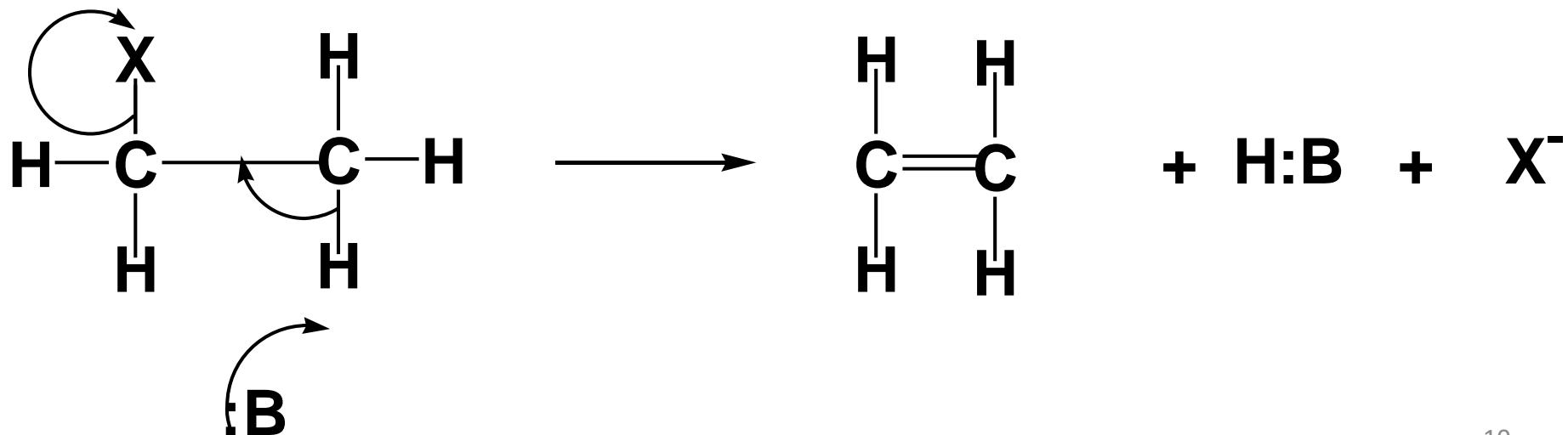
- First cation formation
- Second bond rotation to align empty p orbital & C-H σ bond

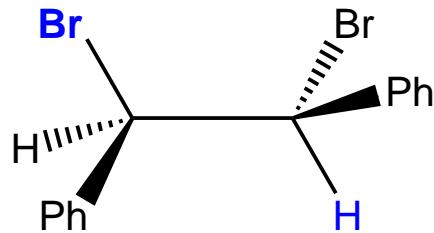


- Conformation with Me & Ph on opposite faces is lower in energy
- Favoured**
- Conformation with Me & Ph on same face is higher in energy as they are closer together
- Disfavoured**

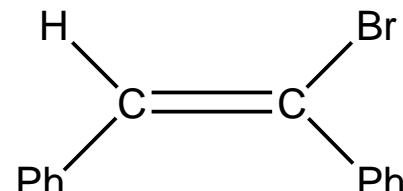
E2 Reaction Mechanism : Elimination bimolecular

- ❖ Reaction involves a single step
- ❖ The base pulls the β -proton, simultaneously the leaving group departs with its electron pair and the double bond forms
- ❖ It is analogous to S_N2 and often competes with it

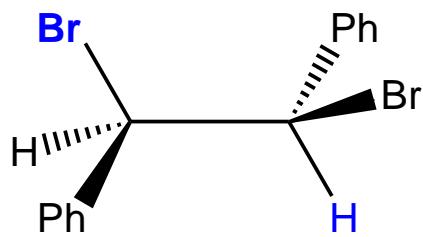




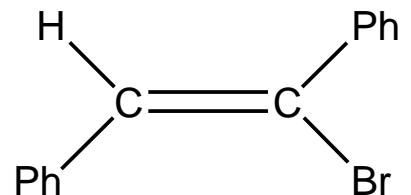
**R,S-1,2-dibromo-1,2-diphenylethane
Meso**



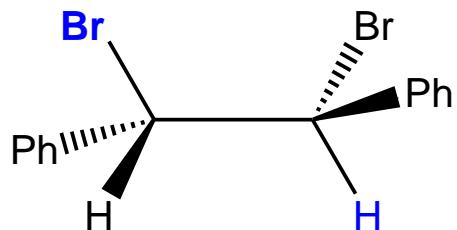
**E-isomer
2-Bromostilbene**



S,S-1,2-dibromo-1,2-diphenylethane



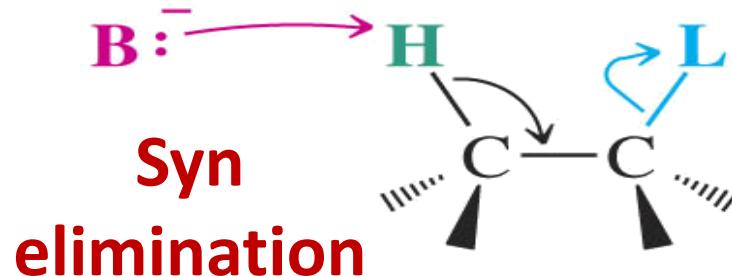
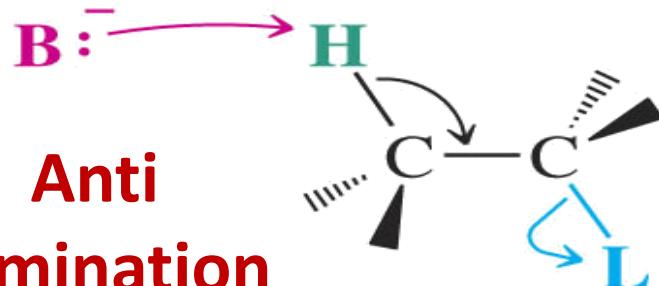
**Z-isomer
2-Bromostilbene**



**R,R-1,2-dibromo-1,2-diphenylethane
d,l-isomer**

E2 Mechanism is stereospecific

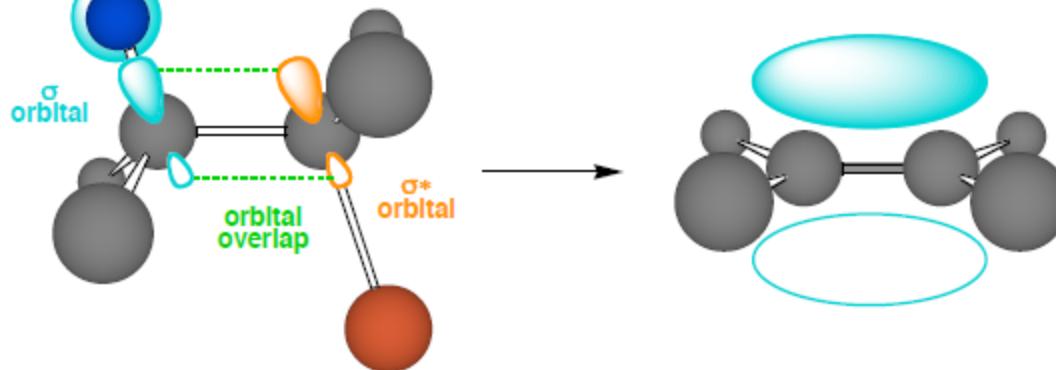
The five atoms involved(including the base) in the transition state must be in one plane. Thus two conformations are possible.



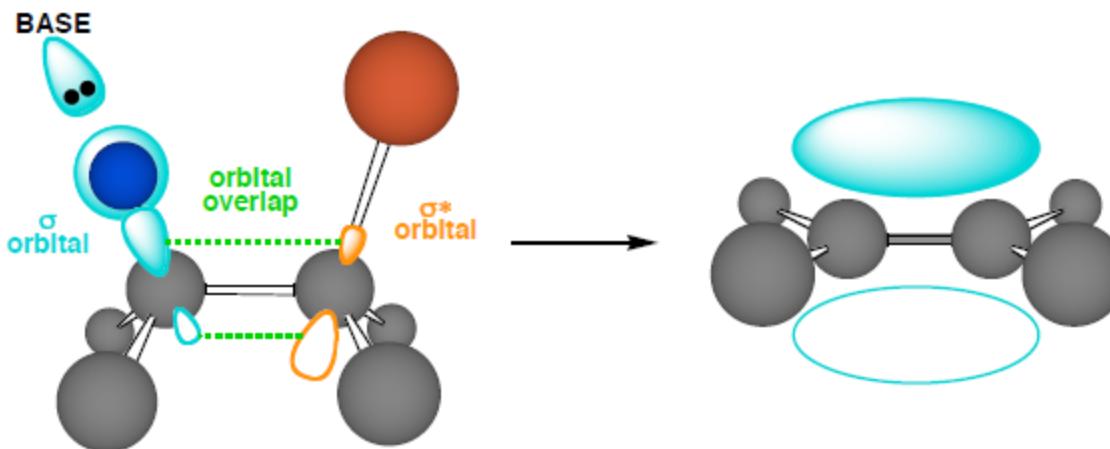
The transition state of anti-elimination is lower in energy than that in syn-elimination because of staggered conformation and thus antielimination is usually greatly favored over syn elimination. Acyclic molecules can easily

