Module:7

Industrial applications

- Water purification methods - zeolites, ion-exchange resins and reverse osmosis;
- Fuels and combustion -LCV, HCV, Bomb calorimeter (numerical)
- Corrosion- Sacrificial anodic protection, Impressed current cathodic protection)
- Overview of computational methodologies: energy minimization and conformational analysis.

Water purification method

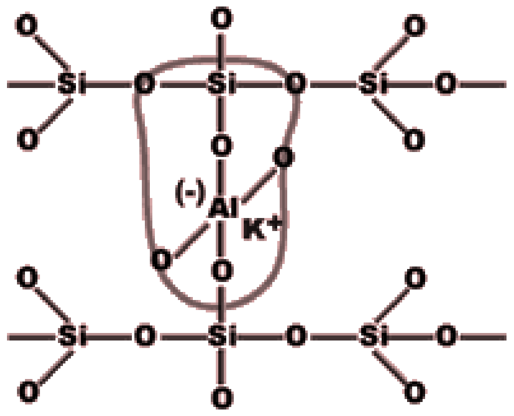
1. Zeolite or permutit process:

Sodium Aluminium Silicate: Complex chemical compound occurs as a natural mineral called '*Zeolite*'. Zeolites are known as permutits and in Greek it means "boiling stone"

- Zeolite is a three-dimensional silicate.
- The chemical formula of zeolite is hydrated sodium aluminum silicate represented as '**$Na_2O.Al_2O_3.xSiO_2.yH_2O$**'.
- It is capable of exchanging reversibly it's sodium ions for Ca^{2+} and Mg^{2+}.

$$\mathbf{Na_2\,Ze + Ca^{2+} \rightarrow CaZe + 2Na^{+}}$$

- Naturally occurring zeolite is **$Na_2O.Al_2O_3.3SiO_2.2H_2O$** and is known as **Natrolite**.



Types of zeolites

Natural

These are non-porous, amorphous and durable.

Ex:

1.Natrolite - $Na_2O. Al_2O_3\ 4SiO_2\ .2H_2O$

2. Laumontite - $CaO. Al_2O_3\ 4SiO_2\ .4H_2O$

3. Harmotome - $(BaO.K_2O). Al_2O_3\ 5SiO_2\ .5H_2O$

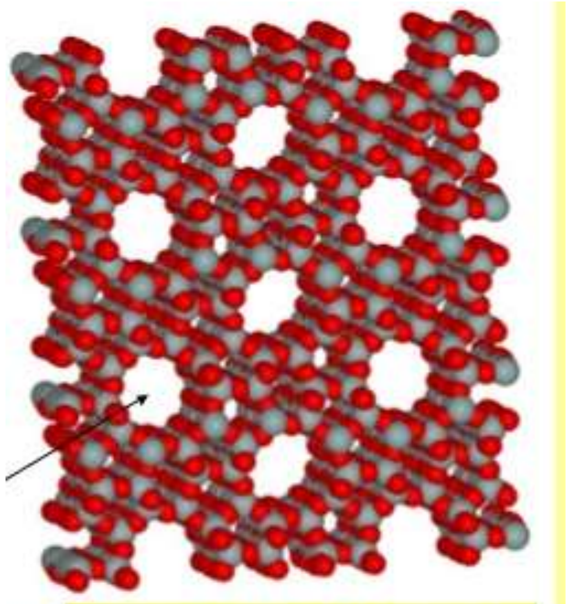
- Capable of exchanging its Na ions

Synthetic

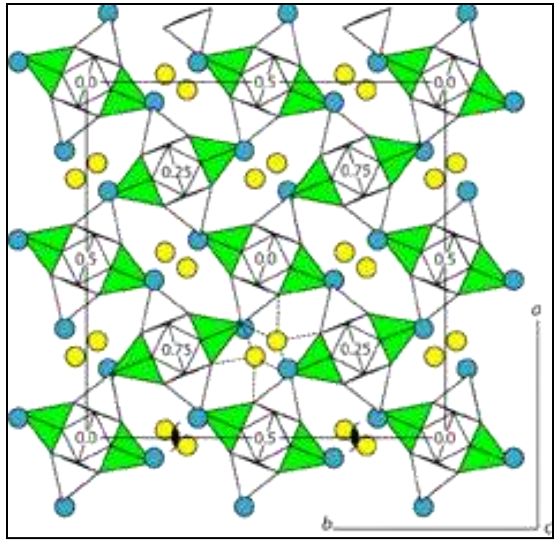
There are porous and possess a gel structure.

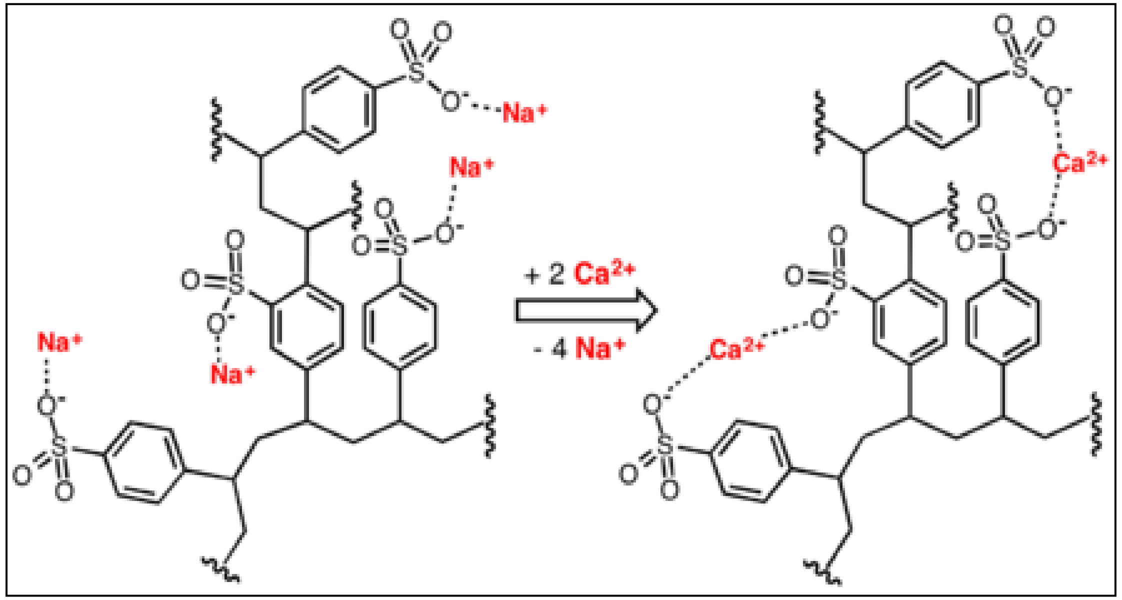
Prepared by heating together Na_2CO_3, Al_2O_3 and SiO_2

They possess high exchange capacity per unit weight compared to natural zeolites



Porous Structure of zeolite





Synthetic Zeolite

- Synthetic zeolite used for softening purpose in permutit process. These are porous and glassy and have greater softening capacity than green sand.
- They are prepared by heating together china clay ($Al_2Si_2O_5(OH)_4$), feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAlSi_3O_8$) are a group of rock-forming tectosilicate minerals which make up as much as 60% of the earth's crust)} and soda ash (Na_2CO_3).
- For softening of hard water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite.
- 'Ze' holds sodium ions loosely and can be represented as 'Na_2Ze'.
- The hardness causing ions (Ca^{2+}, Mg^{2+}) are retained by the zeolite as CaZe and MgZe respectively, while the outgoing water contains sodium salts. During this process, the water becomes free from Ca^{2+} and Mg^{2+}.

Zeolite process

- Method of softening:

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2\ NaHCO_3$$

$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2\ NaHCO_3$$

$$Na_2Ze + CaSO_4 \longrightarrow CaZe + Na_2SO_4$$

$$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2\ NaCl$$

zeolite hardness

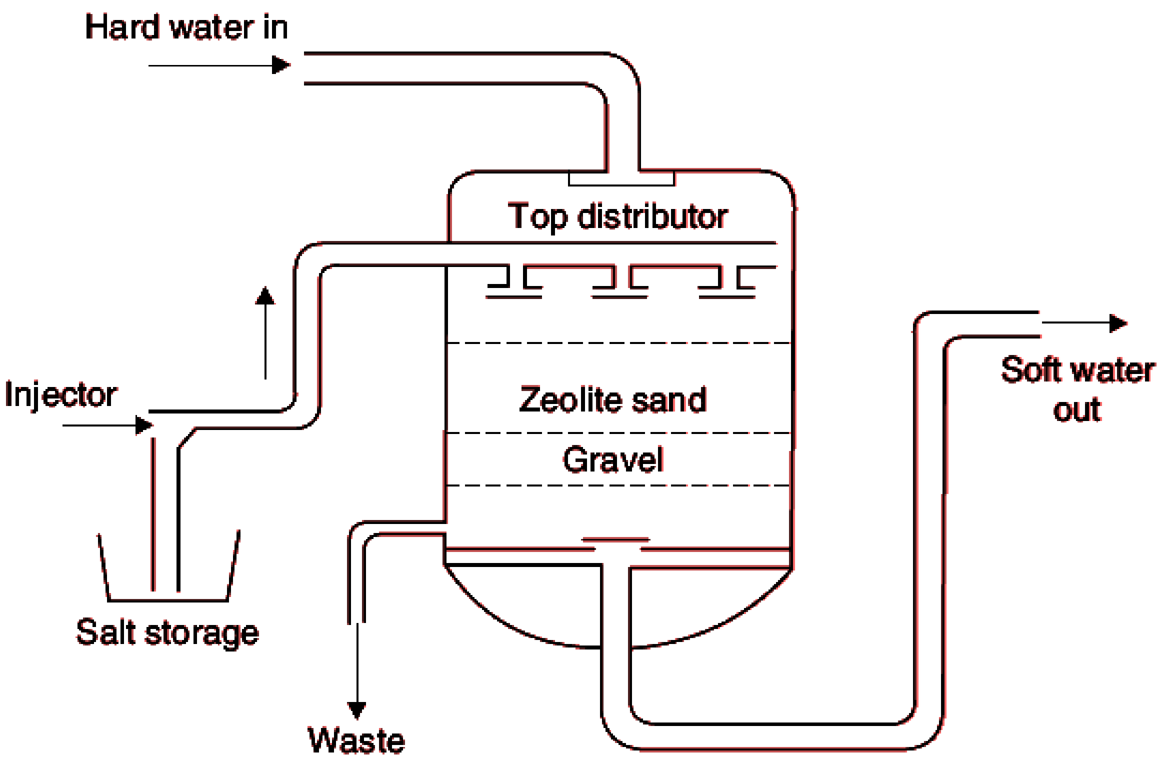
- Regeneration of Zeolite using Brine solution:

$$CaZe\ (or)\ MgZe + 2\ NaCl \longrightarrow Na_2Ze + CaCl_2\ or\ MgCl_2$$

Exhausted zeolite Brine Reclaimed zeolite

The washings are led to the drain and the regenerated zeolites are used for softening purpose again

Zeolite Process



Softening of hard water by permutit process.

Limitations

- If the supplied water is turbid, the suspended matters must be removed before it is being fed into the zeolite bed. Otherwise **results in clogging and becomes inactive.**

- If water contains large quantities of colored ions like Mn^{2+} and Fe^{2+}, they must be removed, as these have the tendency to **form MnZe and FeZe, which cannot be regenerated easily.**

- If mineral acids are present in water, they must be neutralized before feeding into the zeolite bed, as these **can destroy the zeolite bed**.

Advantages

1. Hardness of water can be removed completely up to about 10 ppm
2. The equipment used is small and easy to handle
3. It requires less time for softening
4. There is no sludge formation, hence the process is clean
5. Easy to regenerate with brine solution
6. Any hardness can be removed without any adjustments of the process

Disadvantages

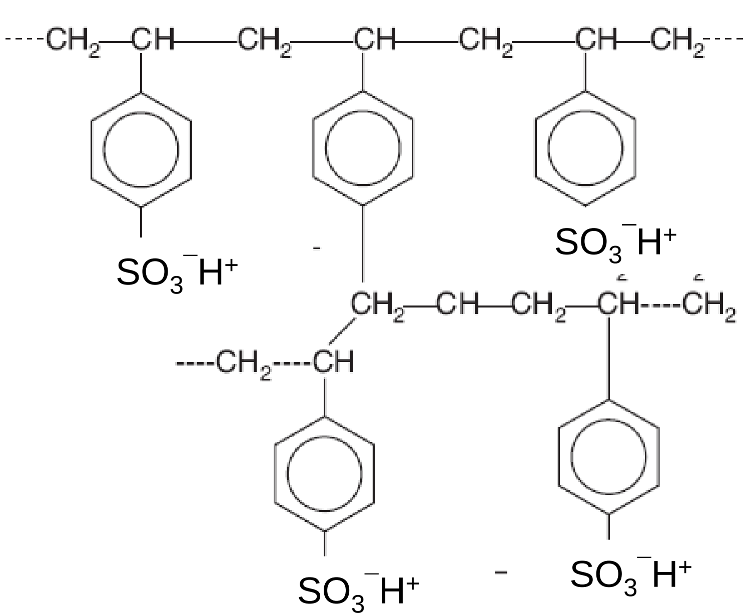
1. Treated water contains more Na^+ ions than in the L-S process.
2. Replaces only Ca^{2+} and Mg^{2+} ions but leaves the acidic ions (HCO_3^- and CO_3^{2-}) as such in the softened water; HCO_3^- decompose to produce CO_2 which causes corrosion in boilers; CO_3^{2-} hydrolyze to NaOH to cause caustic embrittlement.
3. Colored water or water containing suspended impurities cannot be used before filtration.
4. Water containing acid cannot be used for softening since acid may destroy the zeolite

2. Ion-Exchange Process

- Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure.
- Functional groups present are responsible for ion-exchange properties
- Acidic functional groups ($-COO^-H^+$, $-SO_3^-H^+$) exchange H^+ for cations
- Basic functional groups ($-NH_3^+OH^-$) exchange OH^- for anions.