BASE

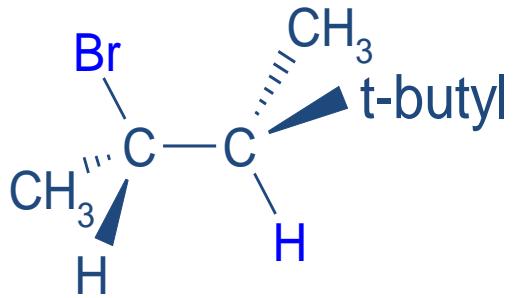
Anti-periplanar



Syn-periplanar



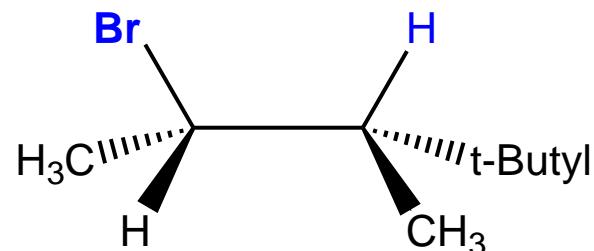
(S,S)-diastereomer



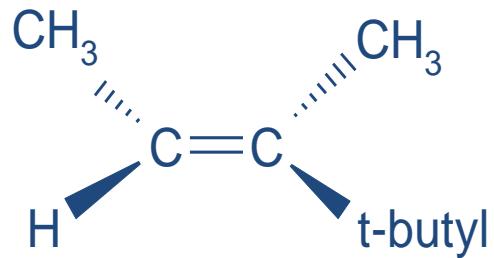
KOH
ethanol
heat

If anti

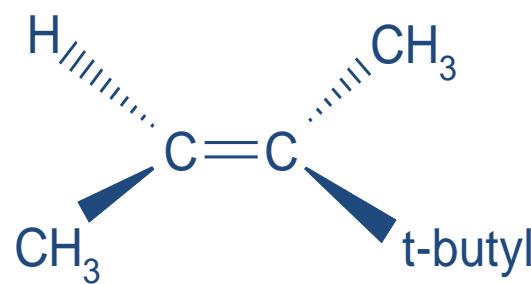
If syn



Actual
product

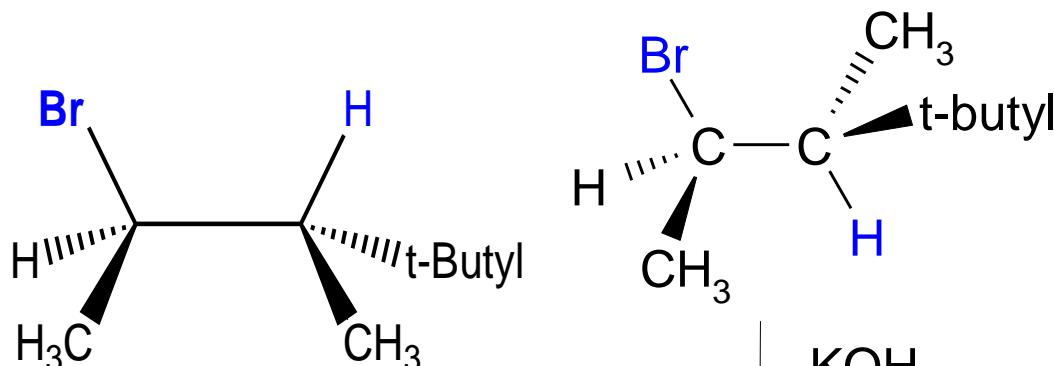


(E)-isomer



(Z)-isomer

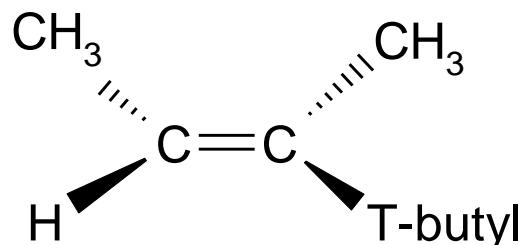
(R,S) -diastereomer



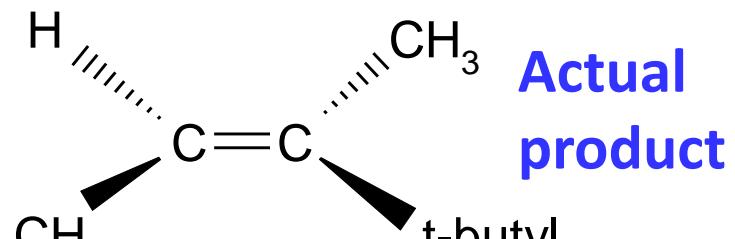
KOH
ethanol
heat

If syn

If anti



(E)-isomer

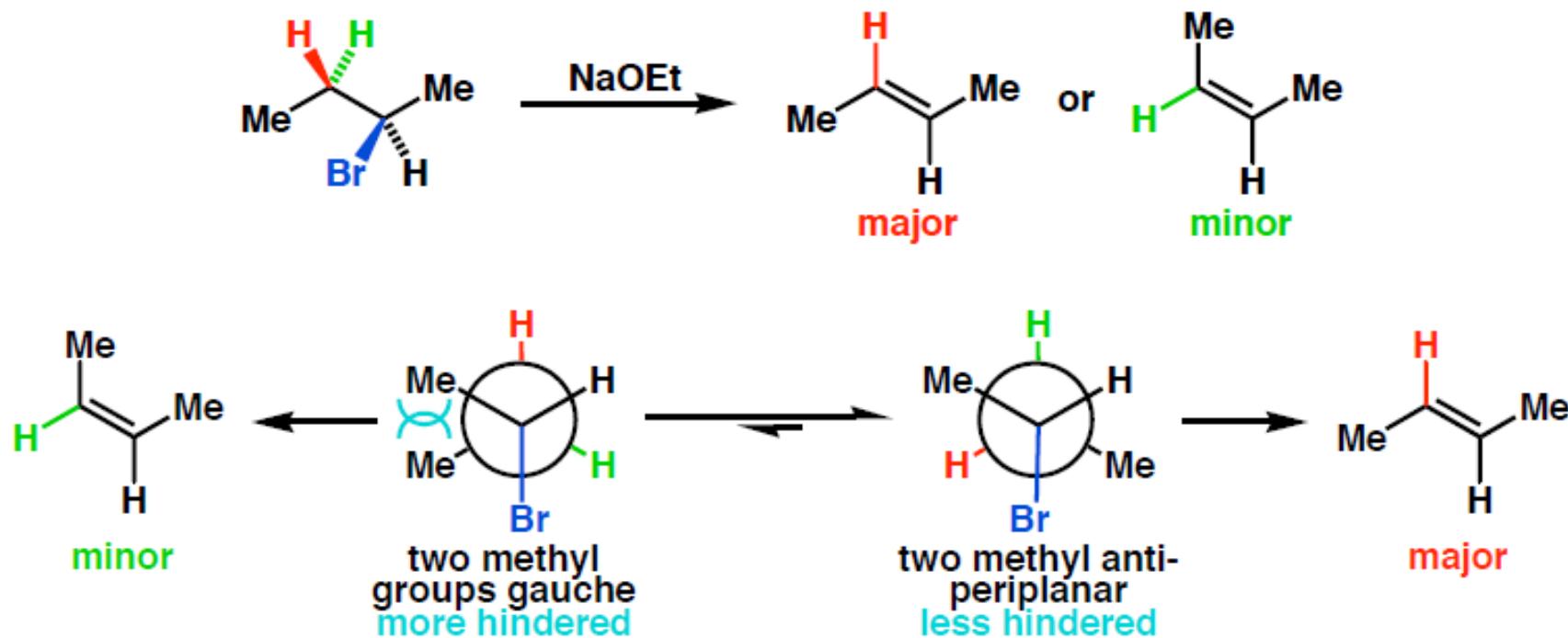


(Z)-isomer

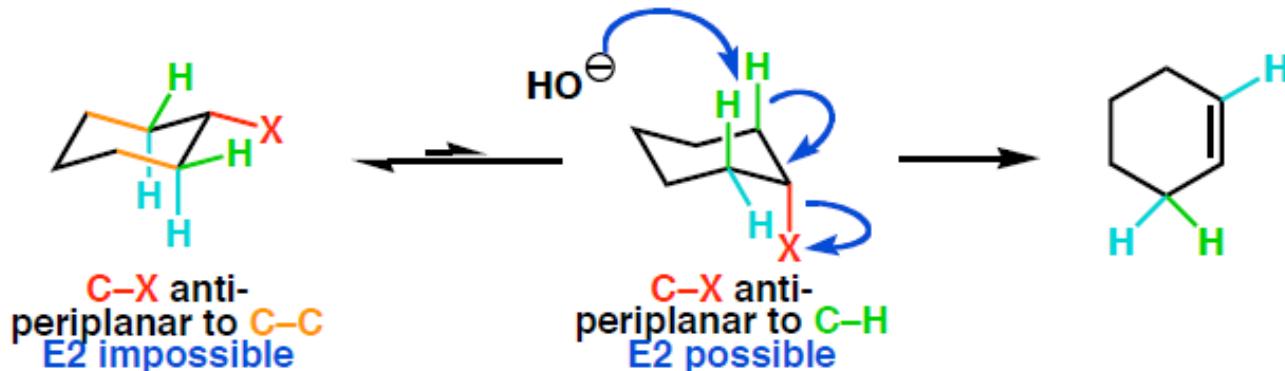
Actual
product

Stereoselectivity in E2

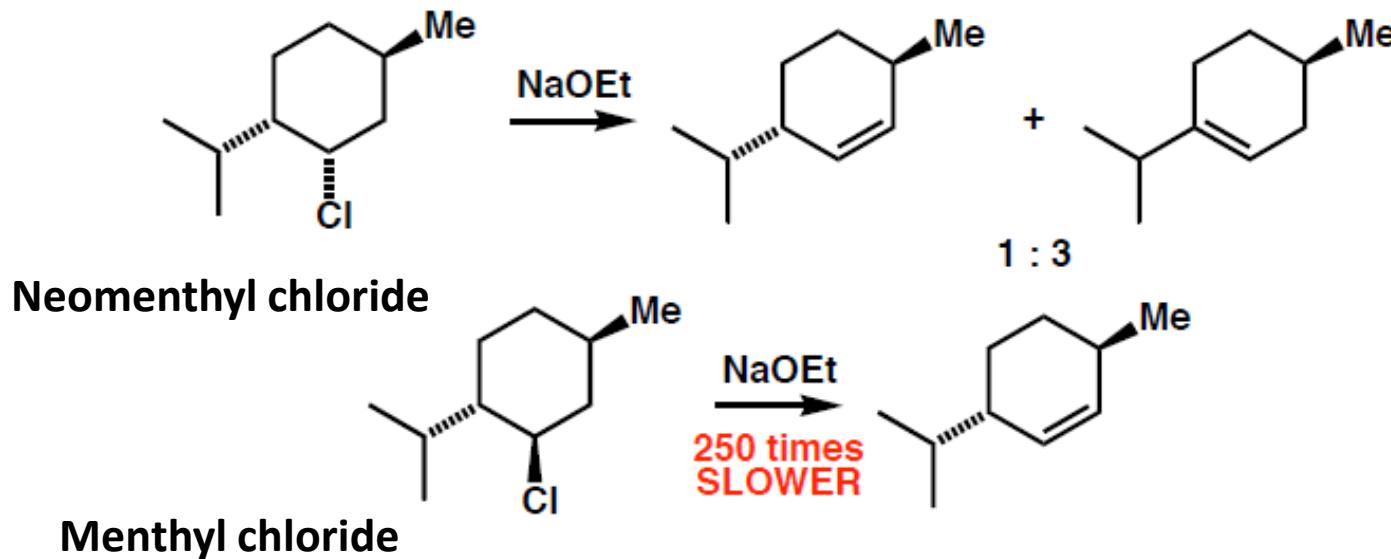
- Stereo**Selectivity** - mechanistically there is a choice of two products but one is favoured - there is a choice
- If two protons can be eliminated the reaction will proceed via the **anti-periplanar** transition state that suffers **least** steric hindrance



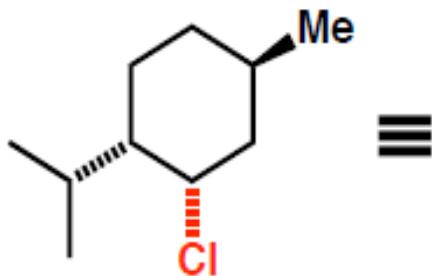
E2 Eliminations from cyclohexanes



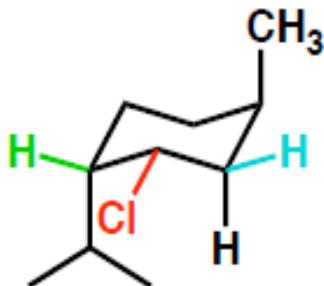
- Necessity for **anti-periplanar** conformation has a huge effect in cyclohexanes
- For **E2** we must have **C-H** & **C-X** both **axial** (trans-diaxial)
- Below shows the effect of this requirement...