Cation Exchange Resin:

- Styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water

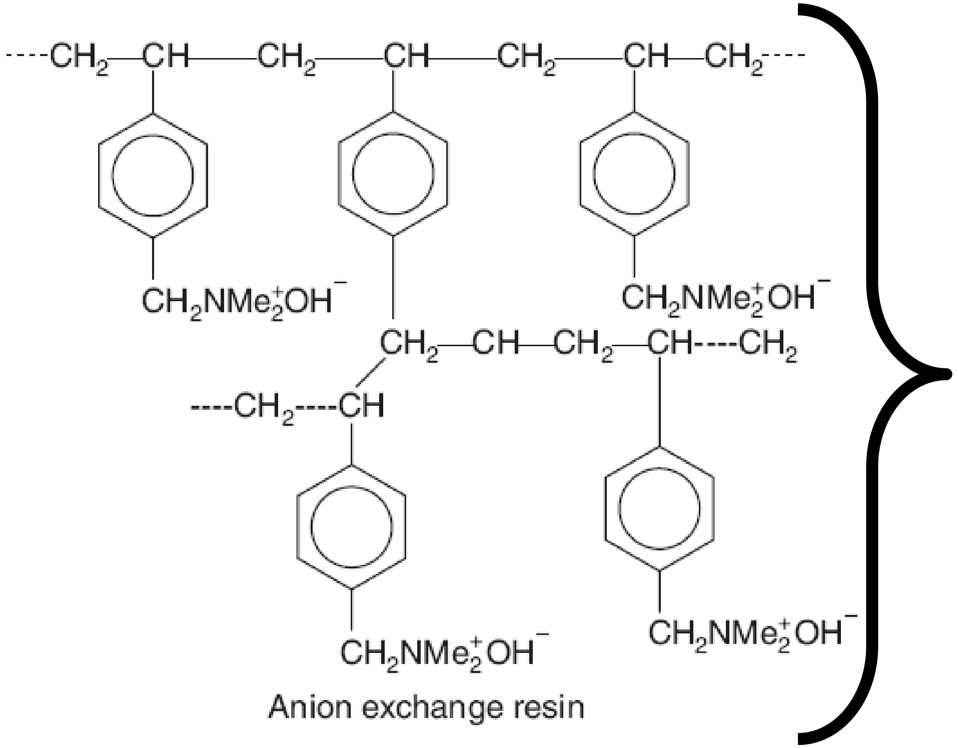


cation exchange resin

RH^+

Anion Exchange Resin:

- **Styrene-divinyl benzene or amine-formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix.**
- **The resin after treatment with dil. NaOH solution capable to exchange their OH^- ions with the anions in the water**



Anion exchange resin

ROH⁻

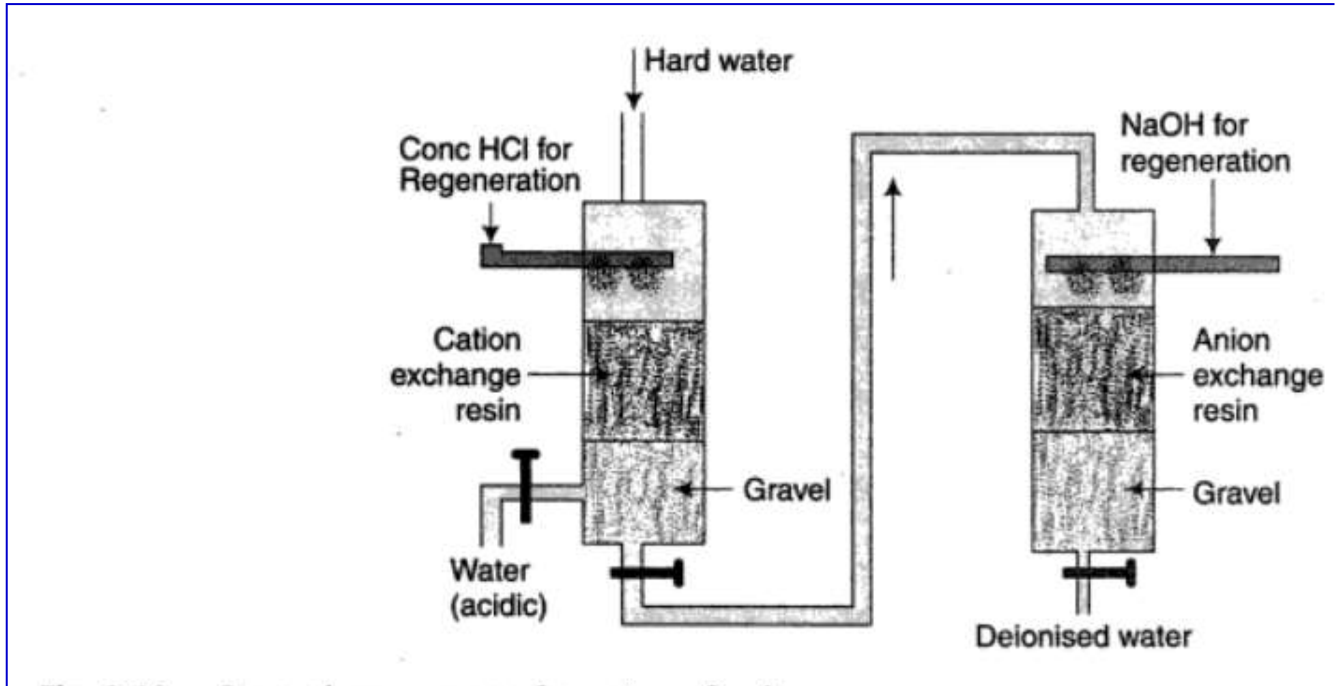
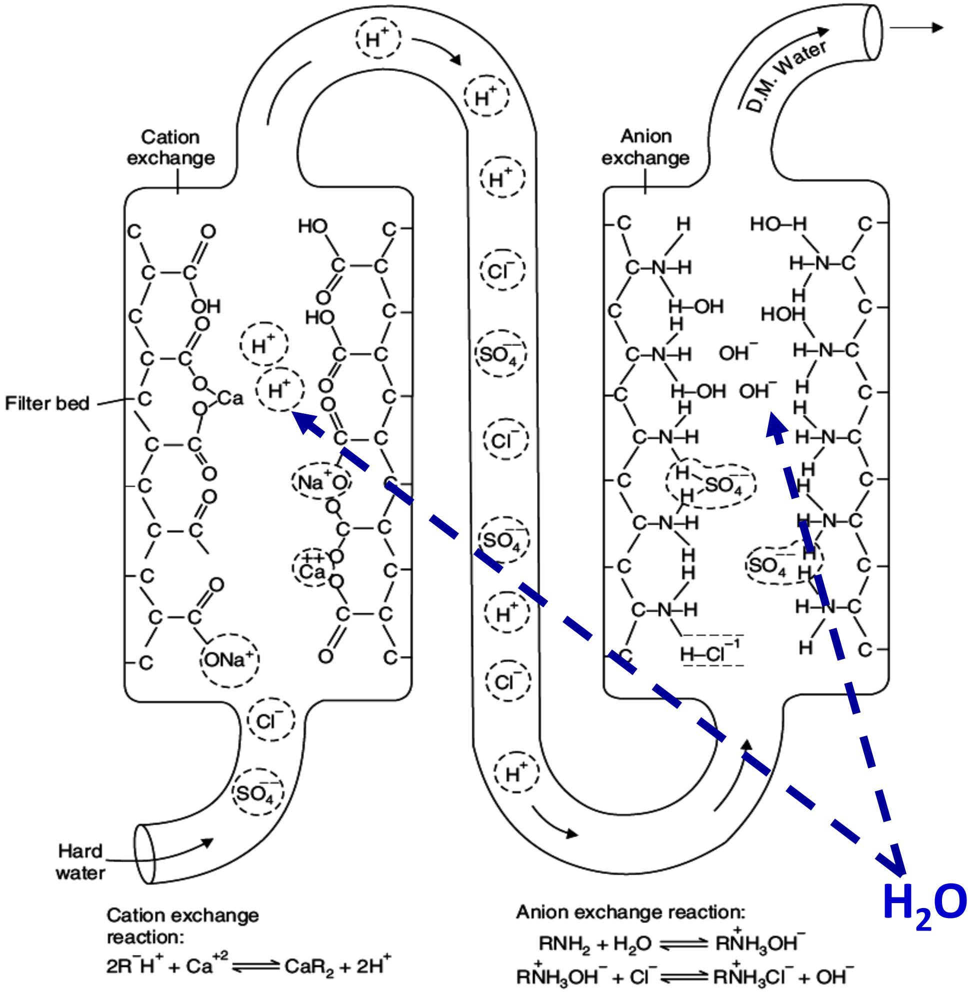


Fig. 8.12 *Ion-exchange process for water softening*



$$2RH^+ + Ca^{2+}/Mg^{2+} \longrightarrow R_2Ca^{2+}/R_2Mg^{2+} + 2H^+$$

$$ROH^- + Cl^- \longrightarrow R^+Cl^- + OH^-$$

Water emerging from the cationic column will be acidic in nature, while passing through the second anionic resin column, H^+ and OH^- ions combine during softening process to give water molecule

If we pass the water through the anion exchanger first then… all the cations present there will be converted in to the **hydroxides** just like **calcium hydroxide and sodium hydroxide**. This phenomenon would result in **higher pH** as the result **hydroxide** will also **get precipitated** and will result in the **blocking of the exchanger**. **This is why water is passed through cation exchanger first.**

In ion exchange method, water is first passed through cation exchanger and then through anion exchanger. Why?

If water pass through the anion exchanger then, **all the cations present in water will be converted in to the hydroxides** i.e., $Ca(OH)_2$, $Mg(OH)_2$. **This phenomenon would increase the pH as the result hydroxides will also get precipitated, resulting the blocking of the exchanger**. Hence, water is passed through cation exchanger first.

Regeneration

When the capacity of the ion exchange resins to exchange H+ and OH- ions are exhausted, they are treated with dil HCl and dil NaOH for regeneration

Regeneration of cation exchange column

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

Regeneration of anion exchange column

$$R_2SO_4^{2-} + 2OH^- \longrightarrow 2ROH^- + SO_4^{2+}$$

Advantage

- **The process can be used to soften highly acidic or alkaline water**
- **it produces water of very low hardness (2 ppm)**

Disadvantage

- **The equipment is costly and more expensive chemical are needed**
- **If the water contains turbidity (>10 ppm), then the output of the process is reduced**

Advantages & Disadvantages of ion-exchange process

Advantages:

- Can be used for highly acid and highly alkaline water
- Residual hardness of water is as low as 2 ppm.
- Very good for treating water for high pressure boilers

Disadvantages:

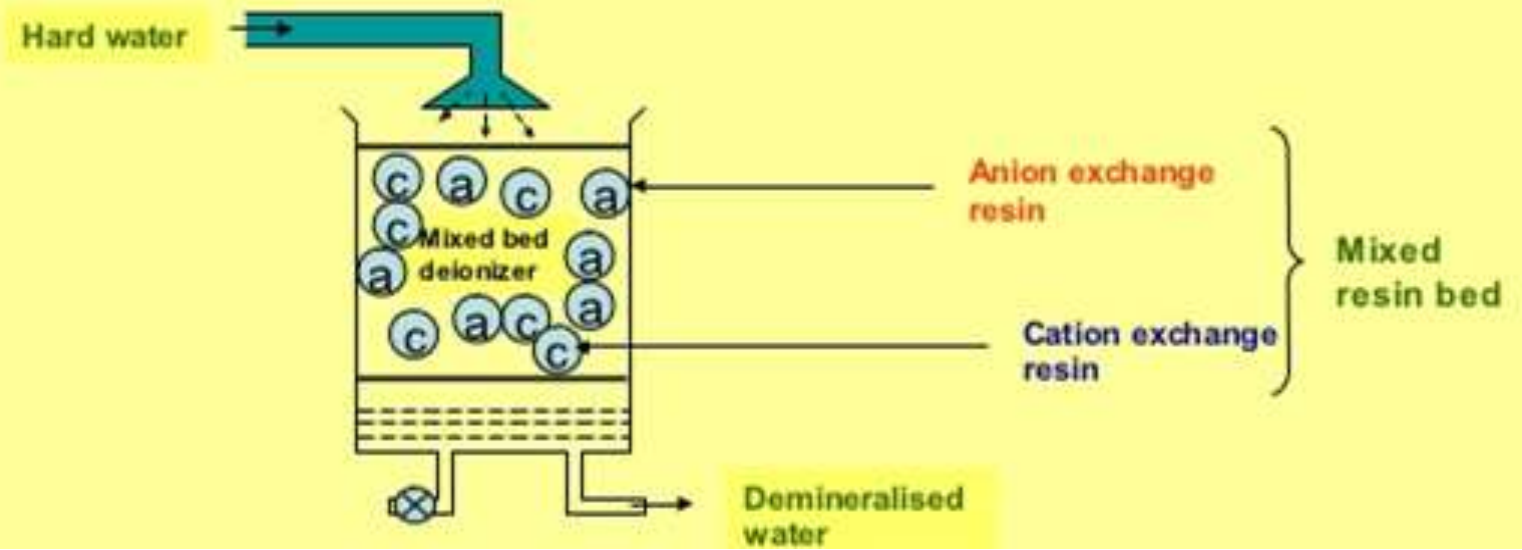
- Expensive equipment and chemicals
- Turbidity of water should be < 10 ppm. Otherwise output will reduce; turbidity needs to be coagulated before treatment.
- Needs skilled labour

S.No	Characteristic	Ion-exchange process	Zeolite process
1	Requirements	Cation and anion exchangers	Zeolite
2	Exchange of ions	Exchange of both cations and anions takes place	Exchange of only cations takes place
3	Capital cost	Very high	High
4	Operating expenses	High	Low
5	Raw water	i)Should be non-turbid ii)Both acidic or alkaline water can be treated iii)Prior knowledge of hardness not	i)Should be non-turbid ii)Should not be acidic iii)Prior knowledge of hardness not required.

Mixed Bed Deionizer

Description and process of mixed bed deionizer

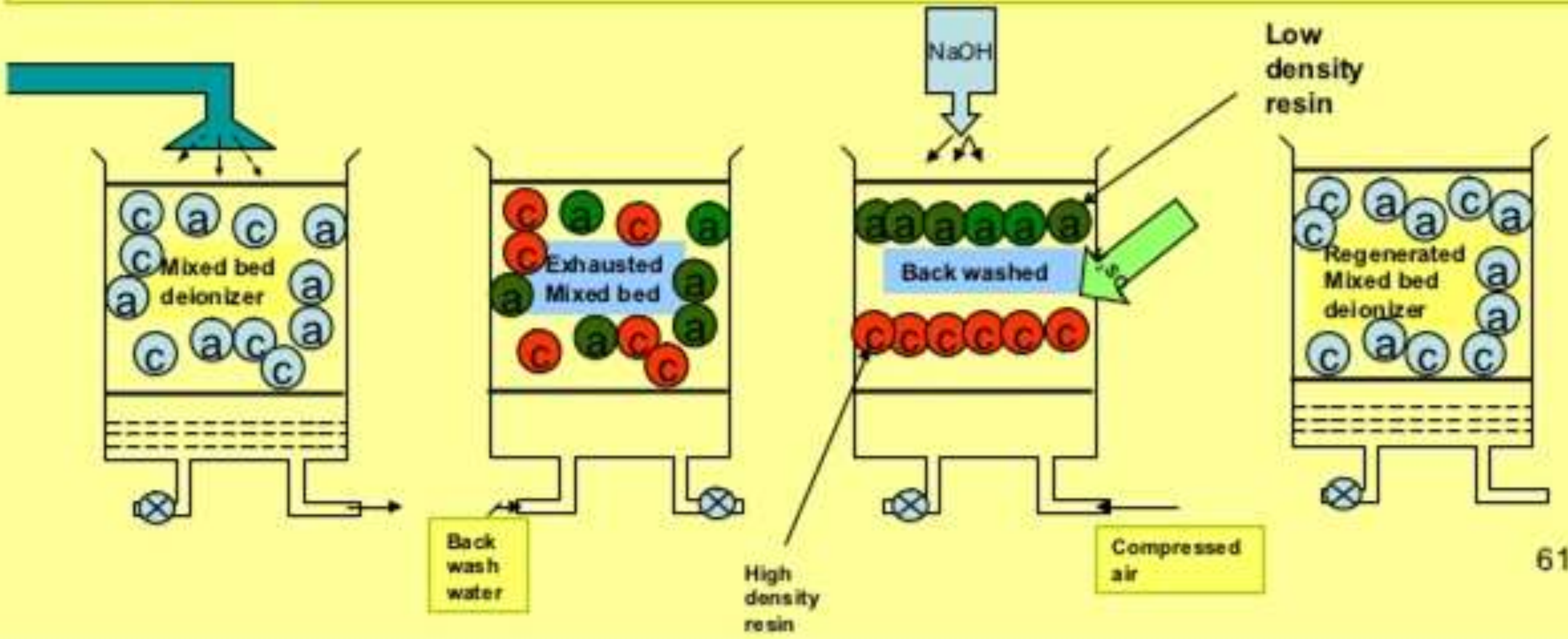
1. It is a single cylindrical chamber containing a mixture of anion and cation exchange resins bed
2. When the hard water is passed through this bed slowly the cations and anioins of the hard water comes in to contact with the two kind of resins many number of times
3. Hence, it is equivalent to passing the hard water many number of times through a series of cation and anion exchange resins.
4. The soft water from this method contains less than 1ppm of dissolved salts and hence more suitable for boilers



- **Contains essentially of a single cylinder containing an intimate mixture of cation exchanger and anion exchanger.**
- **The outgoing water from the mixed-bed contains even less than 1 ppm of dissolved salts**

Regeneration of mixed bed deionizer

1. When the bed (resins) are exhausted or cease to soften the water, the mixed bed is back washed by forcing the water from the bottom in the upward direction
2. Then the light weight anion exchanger move to the top and forms a upper layer above the heavier cation exchanger
3. Then the anion exchanger is regenerated by passing caustic soda solution (NaOH) from the top and then rinsed with pure water
4. The lower cation exchanger bed is then washed with dil.H_2SO_4 solution and then rinsed.
5. The two beds are then mixed again by forcing compressed air to mix both and the resins are now ready for use



Regeneration:

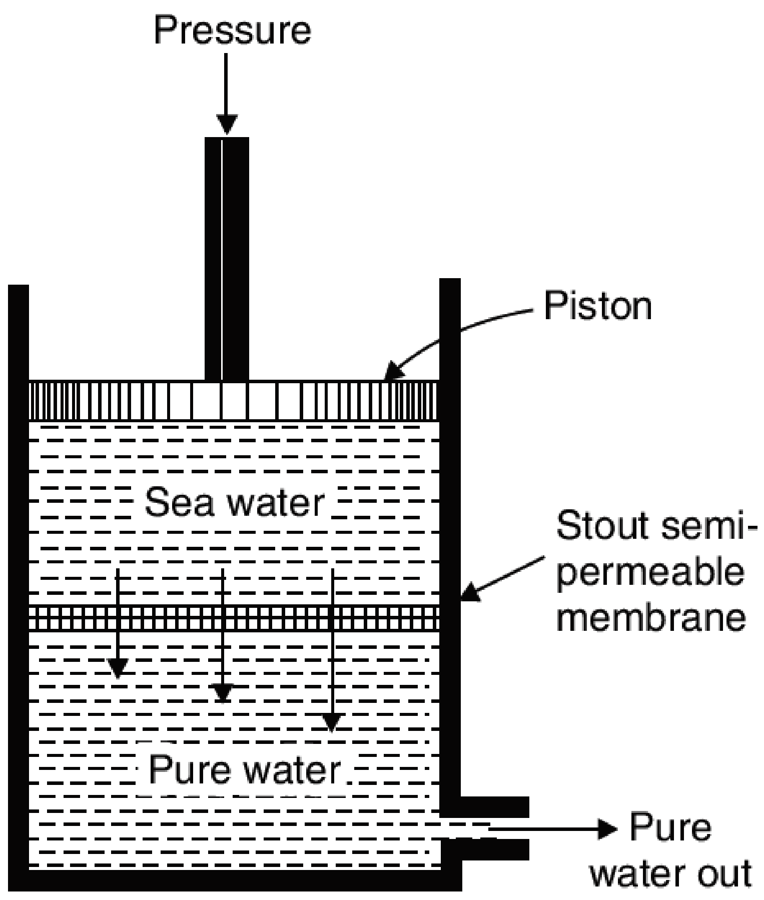
- When the resins are exhausted, the mixed-bed is backwashed using compressed air.
- The lighter anion exchanger gets displaced to the top and the heavier cation exchanger stays below.
- **Anion and cation exchanger were regenerated using NaOH and H_2SO_4 respectively.**

3. Reverse Osmosis

- When two solutions of unequal concentrations are separated by a Semi-permeable membrane, solvent will flow from lower conc. to higher conc.
- This phenomenon can be reversed (solvent flow reversed) by applying hydrostatic pressure on the concentrated side.
- In reverse osmosis, pressure of 15-40 kg/cm^2 is applied to sea water.
- The water gets forced through the semi-permeable membrane leaving behind the dissolved solids.

Advantages:

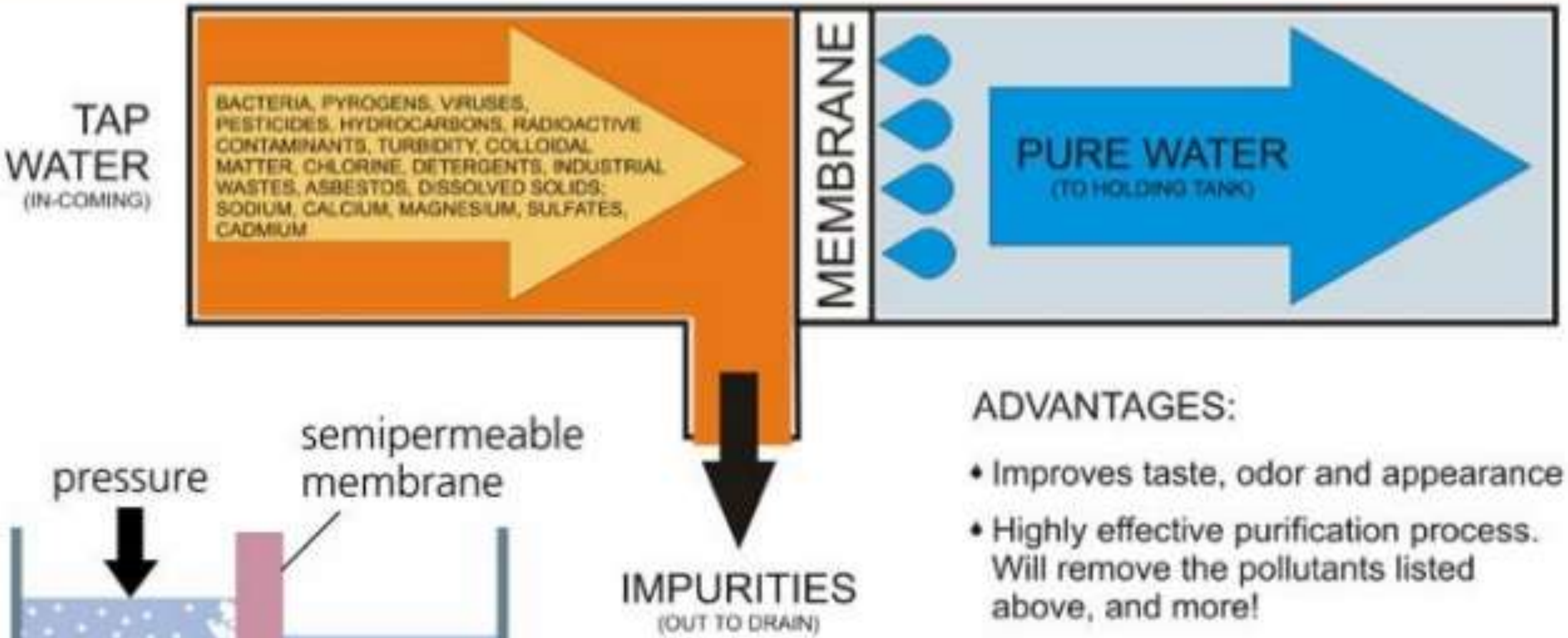
- Advantage is in removing ionic, non-ionic, colloidal and high molecular wt. organic matter.
- **Removes colloidal silica**
- **Cost is only the replacement cost of membranes (life is 2 years)**
- **Easy Membrane replacement** and hence uninterrupted water supply can be ensured
- **Low operating cost, high reliability**
- Because of the above reasons this process is being adopted for converting sea water into potable water and for high pressure boilers.

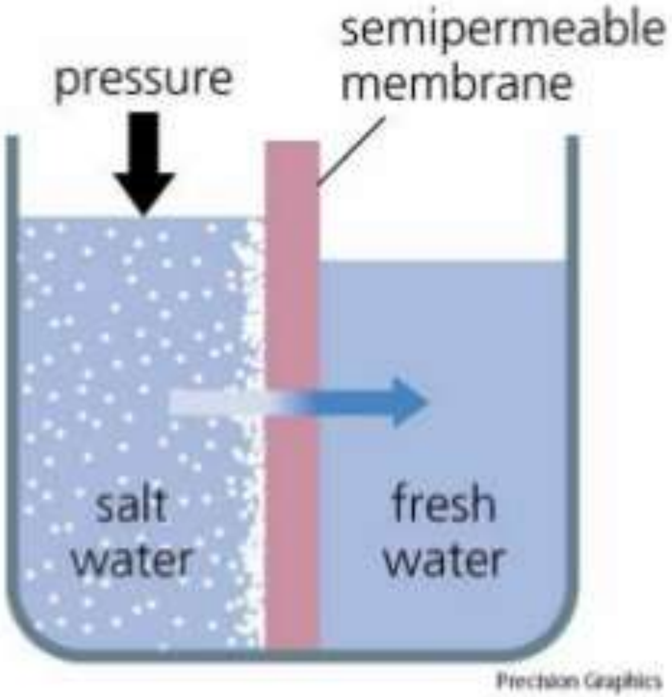


Reverse osmosis cell

- Cellulose acetate
- Polysulfone
- Polysulfone amide
- Polyamide
- Poly-acrylonitrile

Reverse Osmosis





ADVANTAGES:

- Improves taste, odor and appearance
- Highly effective purification process. Will remove the pollutants listed above, and more!
- Consumes no energy
- Very convenient
- Flushes away pollutants, does not collect them
- Easy to keep clean
- Low production cost - gives you water of a guaranteed quality for pennies per gallon

Fuels and combustion

Fuel is substance, which on combustion produces a large amount of heat, which can be used for various domestic and industrial purposes

Combustion

The process of combustion involves oxidation of carbon, hydrogen etc. of the fuels to CO_2, H_2O, and the difference in the energy of reactants and the products are liberated as large amount of heat energy which is utilized.