disfavoured: *i*-Pr axial
E2 not possible
no anti-periplanar C–H

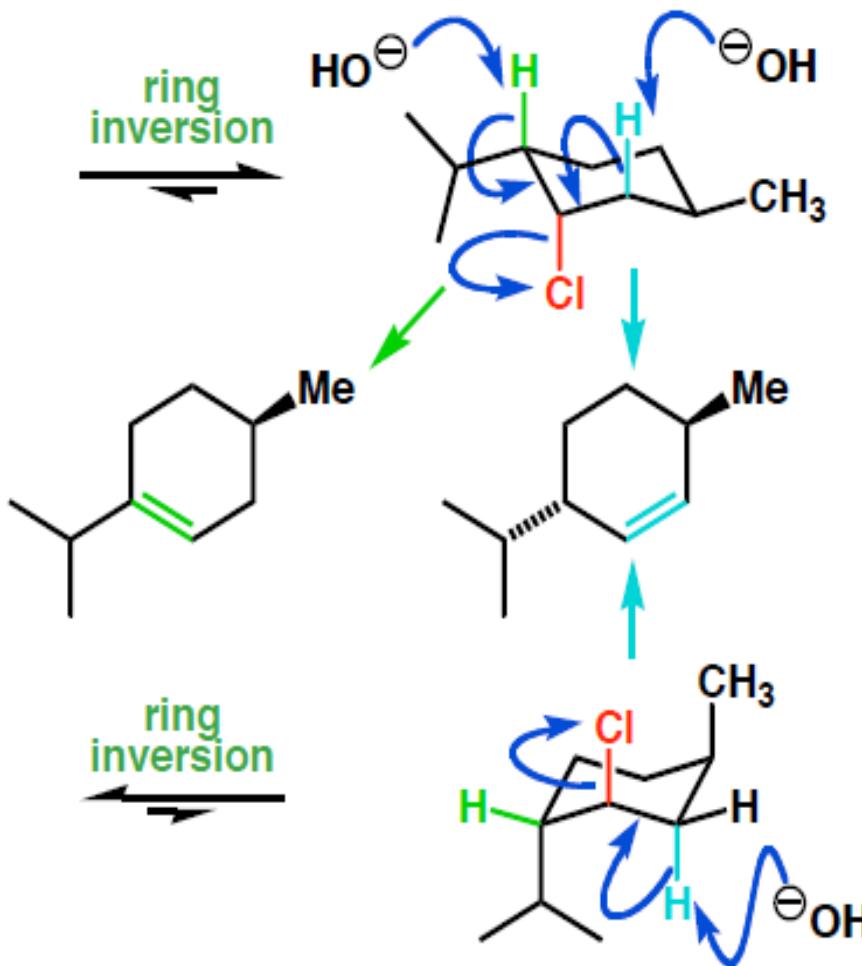


\equiv

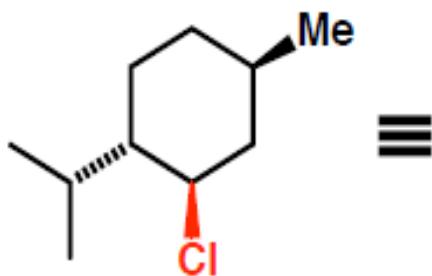


ring inversion

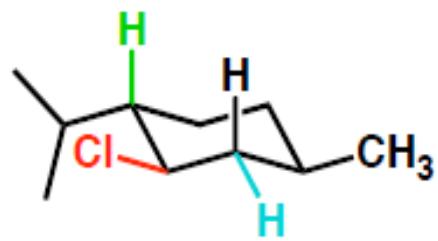
favoured: *i*-Pr equatorial
E2 possible
2 anti-periplanar C–H



favoured: *i*-Pr equatorial
E2 not possible
no anti-periplanar C–H

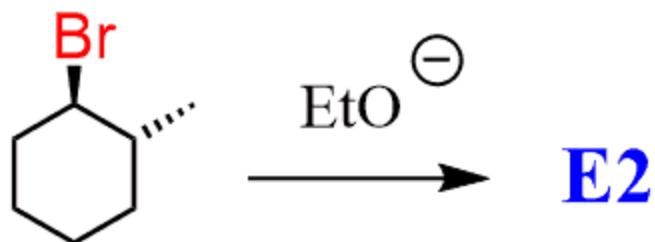


\equiv

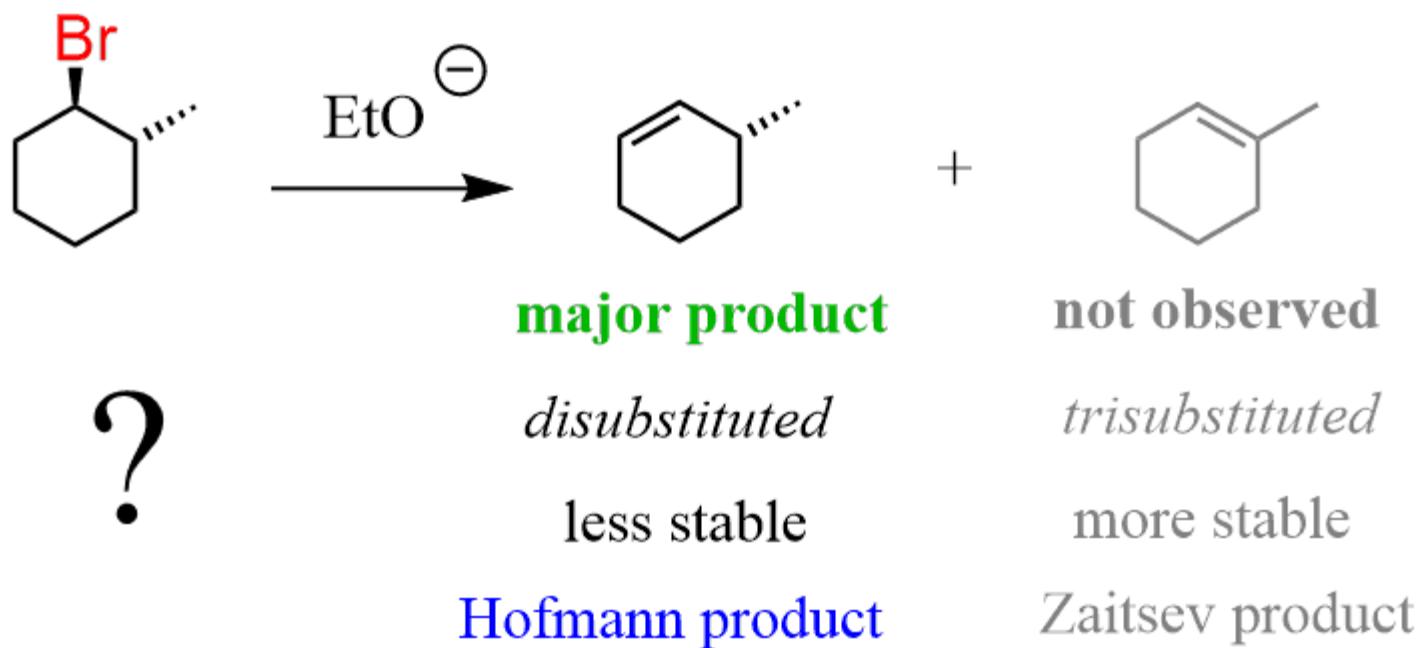


ring inversion

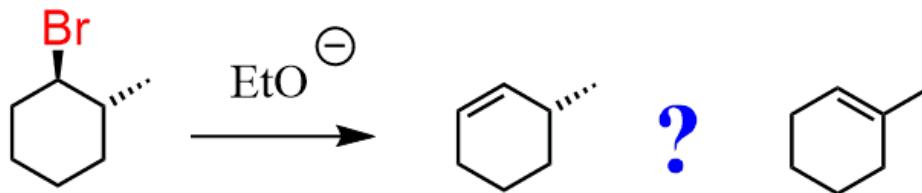
disfavoured: *i*-Pr axial
but E2 possible
Slow as rarely in this conformation



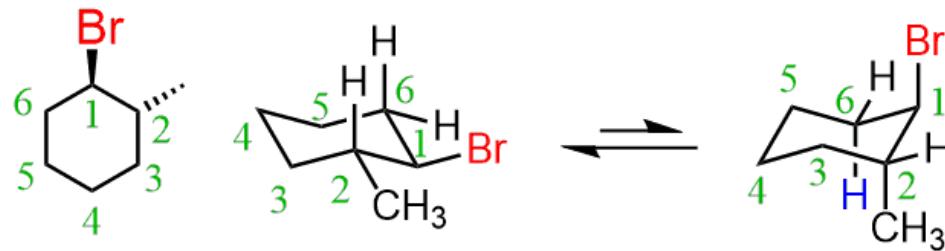
Sterically unhindered base - Zaitsev expected major product



Regiochemistry in E2 Reactions of Cyclohexanes

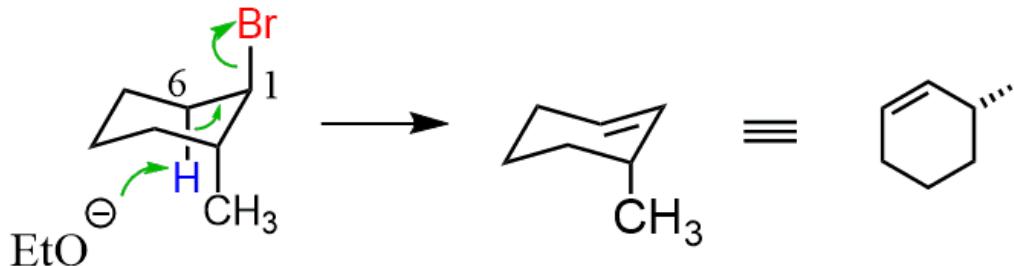


Step 1. Draw the ring flip of the cyclohexane:



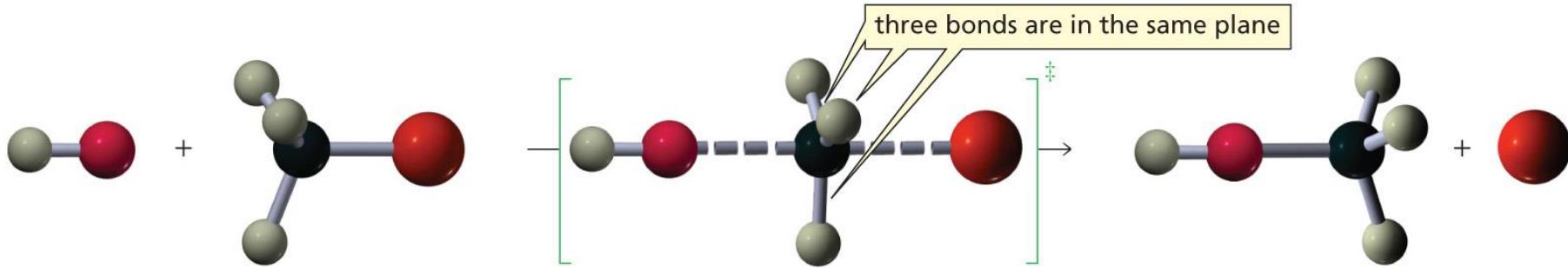
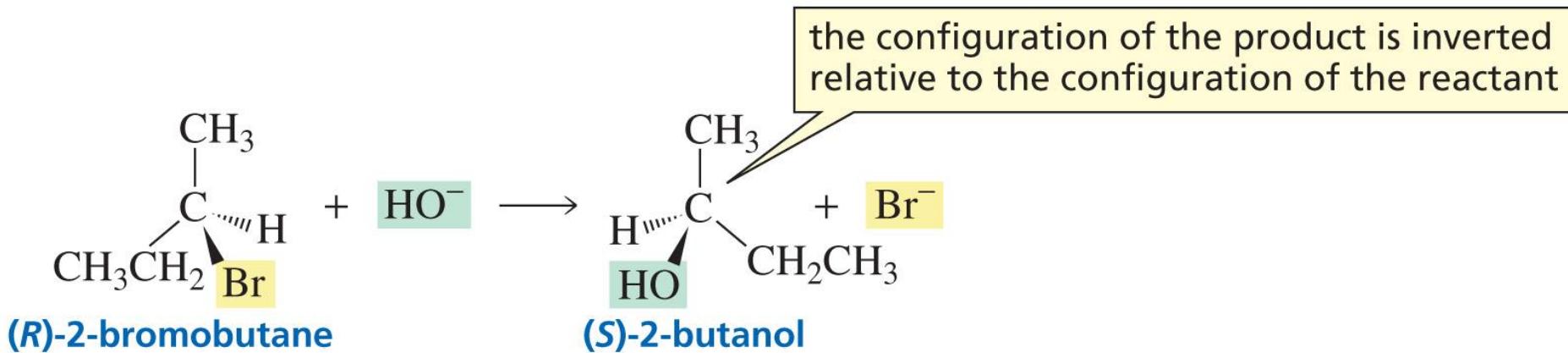
only the β -H on carbon 6
can do E2.