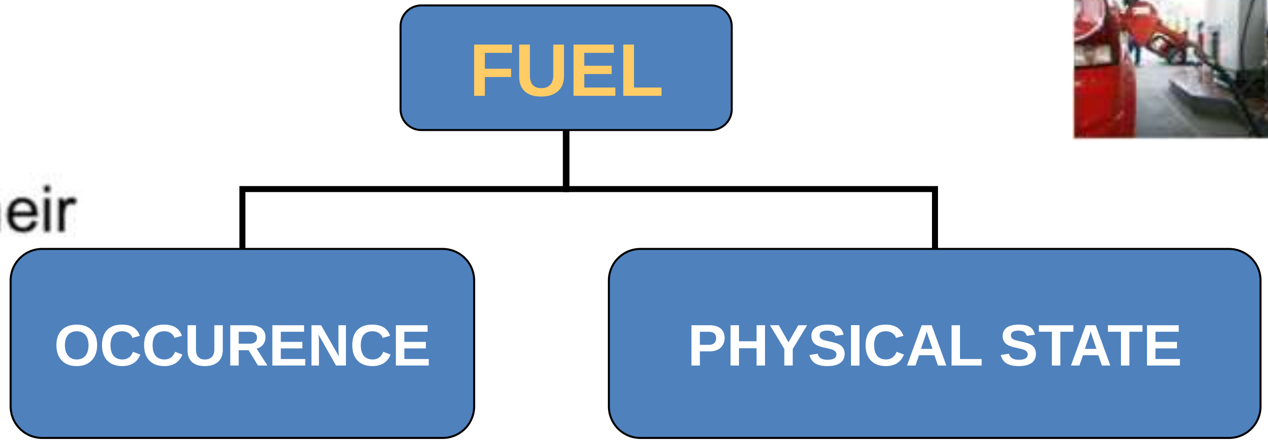
$$\text{Fuel} + O_2 \longrightarrow \text{Products} + \textbf{Heat}$$

The primary or main source of fuels are coal and petroleum oils, the amounts of which are dwindling day by day. These are stored fuels available in earth's crust and are generally called **"fossil fuels"**.

The term combustion refers to the exothermal oxidation of a fuel, by air or oxygen

Classification of Fuels

These can be classified on the basis of their occurrence and physical state



Classification of Fuels

On the basis of occurrence

Primary or Natural

On the basis of state

- **Solid**: Wood, Coal, Dung
- **Liquid**: Crude oil
- **Gaseous**: Natural gas

Secondary or Derived

- **Solid**: Coke, Charcoal
- **Liquid**: Tar, Kerosene, Diesel, Petrol, Fuel oil, LPG, Synthetic gasoline
- **Gaseous**: Coal gas, Water gas, Oil gas, Biogas, Coke oven gas, Blast furnace gas

Does the efficiency of the same quantity of different kind of fuels are the same?

For example

Answer is No!

Calorific Value ***or the capacity to supply heat***

"the total quantity of heat liberated when a unit mass or volume of the fuel is burnt completely".

Units of heat

1. Calorie

The amount of heat required to raise the temperature of one gram of water through one degree centigrade

2. Kilocalorie (or) kilogram centigrade units

the unit of metric system and is equal to 1000 calories. This may be defined as "the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade".

Thus 1 kcal = 1000 cal

3. British thermal unit (B. Th. U.)

"the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit"

1 B. Th. U. = 252 cal = 0.252 k cal.

1 k cal = 3.968 B. Th. U.

4. Centigrade Heat Unit (C. H. U.)

"quantity of heat required to raise the temperature of one pound of water through one degree centigrade".

Thus, 1 k cal = 3.968 B. Th. U. = 2.2 C. H. U.

Higher or Gross Calorific Value (HCV or GCV)

- Most of the fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted to steam
- *If the products of combustion are condensed to room temperature (15 ℃ or 60 ℉), the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross calorific value".*
- So gross or higher calorific value may be defined as…
- *"the total amount of heat produced when one unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature"*

Higher or Gross Calorific Value (HCV or GCV)

As the products of combustion are cooled down to room temperature, the steam gets condensed into water and latent heat is evolved. Thus in the determination of gross calorific value, the latent heat also gets included in the measured heat. Therefore, gross calorific value is also called the higher calorific value.

The calorific value which is determined by Bomb calorimeter gives the higher calorific value (HCV)

Lower or Net Calorific Value (LCV)

In actual case of any fuel, the water vapour and moisture etc are not condensed and escapes as such along with hot combustion gases. Hence a lesser amount of heat is available. So, net or lower calorific value may be defined as…

"The net heat produced when unit mass / volume of the fuel is burnt completely and the products are permitted to escape."

Net or lower calorific value can be found from GCV value

NCV = GCV - Latent heat of water vapour formed

= GCV - Mass of hydrogen × 9 × latent heat of steam

1 part by mass of hydrogen produces 9 parts by mass of water.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

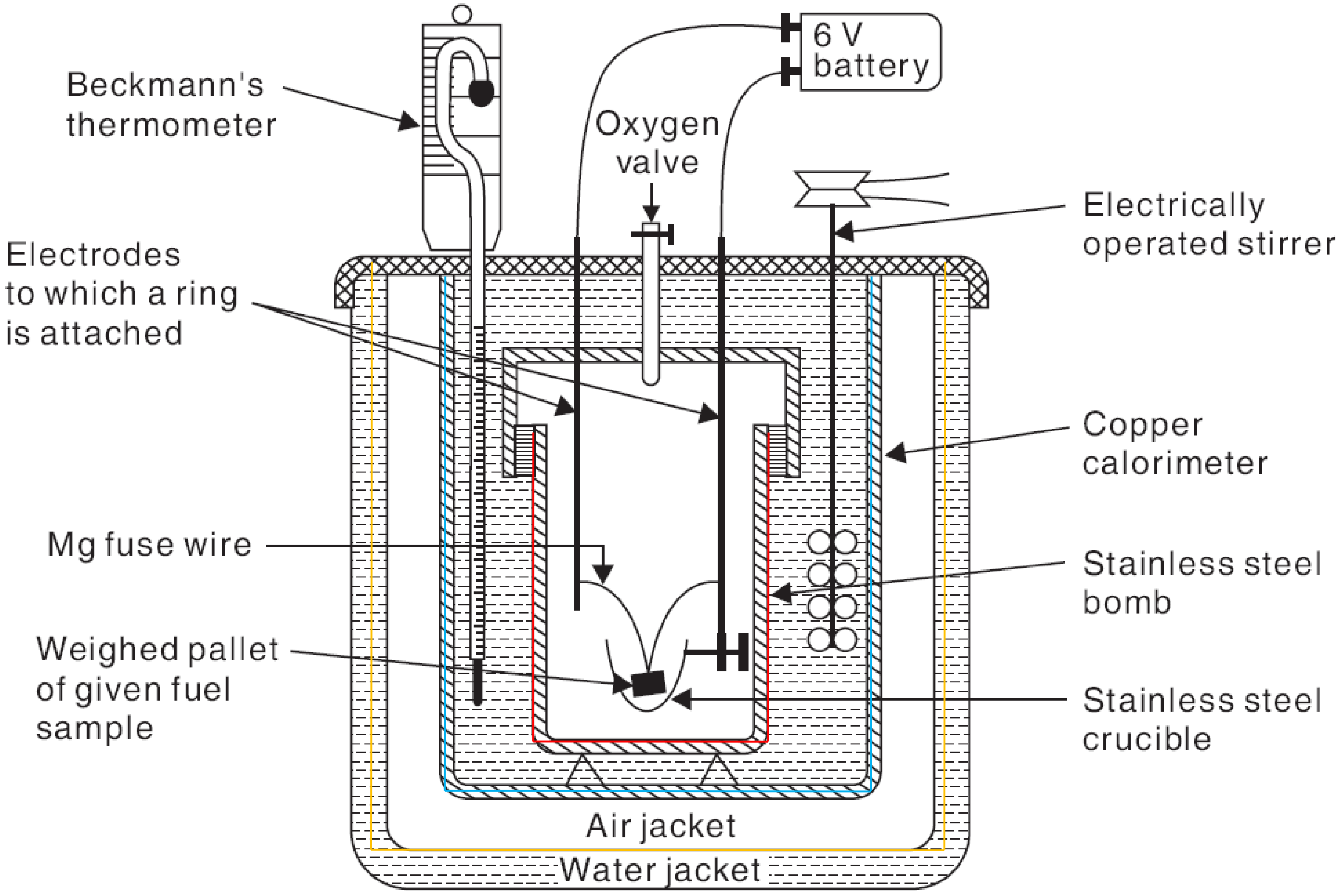
The latent heat of steam is 587 k cal/kg or 1060 B. Th. U. /b of water vapour formed at room temperature. (i.e. 15 ℃)

Determination of Calorific value

1. **Determination of calorific value of solid and non volatile liquid fuels:** It is determined by bomb calorimeter.

Principle: A known amount of the fuel is burnt in excess of oxygen and heat liberated is transferred to a known amount of water. The calorific value of the fuel is then determined by applying the principle of calorimetery i.e. Heat gained = Heat lost

Bomb calorimeter



What is a Bomb- or Combustion Calorimeter?

A Bomb-Calorimeter is used to measure the heat created by a sample burned under an oxygen atmosphere in a closed vessel, which is surrounded by water, under controlled conditions.

- The measurement result is called the Combustion-, Calorific- or BTU-value
- 1g of solid or liquid matter is weighed into a crucible, and placed inside a stainless steel container (the "Decomposition vessel") filled with oxygen. Then the sample is ignited through an ignition wire inside the decomposition vessel and burned
- The reaction is carried out in insulated container, where the heat evolved by the reaction causes the temperature of the contents to change
- All organic matter is burned under these conditions, and oxidized. Even inorganic matter will be oxidized to some extend
- The heat created during the burning process can be determined in different ways
- By measuring the temperature increase
- The heat created by the combustion process is transferred to known amount of water

Calculations

Let weight of the fuel sample taken = x g

Weight of water in the calorimeter = W g

Water equivalent of the Calorimeter, stirrer, bomb, thermometer = w g

Initial temperature of water = t_1°C

Final temperature of water = t_2°C

L= Higher calorific value of fuel in cal/g.

$$L = \frac{(W+w)(t_2-t_1)}{x} \text{ Cal/g}$$

Water Equivalent of the calorimeter (w) is determined by burning a fuel of known calorific value (benzoic acid (HCV = 6,325 kcal/kg) and naphthalene (HCV = 9,688 kcal/kg)

If H is the percentage of hydrogen in fuel,
the mass of water produced from 1 g of fuel = (9/100) × H = 0.09 H

Heat taken by water in forming steam = 0.09 H × 587 cal (latent heat of steam = 587 cal/kg)

LCV = HCV – Latent heat of water formed

$$LCV = \left[HCV - \frac{9}{100} H \times 587\right] \text{kcal/kg.}$$

$$= [HCV - 0.09\ H \times 587]\ \text{kcal/kg.}$$

LCV or NCV = [HCV or GCV – 0.09 H × 587]

1. 0.72 gram of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3° to 29.1°C. If the calorimeter contains 250 grams of water and its water equivalents is 150 grams, calculate the HCV of the fuel. Give your answer in J/g.

$$L = \frac{(W+w)\,(t_2 - t_1)}{x}\ \text{Cal/g}$$

Solution. Here $x = 0.72$ gm $W = 250$ g, $w = 150$ g

$t_1 = 27.3°C$, $t_2 = 29.1°C$.

$$\text{HCV of fuel (L)} = \frac{(W + w)\,(t_2 - t_1)}{x}\ \text{cal/gm}$$

$$= \frac{(250 + 150) \times (29.1 - 27.3)}{0.72} = 1000\ \text{cal/gm}$$

(1 cal = 4.18 Joules).

1000×4.18 J/g = 4180 J/g

2. On burning 0.83 gm of a solid fuel in a bomb calorimeter , the temperature of 3500 g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385 g of and 587 cal/g respectively. If the fuel contains 0.7% hydrogen, calculate its Gross and Net Calorific value.

Solution. Here wt. of fuel (x) = 0.83 g of ;

wt of water (W) = 3500 g;

water equivalent of calorimeter (w) = 385 g ;

$(t_2 - t_1) = (29.2°C - 26.5°C) = 2.7°C$;

percentage of hydrogen (H) = 0.7% ; latent heat of steam = 587 cal/g

$$\text{Gross calorific value} = \frac{(W + w)(t_1 - t_2)}{x} \text{ cal/g}$$

$$= \frac{(3500 + 385) \times 2.7}{0.83} = 12638 \text{ cal/g}$$

$$\text{NCV} = [\text{GCV} - 0.09\ H \times 587]$$

$$= (12638 - 0.09 \times 0.7 \times 587) \text{ cal/g}$$

$$= (12638 - 37) \text{ cal/g} = 12601 \text{ cal/g}$$

Corrections

Corrections: For accurate results the following corrections are also incorporated:

1. **Fuse wire correction**
2. **Acid correction**
3. **Cooling correction**

Fuse wire correction:

Heat liberated during sparking should be _????????_ from calorific value

Fuse wire correction: As Mg wire is used for ignition, the heat generated by burning of Mg wire is also included in the gross calorific value. Hence this amount of heat has to be subtracted from the total value.

Acid correction:

Fuels containing Sulphur and Nitrogen if oxidized, the heats of formation of H_2SO_4 and HNO_3 should be subtracted (as the acid formations are exothermic reactions)

Acid Correction: During combustion, sulphur and nitrogen present in the fuel are oxidized to their corresponding acids under high pressure and temperature.

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \Delta H = -144{,}000 \text{ Cal}$$

$$2N_2 + 5O_2 + 2H_2O \rightarrow 4HNO_3 \qquad \Delta H = -57{,}160 \text{ Cal}$$

The corrections must be made for the heat liberated in the bomb by the formation of H_2SO_4 and HNO_3. The amount of H_2SO_4 and HNO_3 is analyzed by washings of the calorimeter.

For each ml of 0.1 N H_2SO_4 formed, 3.6 calories should be subtracted.

For each ml of 0.01 HNO_3 formed, 1.43 calories must be subtracted.

Cooling correction:

The rate of cooling of the calorimeter from maximum temperature to room temperature is noted.