Step 2. Show the E2 attacking the β -H at 180° to the LG:



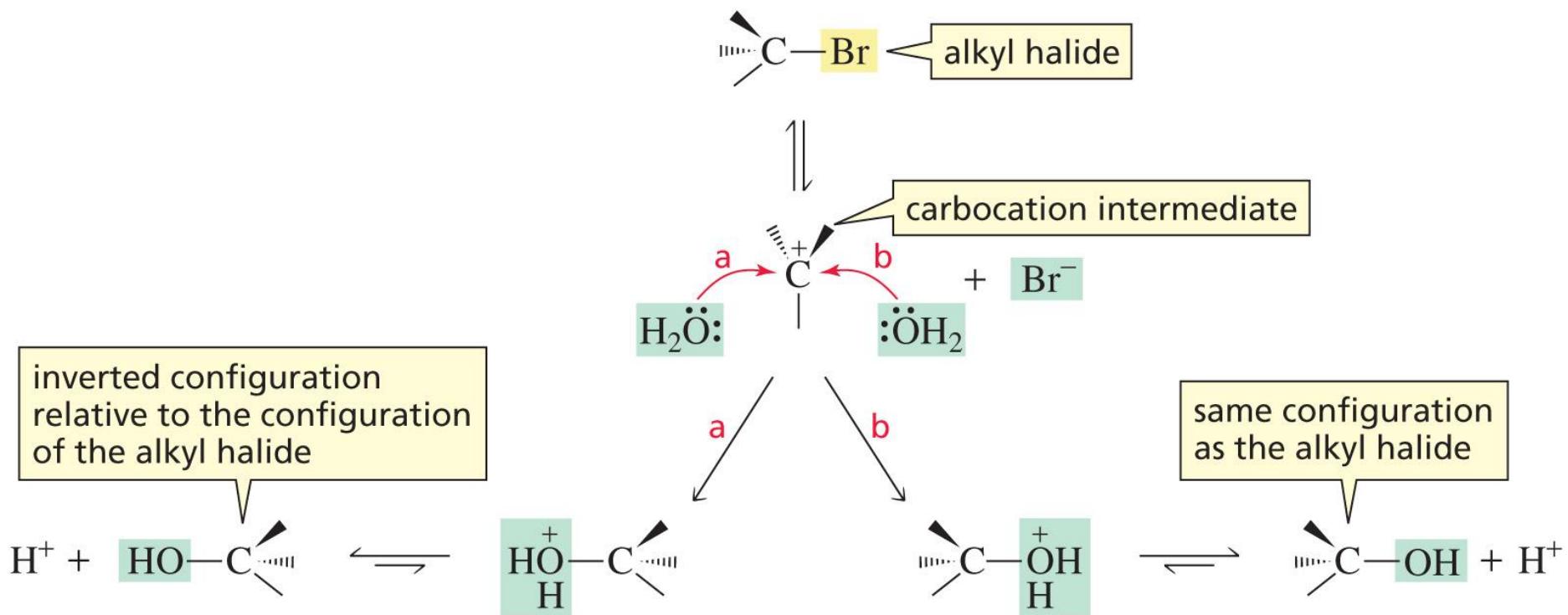
Stereochemistry of S_N1 and S_N2 Reactions

S_N2 is stereospecific; S_N1 is non stereospecific



Inversion of configuration (Walden inversion) in an S_N2 reaction is due to back side attack

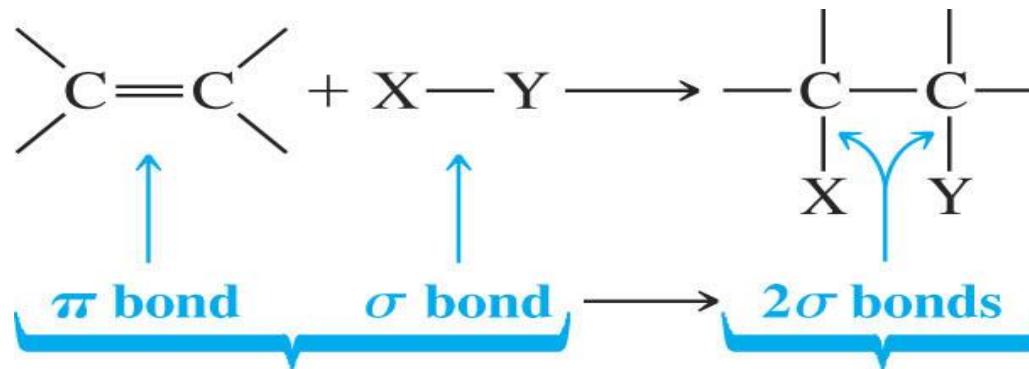
The carbocation intermediate in S_N1 leads to the formation of two stereoisomeric products



Copyright © 2007 Pearson Prentice Hall, Inc.

R-Alkyl halide → R and S Alcohol (Racemic mixture)
S-Alkyl halide → R and S Alcohol (Racemic mixture)

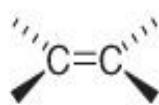
Stereochemistry of Addition Reactions



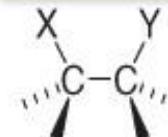
Bonds broken

Bonds formed

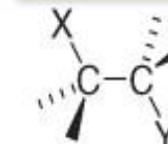
Two modes
of addition



syn addition

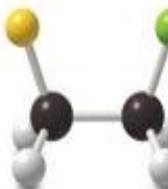
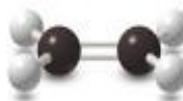


or

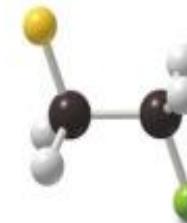


X and Y added from
opposite sides

X and Y added from
the same side

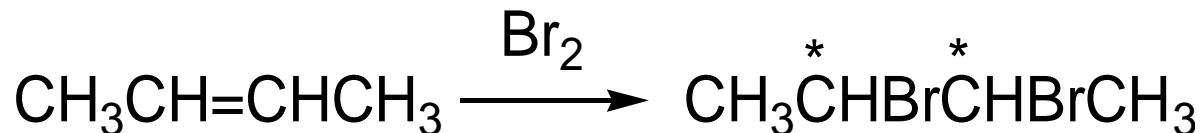


or



- ◆ *Syn addition* takes place when both X and Y are added from the same side.
- ◆ *Anti addition* takes place when X and Y are added from opposite sides.

Addition of Bromine (Br_2) to alkenes are Stereospecific



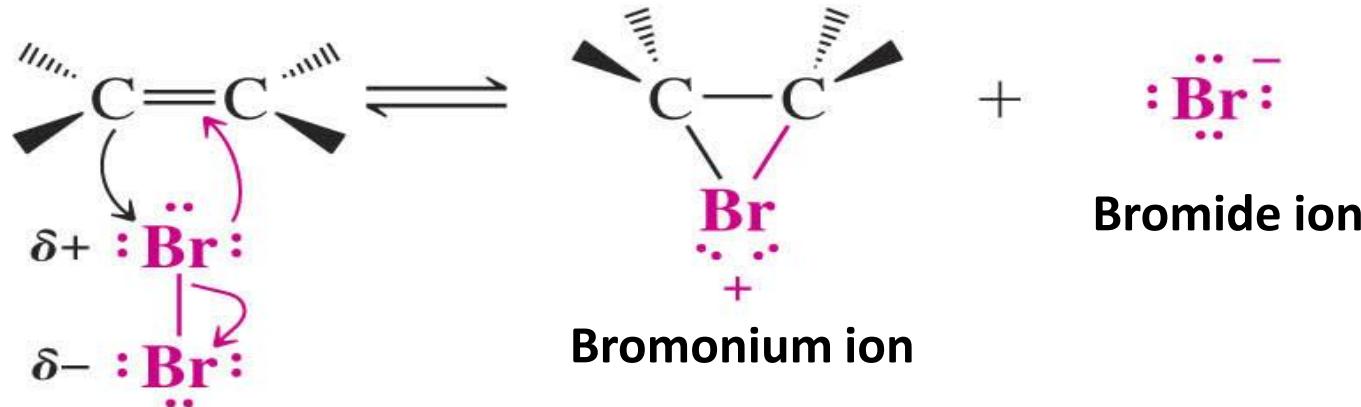
(Z)-2-butene gives racemic 2,3-dibromobutane and no meso compound is formed.

(E)-2-butene gives only meso-2,3-dibromobutane.

A reaction is stereospecific if a particular stereoisomer of the reactant produces a specific stereoisomer of the product.

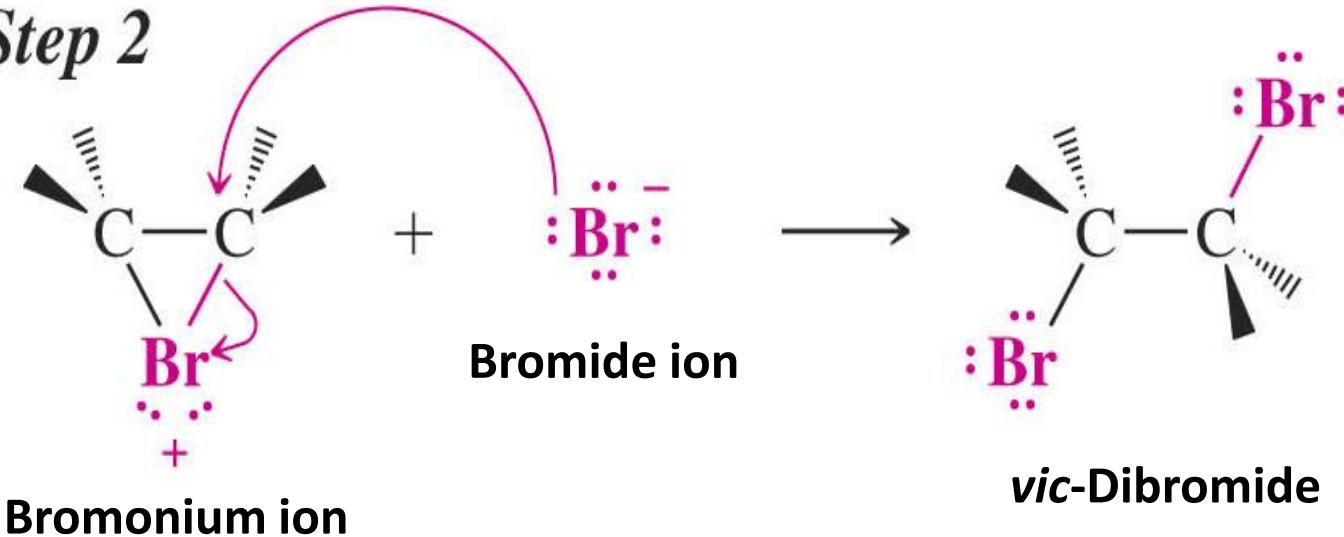
Mechanism

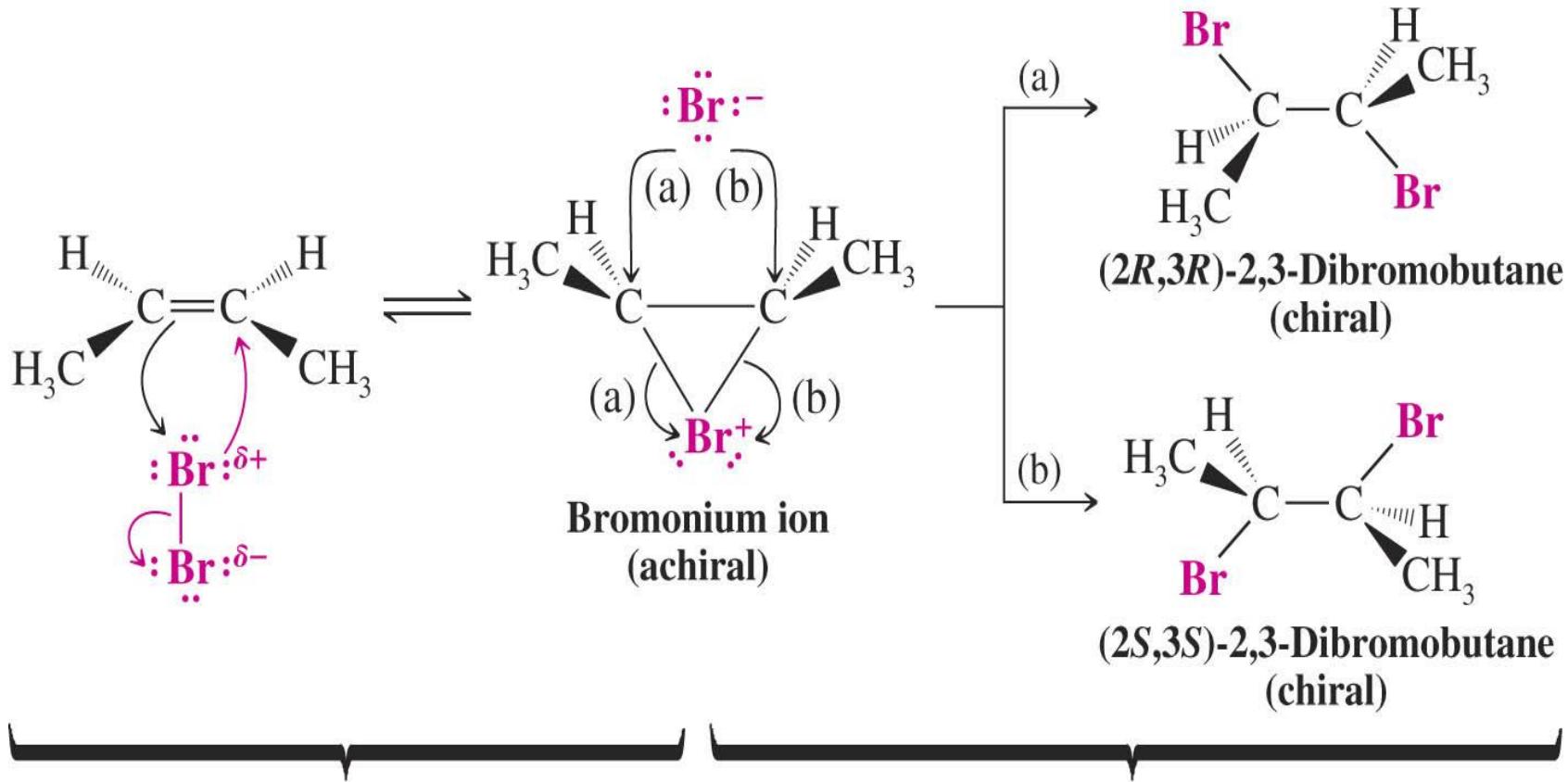
Step 1



The three -membered ring containing a positively charged halogen atom is called a bridged halonium ion.

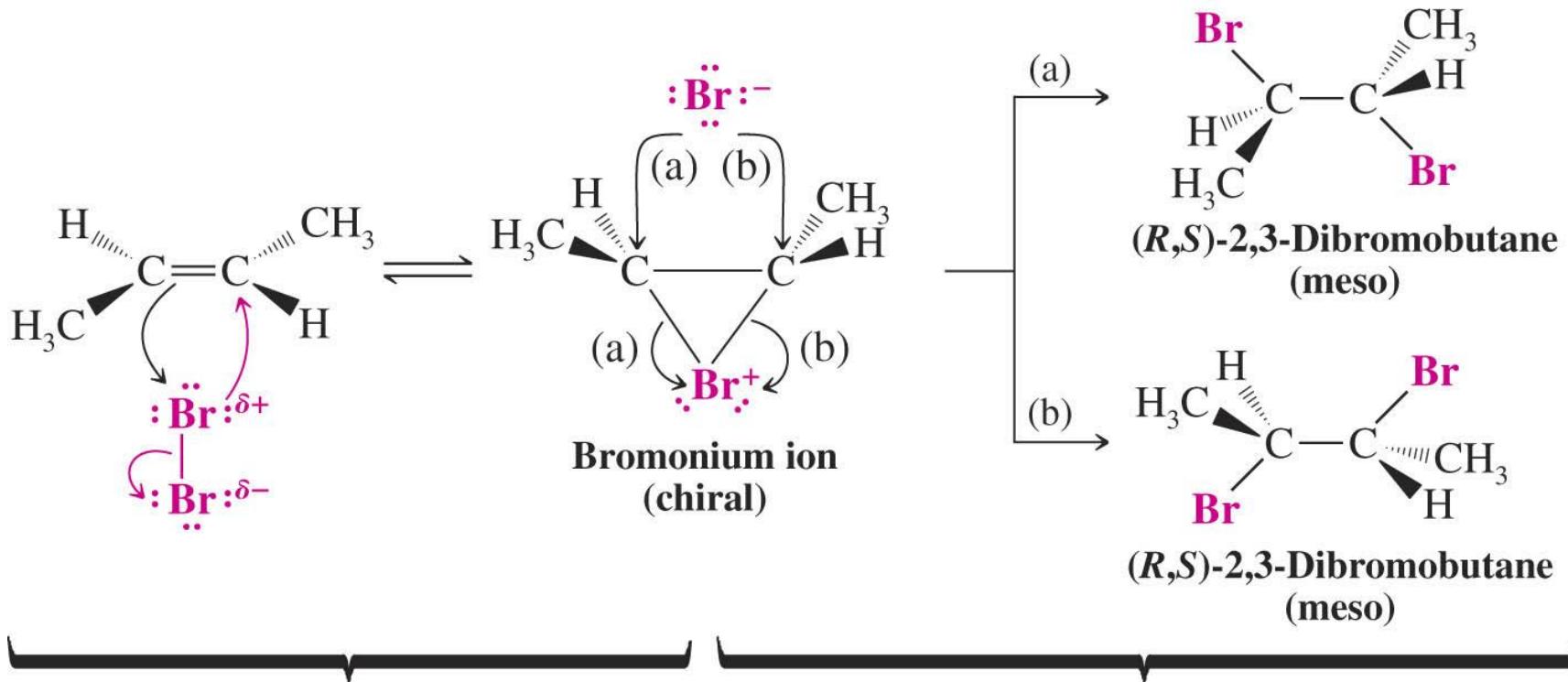
Step 2





cis-2-Butene reacts with bromine to yield an achiral bromonium ion and a bromide ion. [Reaction at the other face of the alkene (top) would yield the same bromonium ion.]

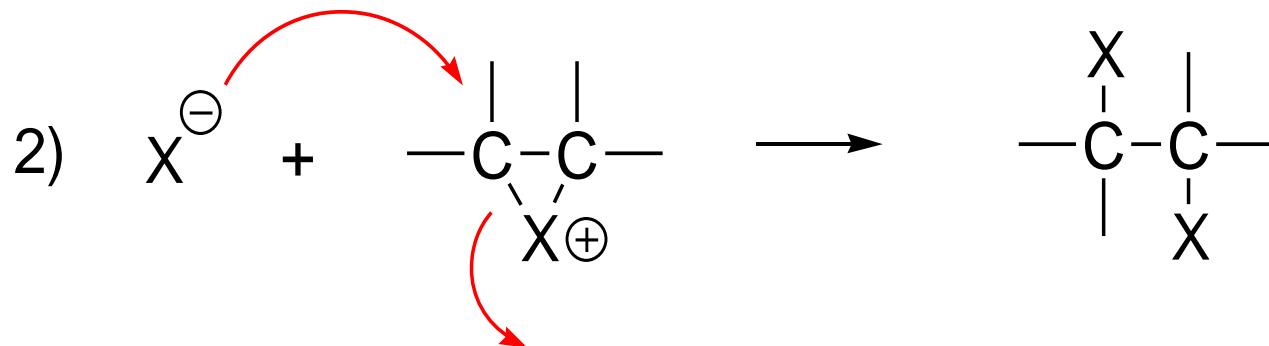
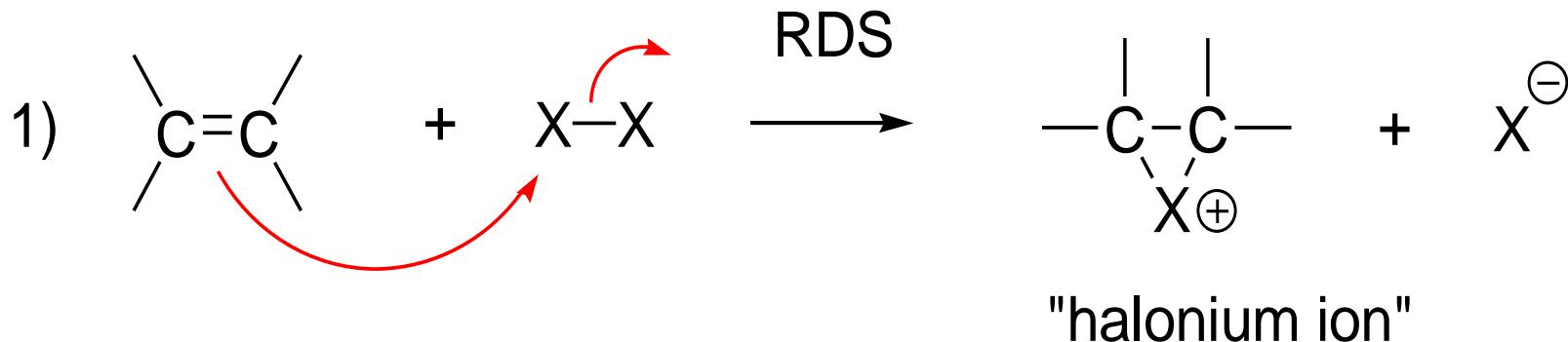
The bromonium ion reacts with the bromide ions at equal rates by paths (a) and (b) to yield the two enantiomers in equal amounts (i.e., as the racemic form).