If the time taken for the water in the calorimeter to cool down from the maximum temperature attained, to the room temperature is x minutes and the rate of cooling is dt/min, then the cooling correction = x × dt. This should be added to the observed rise in temperature.

Therefore, Gross calorific value

=(W+w)(t_2-t_1+Cooling correction)-[Acid+ fuse corrections] / Mass of the fuel.

$$GCV = \frac{(W+w)\,(t_2 - t_1 + \text{Cooling Correction}) - (\text{Acid} + \text{Fuse Correction})}{\text{Mass of the fuel } (x)}$$

3. A sample of coal contains C =93%; H =6% and ash = 1%. The following data were obtained when the above coal was tested in bomb calorimeter. Wt. of coal burnt = 0.92 g, Wt. of water taken = 2200 g, Water equivalent of calorimeter =550 g, Rise in temperature = 2.42 °C, Fuse wire correction = 10 cal., Acid correction = 50 cal. Calculate gross and net calorific value of the coal, assuming the latent heat of condensation of steam as 580 cal/g.

Solution: Wt. of coal sample (x) = 0.92 g;

wt. of water (W) =2200 g;

Water equivalent of calorimeter (w) = 550 g;

Temperature rise (t_2-t_1) = 2.42 °C;

Acid correction = 50 cal;

Fuse wire correction = 10 cal;

Latent heat of steam = 580 cal/g;

Percentage of H =6%

$$GCV = \frac{(W + w)(t_1 - t_2) - [\text{acid + fuse corrections}]}{x}$$

$$= \frac{(2200 + 550) \times 2.42 - [50 + 10] \text{ cal}}{0.92\text{g}}$$

$$= 7168.5 \text{ cal/g.}$$

$$NCV = [GCV - 0.09 \text{ H} \times \text{latent heat steam}]$$

$$= (7168.5 - 0.09 \times 6 \times 580) \text{ cal/g}$$

$$= 6855.3 \text{ cal/g}$$

4. A sample of coal contains C =90%; H =5% and ash = 5%. The following data were obtained when the above coal was tested in bomb calorimeter. Wt. of coal burnt = 0.95g, Wt. of water taken = 2300 g Water equivalent of calorimeter =550g, Rise in temperature = 2.5C, Fuse wire correction = 10.0 cal, Acid correction = 60.0 cal, Calculate gross and net calorific value of the coal, assuming the latent heat of condensation of steam as 580 cal/g

Solution: Wt. of coal sample (x) = 0.95 g; wt. of water (W) =2300 g;

Water equivalent of calorimeter (w) = 550 g;

Temperature rise (t_2-t_1) = 2.5°C;

Acid correction = 60 cal;

Fuse wire correction = 10 cal;

Latent heat of steam = 580 cal/g;

Percentage of H =5%

$$GCV = \frac{(W + w)(t_1 - t_2) - [\text{acid + fuse corrections}]}{x}$$

$$= \frac{(2300 + 550) \times 2.5 - [60 + 10] \text{ cal}}{0.95\text{g}}$$

$$= 7125\text{-}70/95 = 7426.32 \text{ cal/g.}$$

$$NCV = [GCV - 0.09\ H \times \text{latent heat steam}]$$

$$= (7426.32 - 0.09 \times 5 \times 580) \text{ cal/g}$$

$$= 7165.32 \text{ cal/g}$$

5. A coal sample contains C = 92%; H = 5% and ash = 3%. When this coal sample was tested in the laboratory for its calorific value in a bomb calorimeter, the following data were obtained

Wt of coal burnt = 0.95 g, Wt of water taken = 700 g

Water equivalent of bomb and calorimeter = 2000 g

Rise in temperature = 2.48°C, Fuse wire correction = 10.0 cal

Acid correction = 60.0 cal, Cooling correction = 0.02°C

Calculate the gross and net calorific value of the coal sample in cal/g. Assume the latent heat of condensation of steam as 580 cal/g.

$$GCV = \frac{(W + w)[(t_1 - t_2) + \text{Cooling Coorection}] - [\text{acid} + \text{fuse corrections}]}{x}$$

$$= \frac{(2000+700)(2.48+0.02)-(10+60)}{0.95} = \frac{(2700)(2.50)-(70)}{0.95}$$

$$= \frac{6750-70}{0.95} = \frac{6680}{0.95} = 7031.57 \text{ cal/g}$$

[Ans HCV/GCV = 7031.57 cal/g

LCV/NCV = 6770.57 cal/g]

LCV or NCV = HCV – 0.09H × 580 cal/g

= 7031.570 – 0.09 × 5 × 580

= 7031.57 – 261 = 6770.57 cal/g

6. Calculate the GCV and LCV of a fuel which underwent complete combustion in a bomb calorimeter and the experiment parameters are given below.

- **Fuel contains C =93%; H =6% and ash = 1%, Initial Temperature: 35°C, Final temperature: 40°C, Weight of water: 2.50 Kg, Water Equivalent of calorimeter: 425 gm , Weight of fuel: 2 gm, Acid correction: 7 cal, Fuse wire correction: 13°C, Cooling correction: 32°C**

Solution: **Wt. of coal sample (x) = 2 g; wt. of water (W) =2500 g;**

Water equivalent of calorimeter (w) = 425 g;

Temperature rise (t_2-t_1) = 40-35 = 5°C;

Acid correction =7 cal;

Fuse wire correction = 13 cal;

Cooling correction = 32

Latent heat of steam = 587 cal/g;

Percentage of H = 6%

$$GCV = \frac{(W + w)(t_2 - t_1 + \text{Cooling Correction}) - [\text{acid + fuse corrections}]}{x}$$

$$= \frac{(2500 + 425) \times (5+32) - [7 + 13]\ \text{cal}}{2g} = \frac{108965-20}{2}$$

$$= 54472.5\ \text{cal/g.}$$

NCV $= [GCV - 0.09\ H \times \text{latent heat steam}]$

$$= (54472.5 - 0.09 \times 6 \times 587)\ \text{cal/g}$$

$$= 54155.52\ \text{cal/g}$$

Dulong's Formula

The approximate calorific value of a fuel can be determined by knowing the amount of constituents present:

Gross or higher calorific value (HCV) from elemental constituents of a fuel.

H = 34500 kcal/kg;

C = 8080 kcal/kg;

S = 2240 kcal/kg

Oxygen present in the fuel is assumed to be present as water (fixed hydrogen).

Available Hydrogen = Total hydrogen – Fixed hydrogen

= Total hydrogen – 1/8 mass of oxygen in fuel.

Dulong's formula for calorific value from the chemical composition of fuel is,

$$\mathrm{HCV} = \frac{1}{100}\left[8080\ \mathrm{C} + 34500\left(\mathrm{H} - \frac{0}{8}\right) + 2240\ \mathrm{S}\right]\mathrm{kcal/kg}$$

7. A coal sample on analysis gives C = 75%, H_2= 6 %, O_2= 3.5 %, S = 3 % and the rest ash. Calculate the Gross and Net calorific values of the fuel. Latent heat of steam is = 587 cal/gm .

(i) Gross Calorific Value (GCV)

$$= \frac{1}{100}\left(8080\,C + 34500\,[H - \frac{O}{8}] + 2240\,S\right)\ \text{kcal/kg}$$

$$= \frac{1}{100}\left(8080 \times 75 + 34500\,[6 - \frac{3.5}{8}] + 2240 \times 3\right)\ \text{kcal/kg}$$

$$= \frac{1}{100}[606000 + 191906 + 6720]\ \text{kcal/kg}$$

$$= \frac{1}{100}[804626]\ \text{kcal/kg}$$

$$= \boldsymbol{80462.6\ kcal / kg.}$$

(i) NET Calorific Value (NCV)

$$= \text{GCV} - \frac{9}{100}H \times 587\ \text{kcal/kg}$$

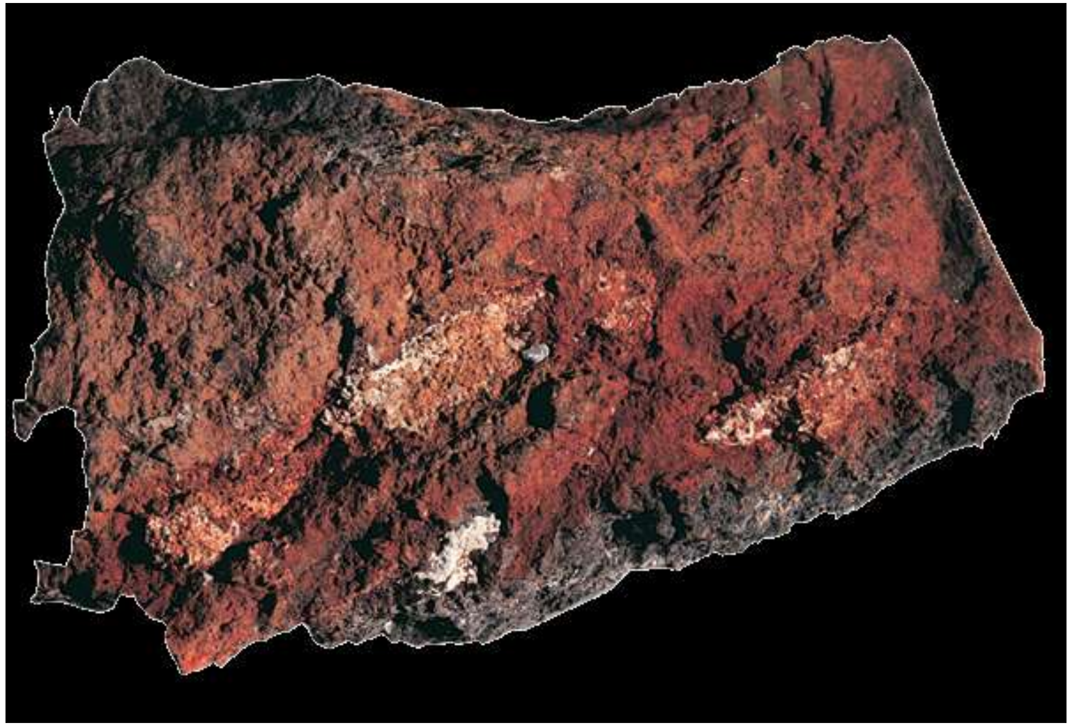
$$= 80462.6 - \frac{9}{100} \times 6 \times 587\ \text{kcal/kg}$$

$$= 80462.6 - 316.98\ \text{kcal/kg}$$

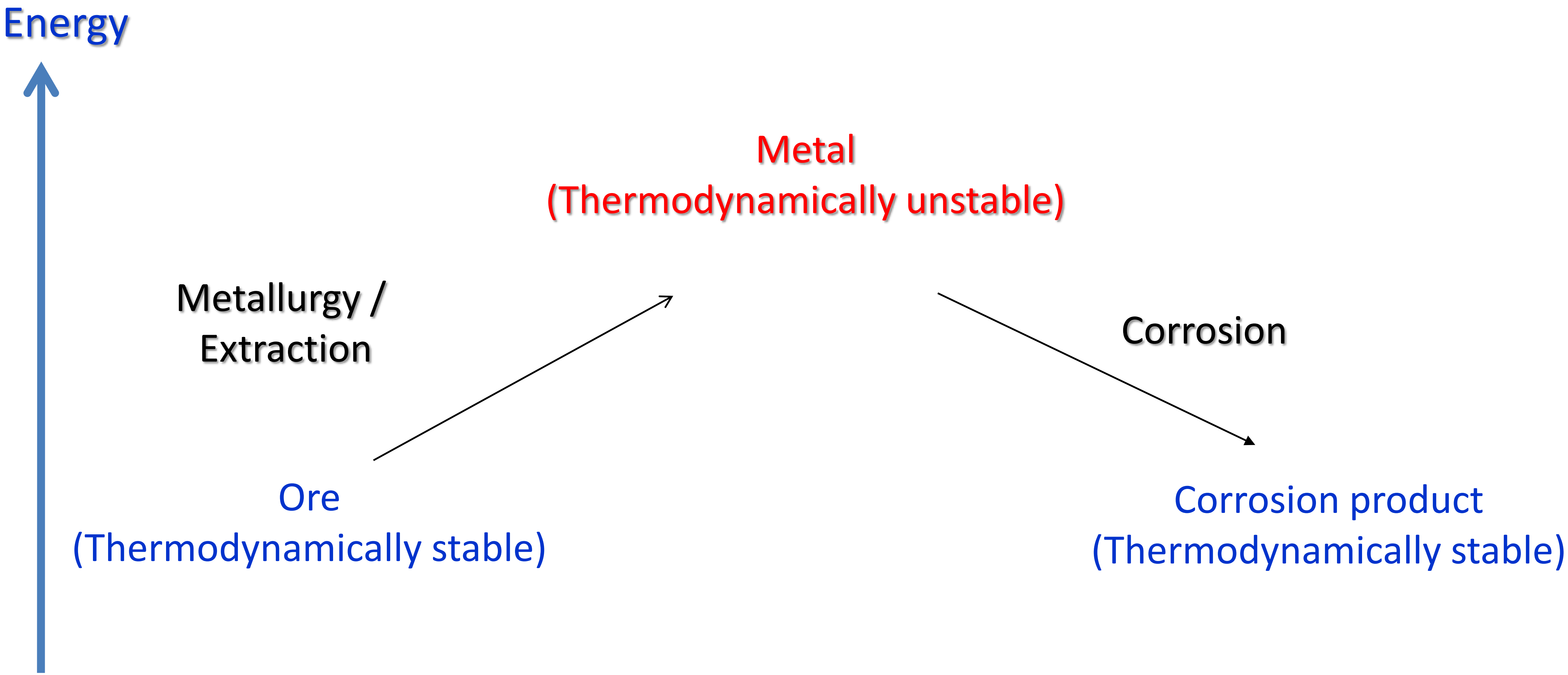
$$= \boldsymbol{80145.62\ kcal / kg}$$

Corrosion

Natural Abundance of Metals



In the form of oxides, carbonates, chlorides, silicates etc. (Ores)