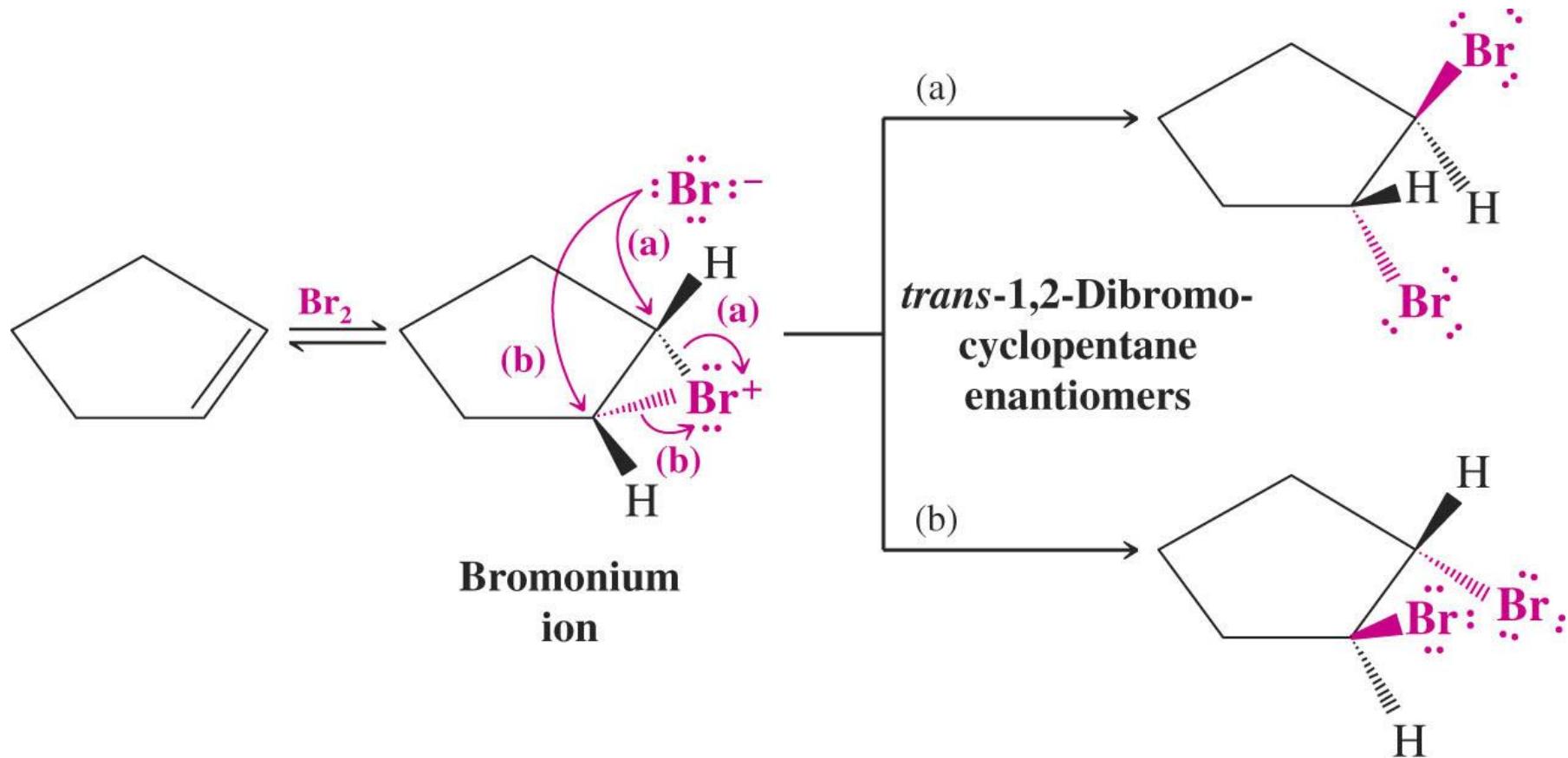
trans-2-Butene reacts with bromine to yield chiral bromonium ions and bromide ions. [Reaction at the other face (top) would yield the enantiomer of the bromonium ion as shown here.]

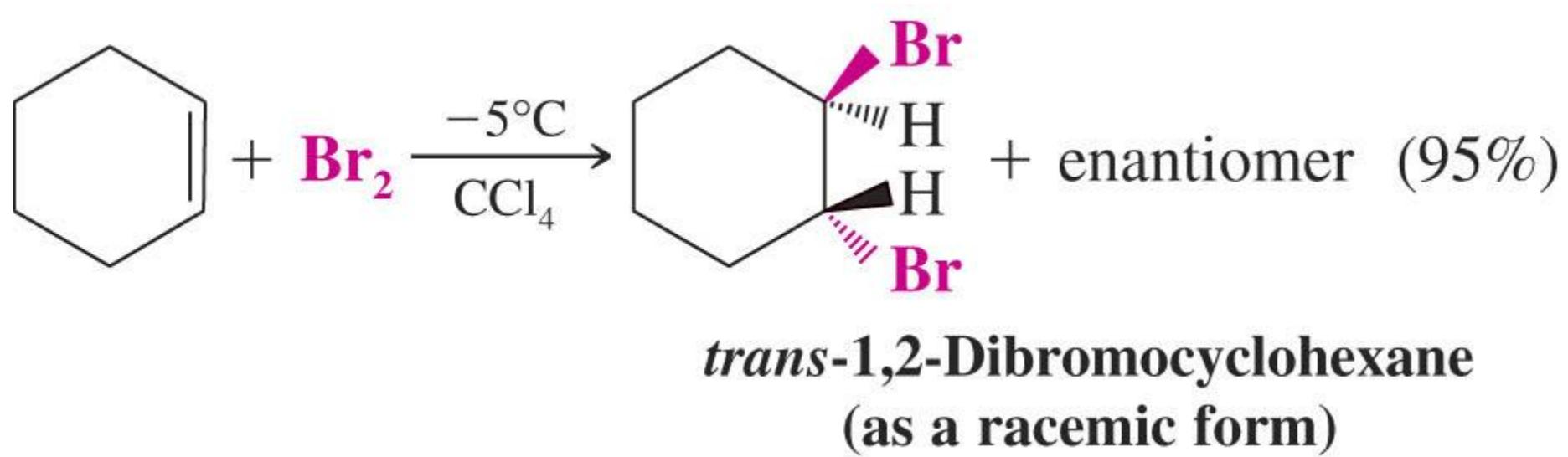
When the bromonium ions react by either path (a) or path (b), they yield the *same* achiral meso compound. [Reaction of the enantiomer of the intermediate bromonium ion would produce the same result.]

What does the stereochemistry tell us about the mechanism of addition of halogens to alkenes?

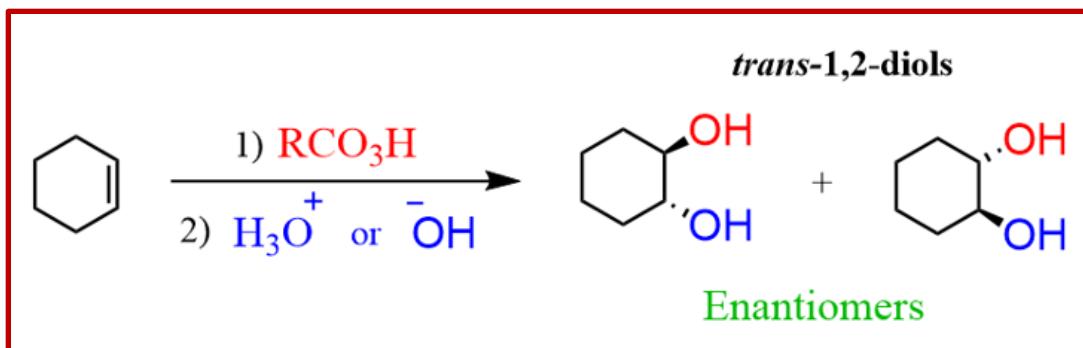
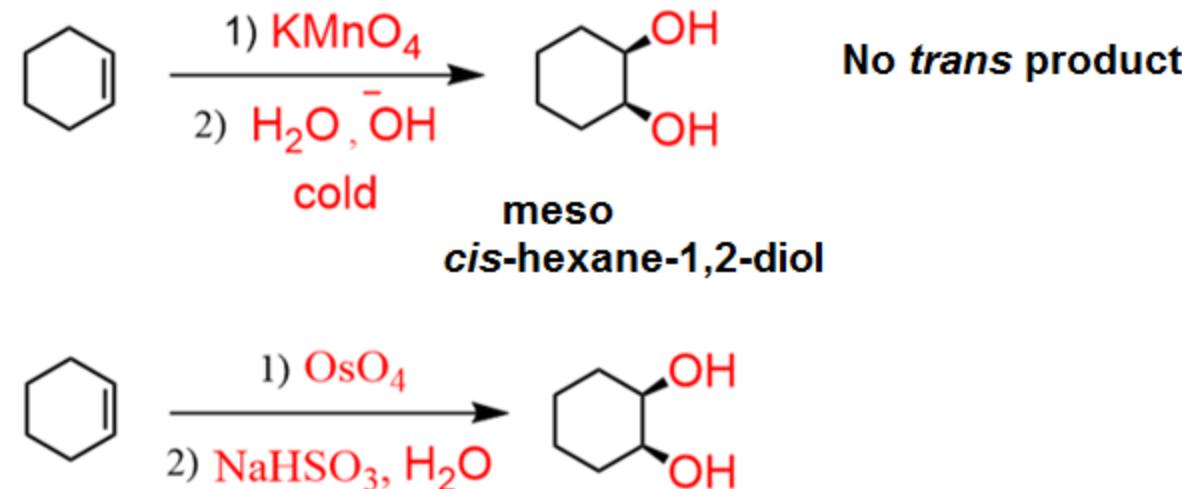


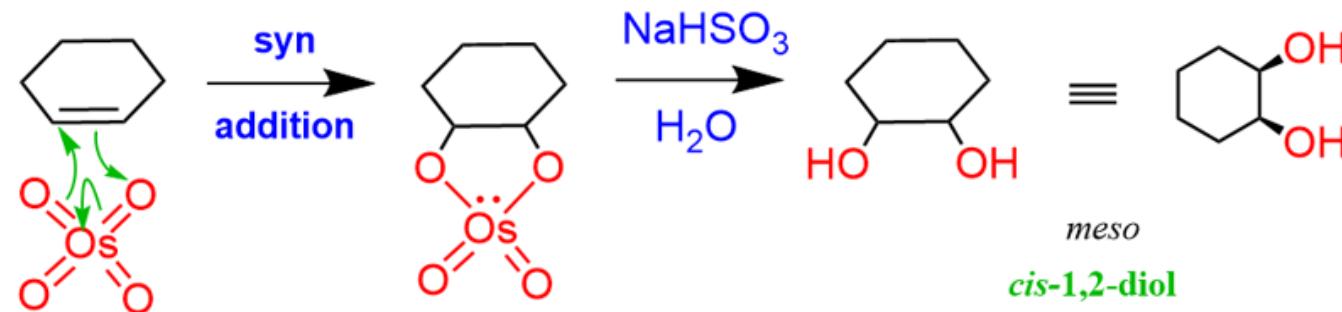
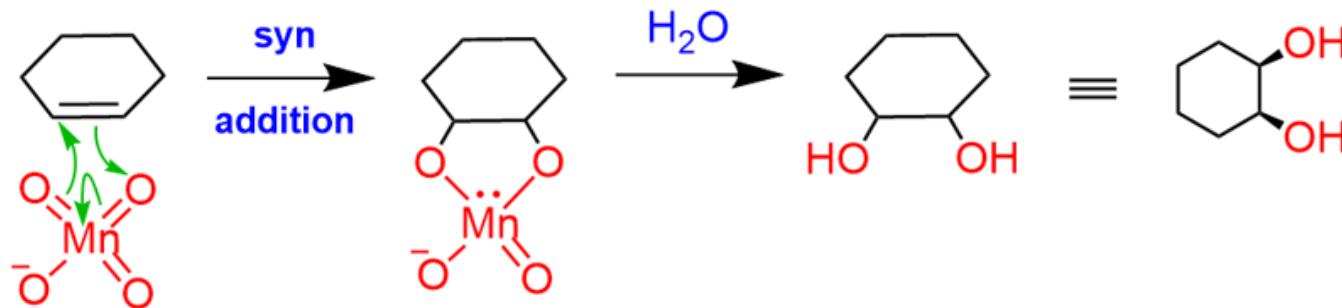
- Anti Addition
- Multi step process
- Cyclic bromonium ion Intermediate





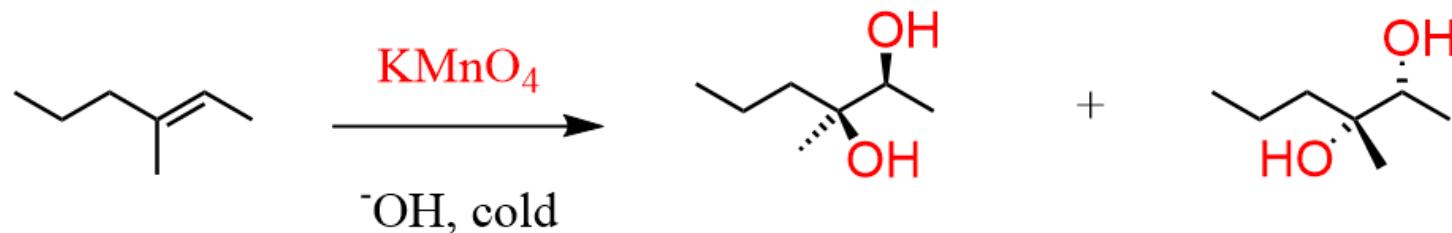
Dihydroxylation of alkenes (Formation of *cis*-1,2-diol and *trans*-1,2-diol)





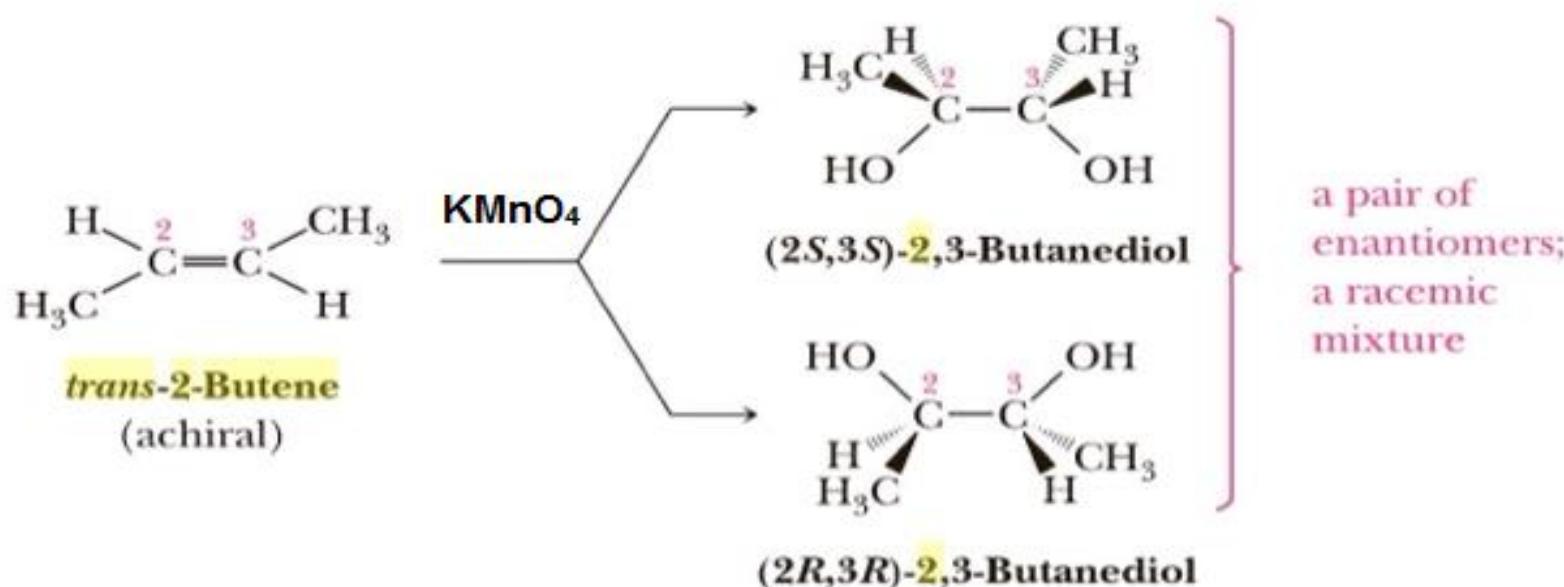
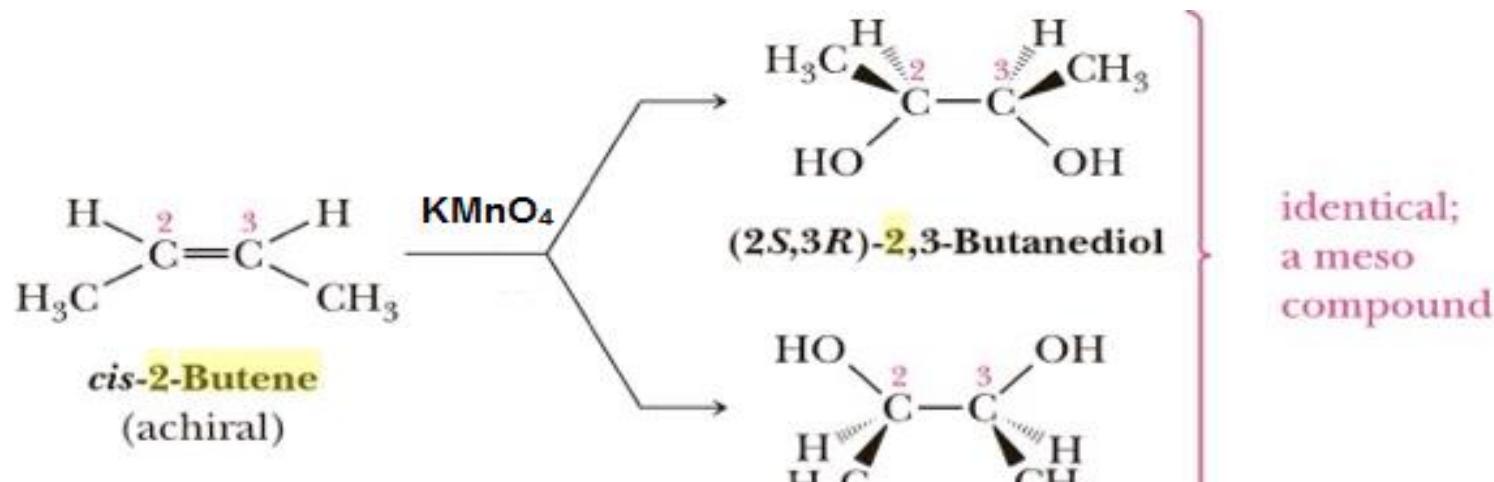
Oxygens add to the same face of the C=C

Stereospecific *Syn* addition



In case of unsymmetrical alkene, the *syn* dihydroxylation produces a pair of enantiomers:

Q: Find out the oxidation products for oxidation of *cis*-2-butene and *trans*-butene with KMnO_4 in basic cold condition. Is it stereospecific, If so why and how???



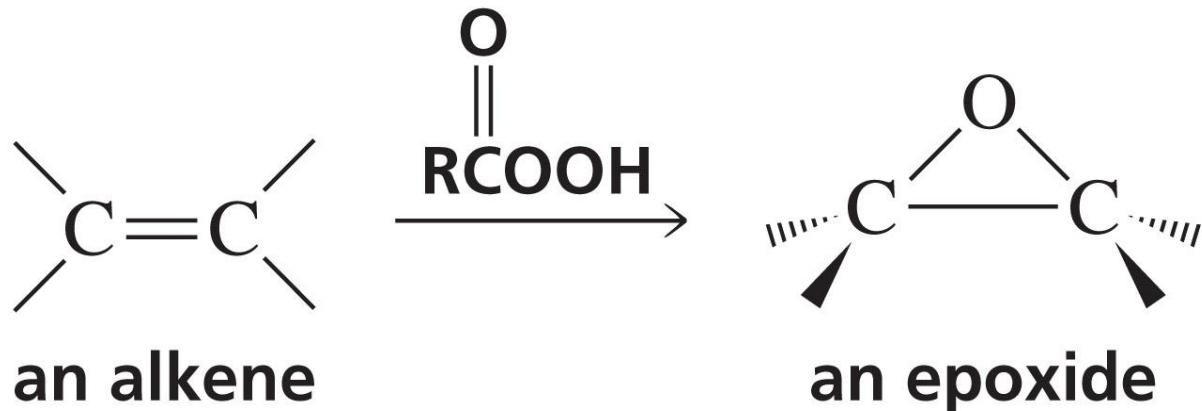
Oxidation with peroxy acids (ex m-CPBA (meta chloroperbenzoic acid), CH₃CO₂OH (peracetic acid) followed by hydrolysis gives the opposite

cis-2-butene → (*S,S*)- & (*R,R*)-2,3-dihydroxybutane

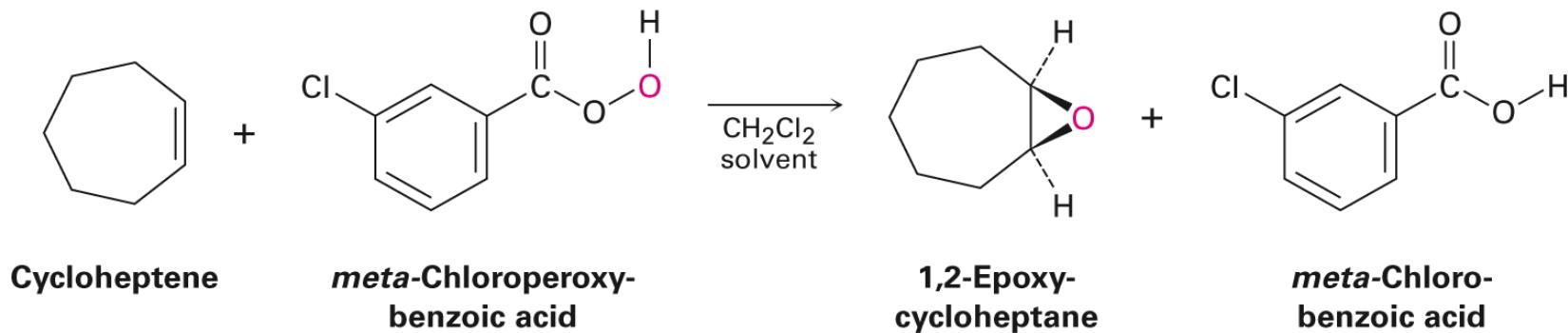
trans-2-butene → *meso*-2,3-dihydroxybutane

Two step process;

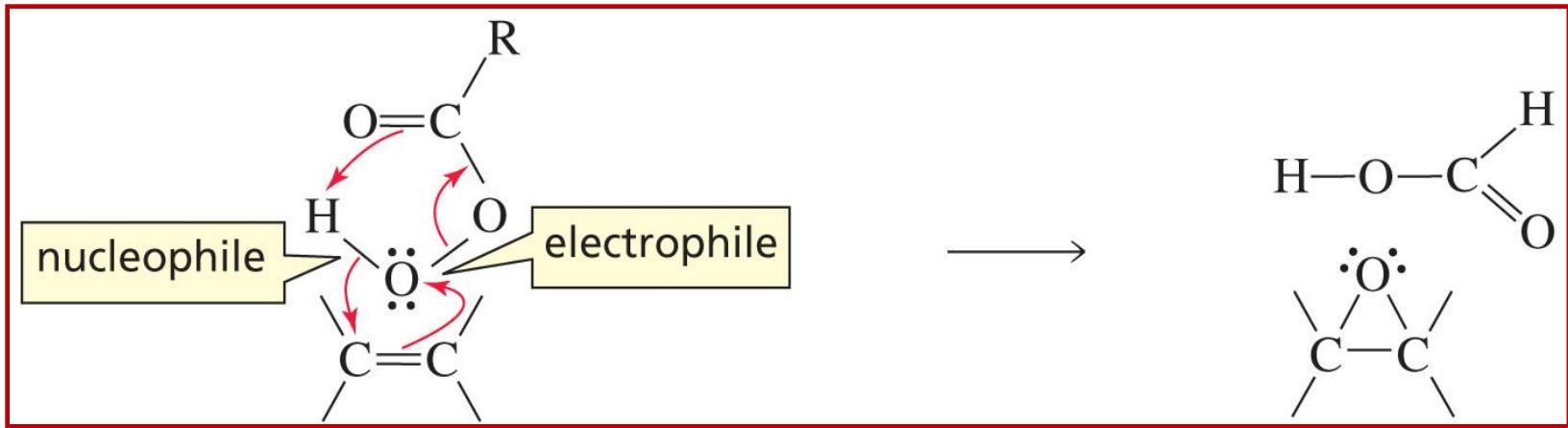
- 1. Epoxidation by peracid**
- 2. Acid-catalyzed ring-opening reaction of epoxide with water**