Energy
Metal
(Thermodynamically unstable)
Metallurgy /
Extraction
Corrosion
Ore
(Thermodynamically stable)
Corrosion product
(Thermodynamically stable)

- **Combined forms are reduced to their metallic states from their ores – extraction process**
- **The isolated pure metals – excited state (high energy state) than their corresponding ores**
- **They have a natural tendency to revert back to combined state (low energy state)**
- **When the metals put into use – Exposed to environment (dry gases, moisture, liquids), the exposed metal surfaces begin to decay – conversion into more stable metal compounds**
- **Destruction or deterioration of the metal starts at the surface**

Corrosion in Metals and Alloys

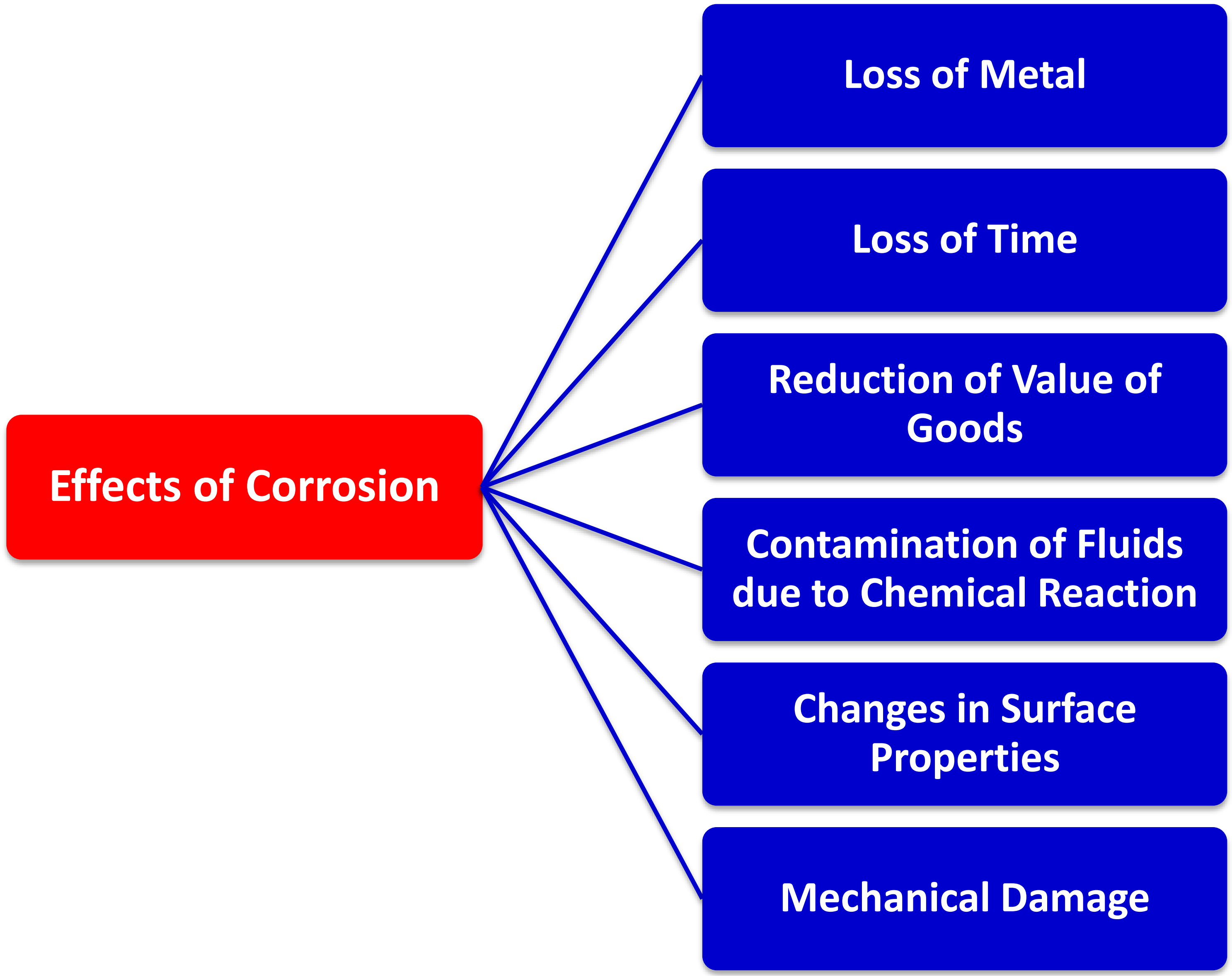
"Any process of destruction and consequent loss of metals or alloys, through an unwanted chemical or electrochemical changes by its surrounding environment"

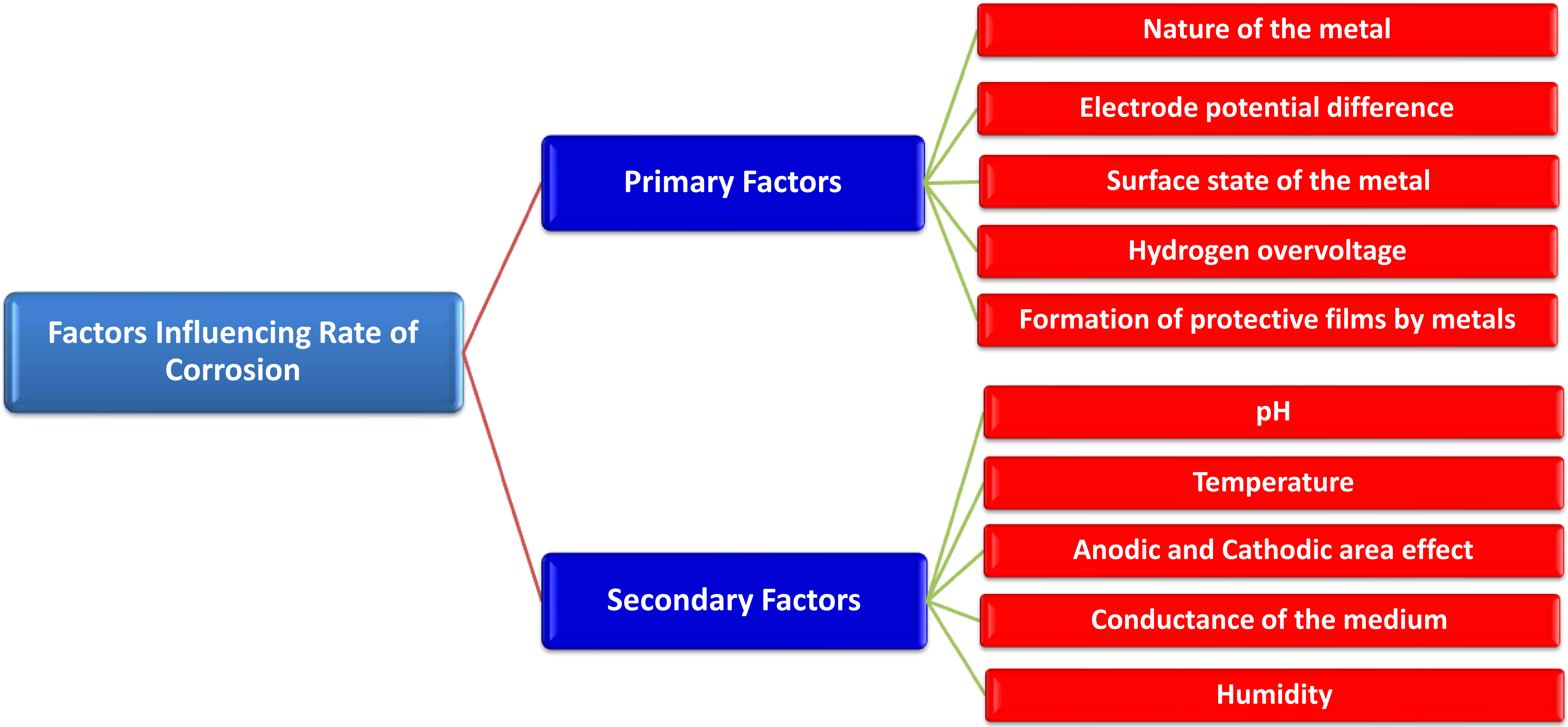
$$\text{Metal ores} \underset{\text{Corrosion}}{\overset{\text{Metallurgical extraction}}{\rightleftharpoons}} \text{Metal}$$

Causes of Corrosion

- Corrosion is due the deterioration of materials by chemical interaction with their environment.
- The most familiar example of corrosion is rusting of iron exposed to the atmospheric conditions.

$$2Fe(s) + \frac{3}{2}O_2(g) + xH_2O(l) \rightarrow \underset{\text{(Chemical composition of rust)}}{Fe_2O_3 \cdot xH_2O(s)}$$


Effects of Corrosion
Loss of Metal
Loss of Time
Reduction of Value of Goods
Contamination of Fluids due to Chemical Reaction
Changes in Surface Properties
Mechanical Damage


Factors Influencing Rate of Corrosion
Primary Factors
Nature of the metal
Electrode potential difference
Surface state of the metal
Hydrogen overvoltage
Formation of protective films by metals
Secondary Factors
pH
Temperature
Anodic and Cathodic area effect
Conductance of the medium
Humidity

Protective coatings for corrosion control

Cathodic Protection

"Corrosion control is achieved by forcing a defined quantity of direct current to flow from auxiliary anodes, through the electrolyte, and onto the metal structure to be protected"

To force the metal to be protected to behave like cathode

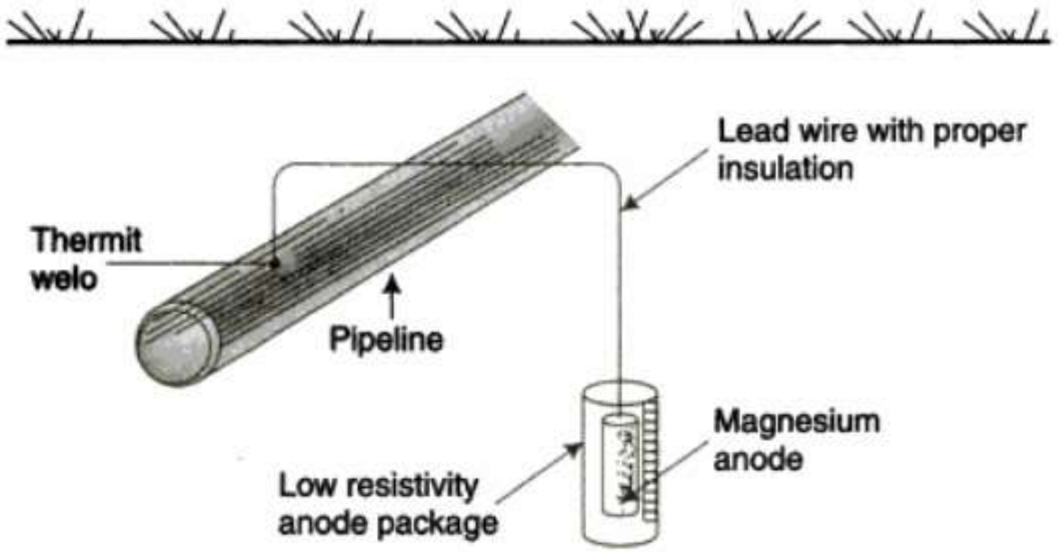
Sacrificial Anodic Protection Method

Involves the use of current that produced when the two electrochemically dissimilar metals or alloys are metallically connected and exposed to the electrolyte

Impressed Current Cathodic Protection

Involves the use of direct current power source and auxliary anode Impressed current cathodic protection system

a. Sacrificial Anodic Protection Method



Metallic structure (to be protected) is connected by a wire to a more anodic metal

Sacrificial anode Eg. Mg, Zn, Al and their alloys

Protection of Buried pipe lines, Underground cables, Marine structures, Ship- Hulls, Water-tanks

Examples

Sacrificial Anode for a Pipeline

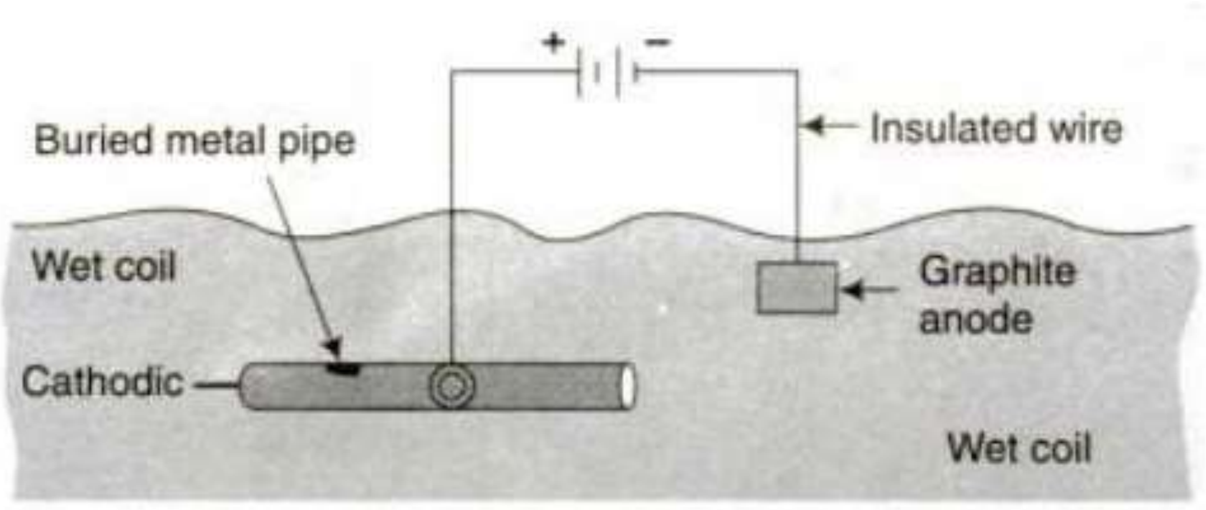
Aluminium anodes mounted on a steel jacket structure – using galvanic corrosion for corrosion control! Called cathodic protection (aka sacrificial anode)

Zinc is attached to the steel hull of the vessel

b. Impressed Current Cathodic Protection

An impressed current is applied in opposite direction to nullify the corrosion current, and covert corroding metal from anode to cathode

The impressed current is obtained from a dc source (battery) with an inert anode graphite (insoluble metal).



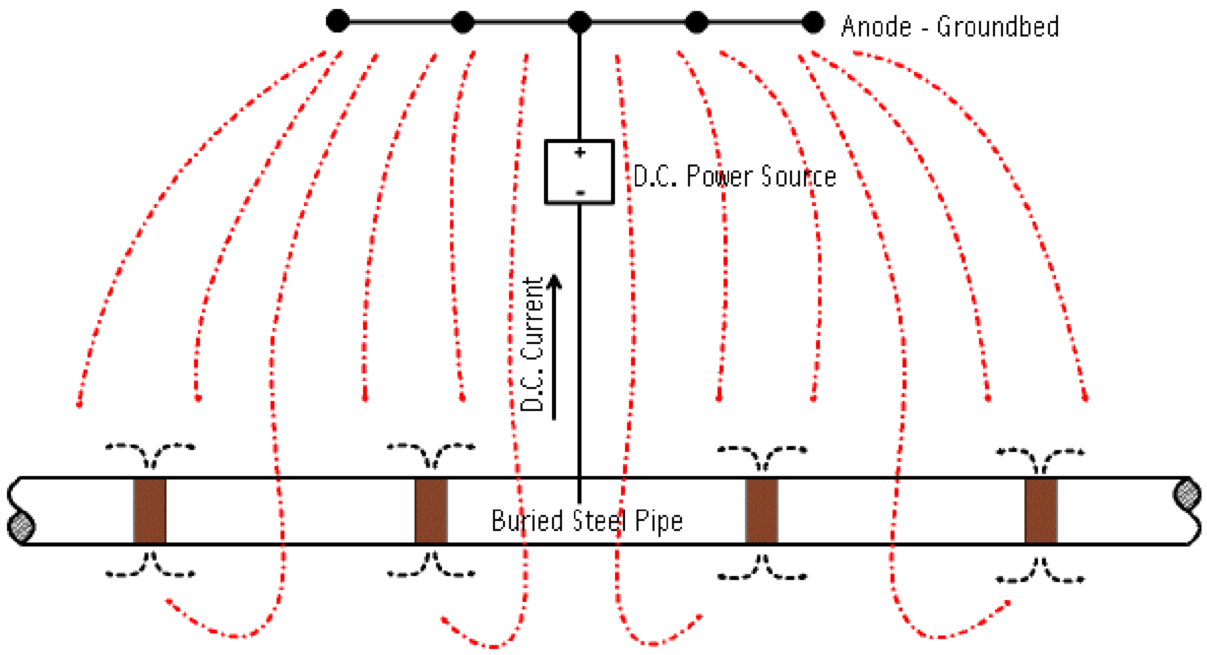
Water pipeline

Oil pipeline

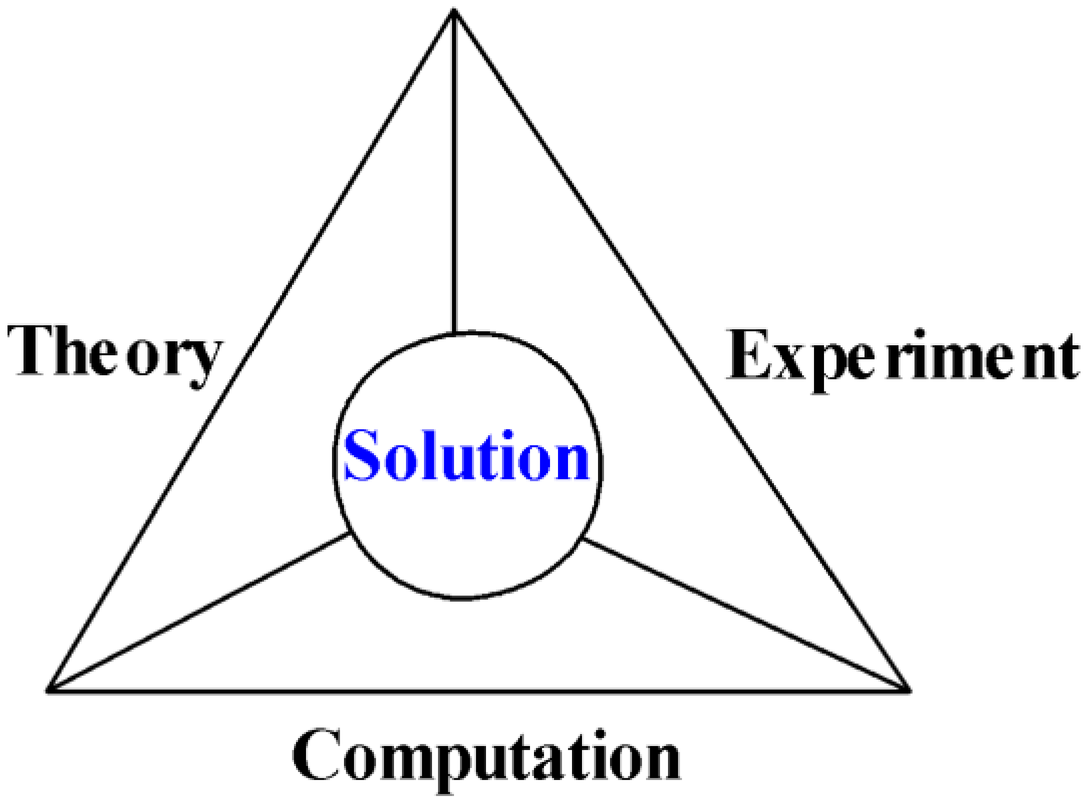
Transmission line

Marine piers

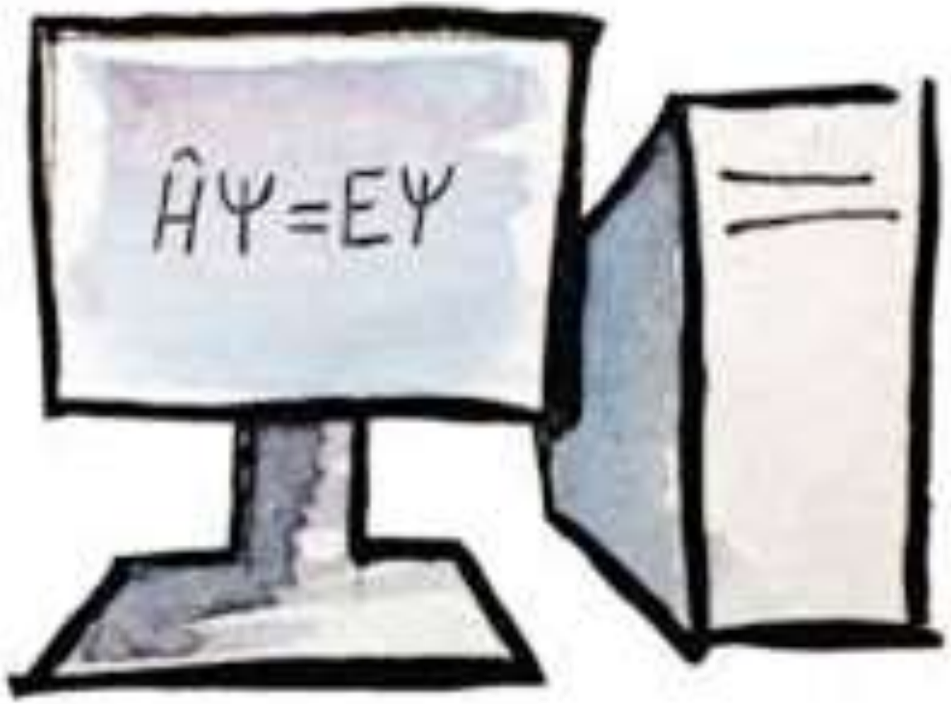
Exxon Mobil example

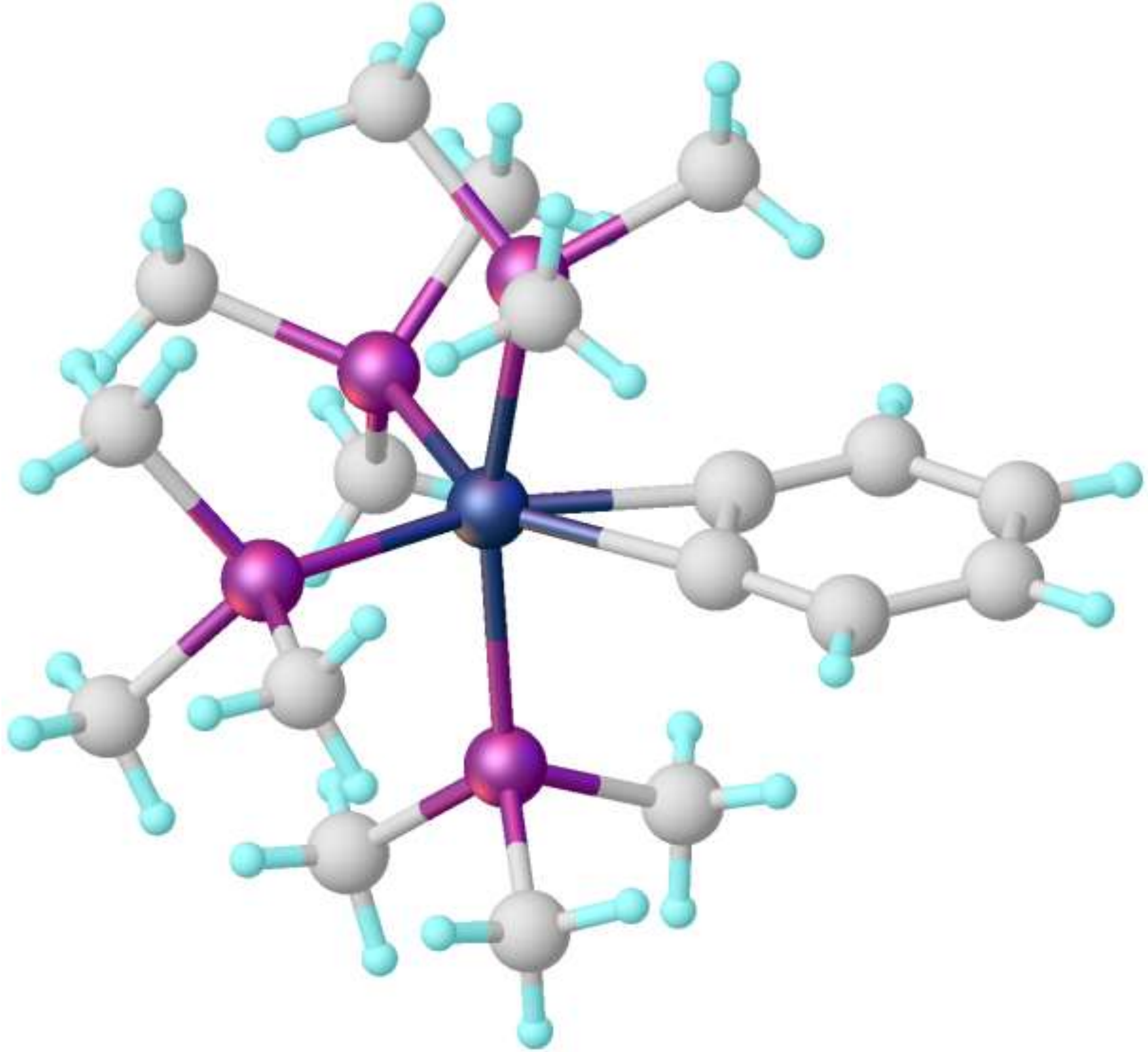


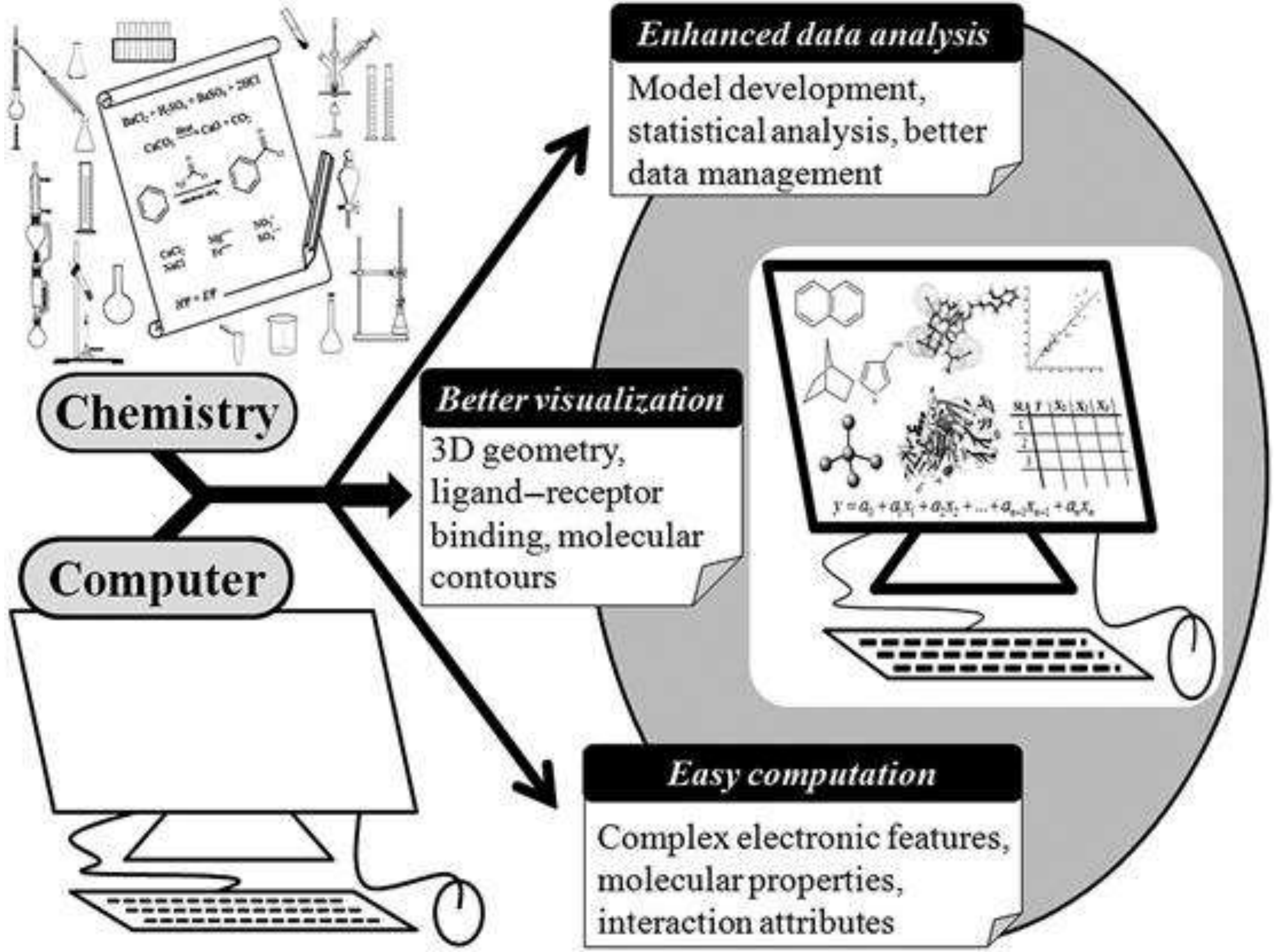
In Computational chemistry, computers are used to solve the theoretical equations or model for the properties of a chemical system.



Doing Chemistry with Computers



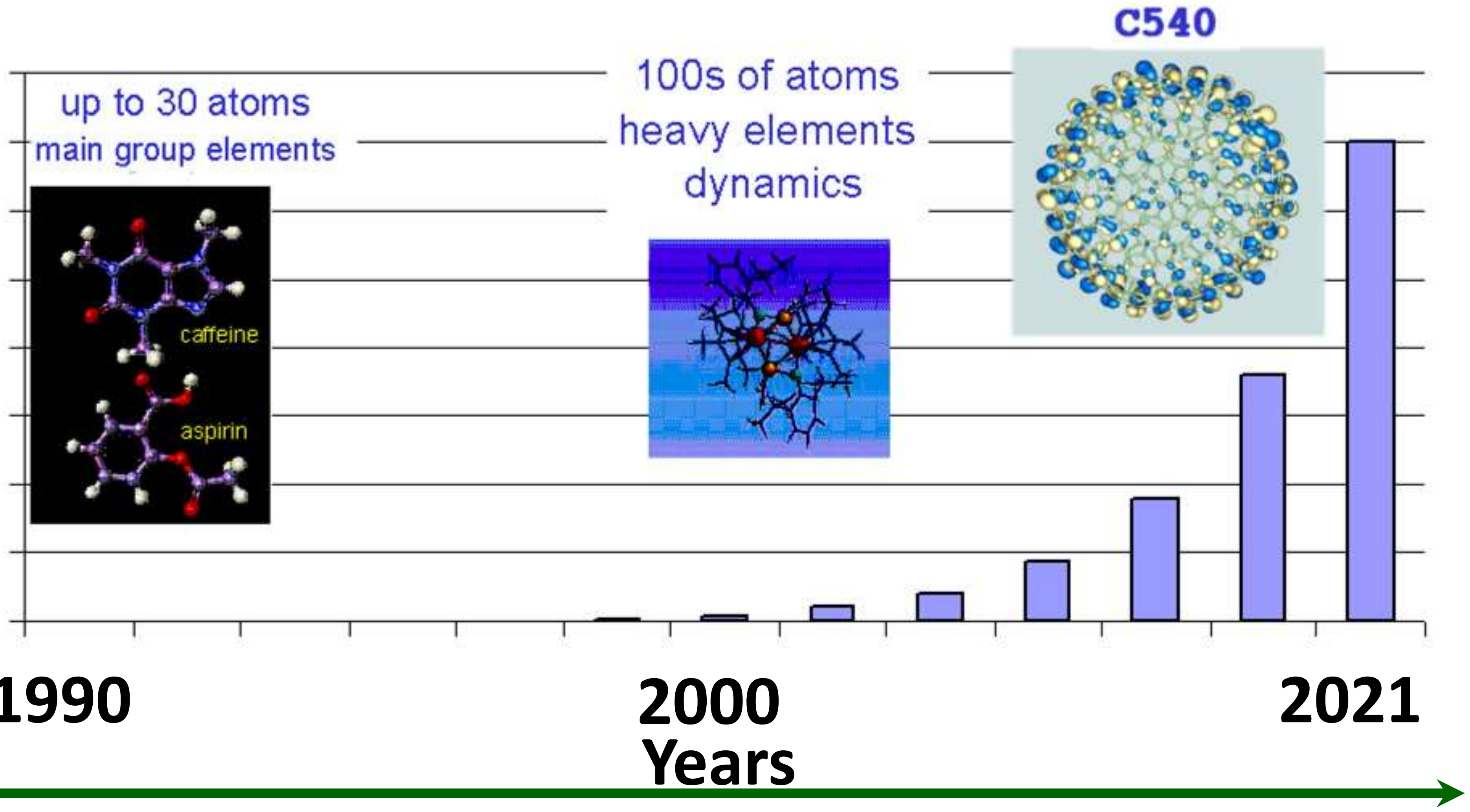



Chemistry
Computer
Enhanced data analysis
Model development, statistical analysis, better data management
Better visualization
3D geometry, ligand–receptor binding, molecular contours
Easy computation
Complex electronic features, molecular properties, interaction attributes

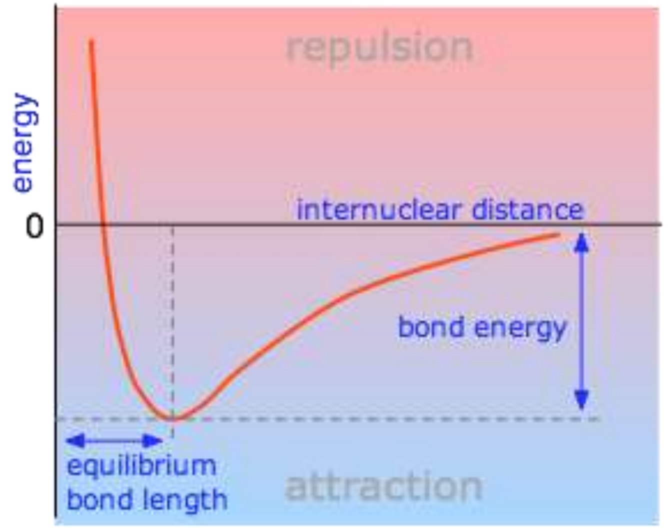
Using computational chemistry software you can perform:

- Electronic structure predictions