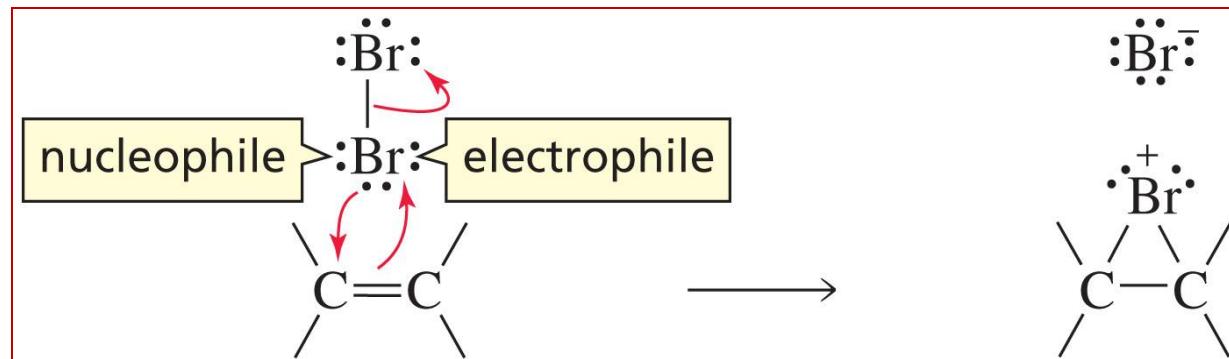
addition of peroxyacid is a syn addition



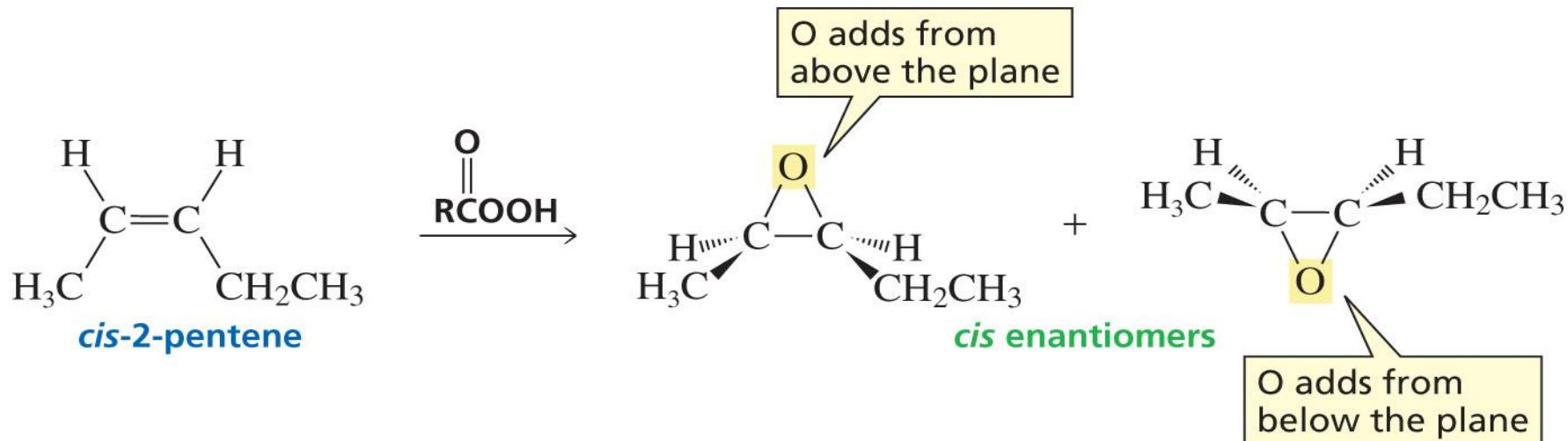
Mechanism for Epoxidation



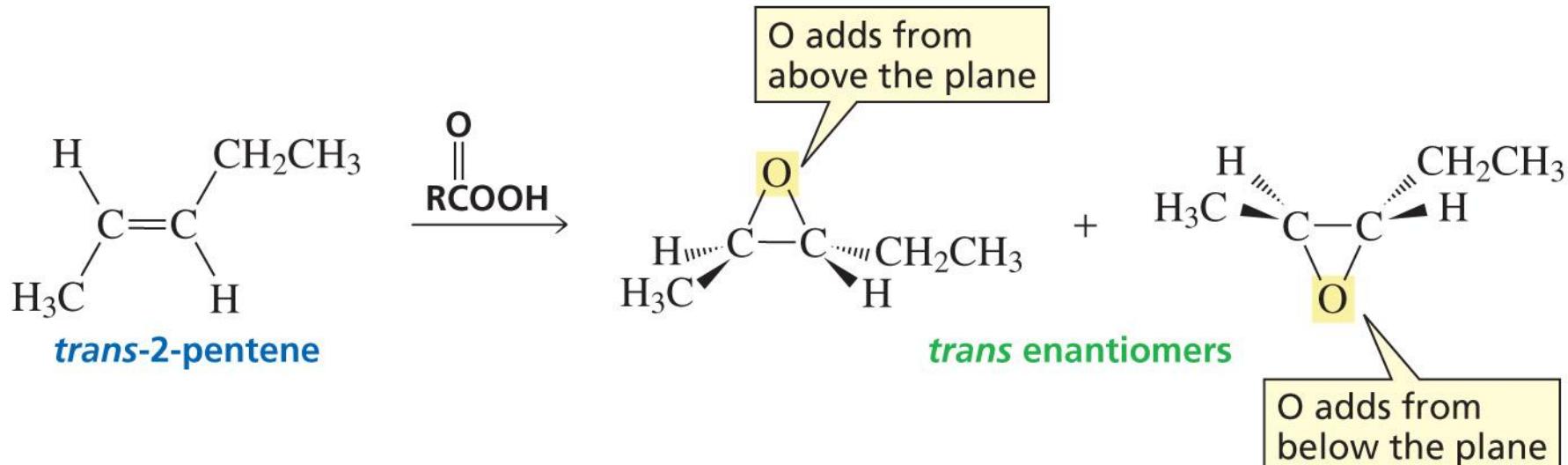
The mechanism is similar to that for the addition of Br₂.



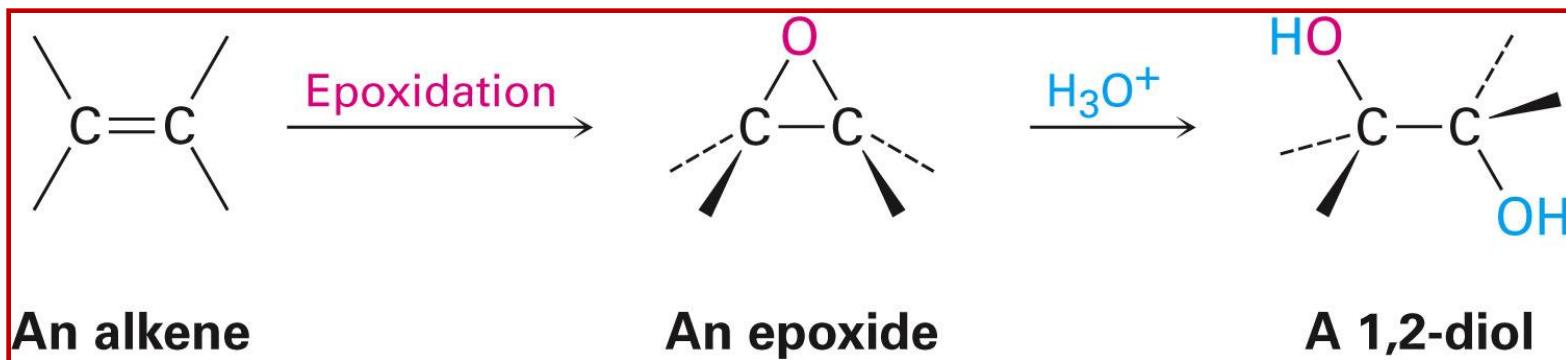
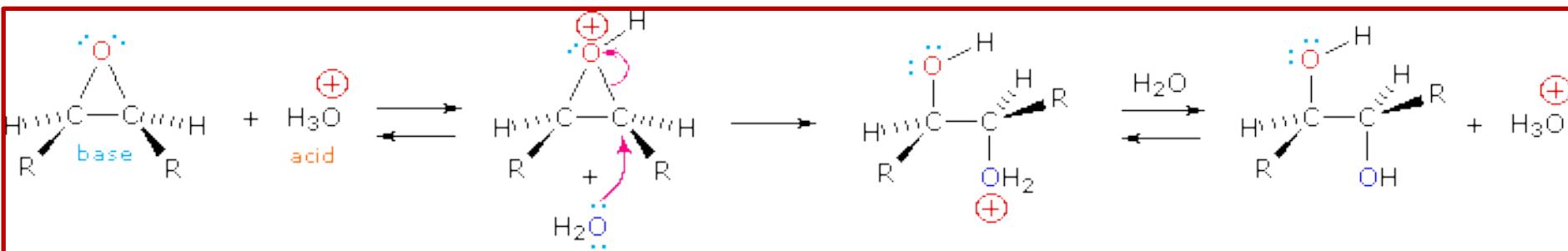
Syn Addition to a Cis Isomer Forms Only the Cis Stereoisomers



Syn Addition to a Trans Isomer Forms Only the Trans Stereoisomers

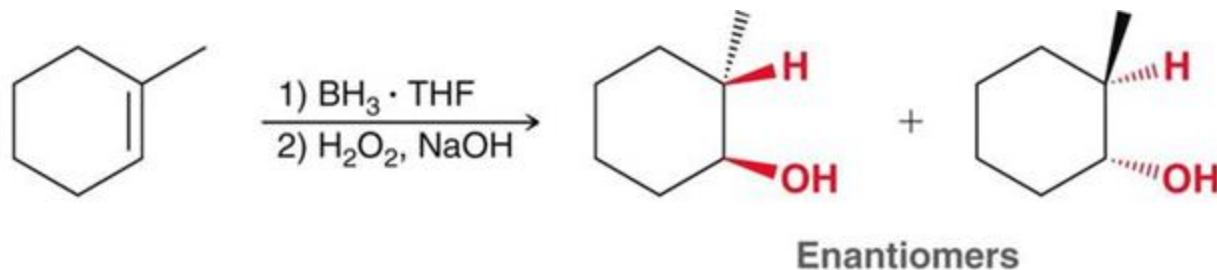


- Epoxides undergo an acid-catalyzed ring-opening reaction with water
- Gives corresponding 1,2-dialcohol, or diol, also called a **glycol**



Stereospecificity in addition of water through Hydroboration-Oxidation reaction

Formation of stereospecific *syn*-addition and *trans* products are obtained.



Anti addition is NOT observed