- Geometry optimizations or energy minimizations
- Conformational analysis and potential energy surfaces (PES)
- Frequency calculations
- Finding transition structures and reaction paths
- Molecular docking: Protein – Protein and Protein-Ligand interactions
- Electron and charge distributions calculations
- Chemical kinetics: Calculations of rate constants for chemical reactions
- Thermochemistry: heat of reactions, energy of activation, etc.
- Calculation of many other molecular and physical and chemical properties
- Orbital energy levels and electron density
- Electronic excitation energy

Computer Performance

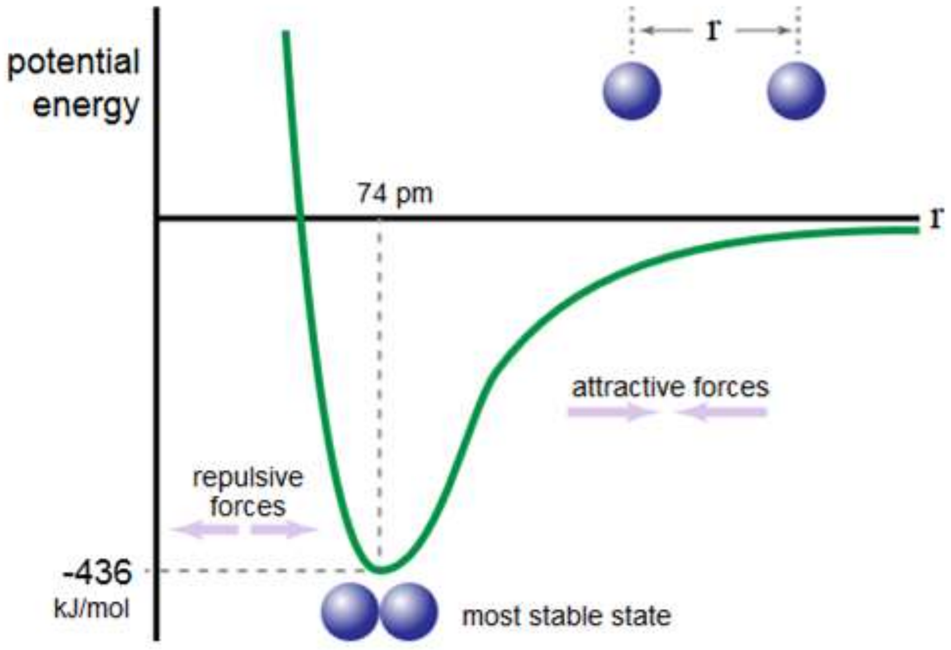


- **Structure of a molecule in general is how atoms are arranged in the molecule in the three dimensional space.**

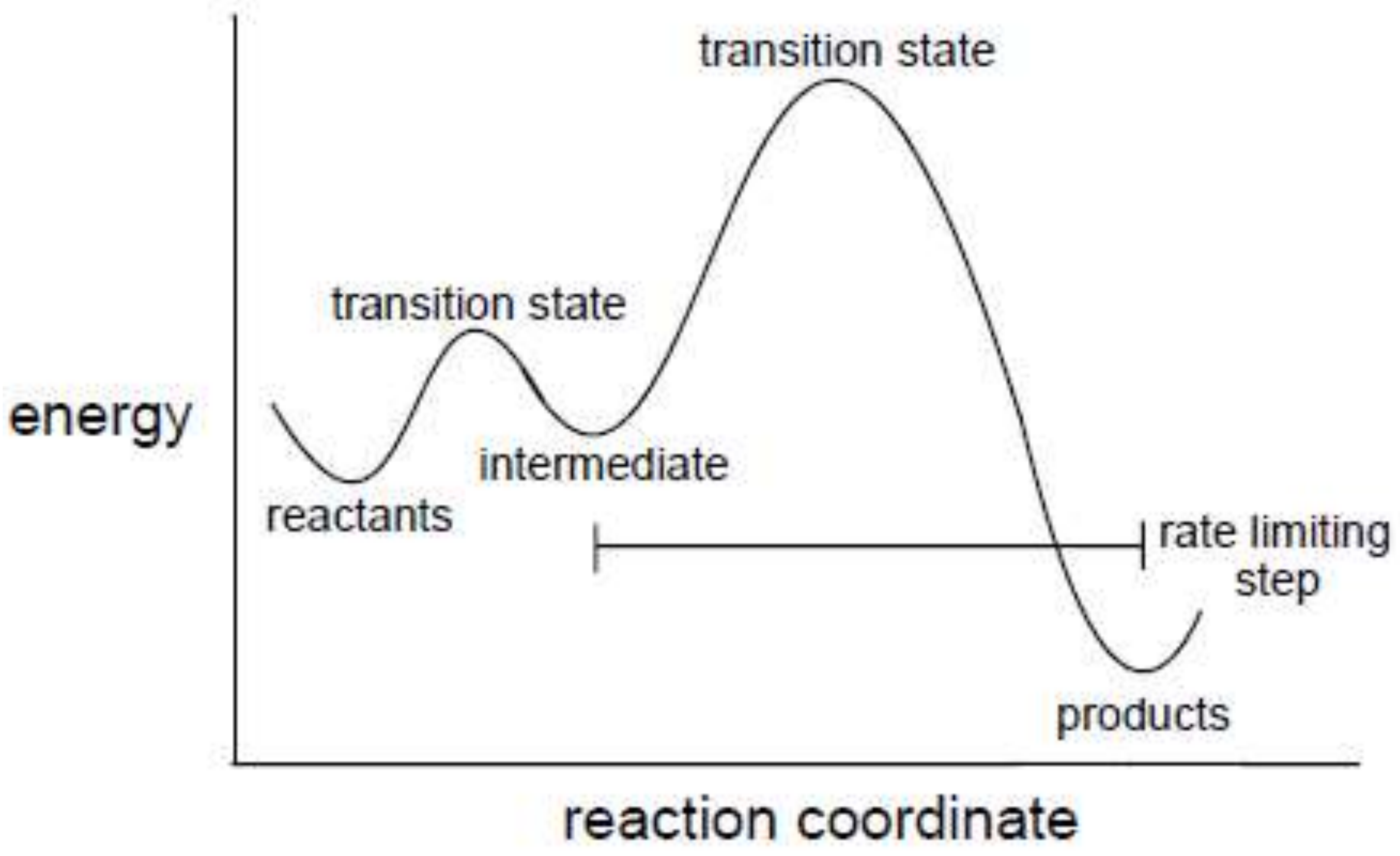


Potential energy for nuclear motion in a diatomic molecule

- **Potential energy surface (PES) is a plot of energy with respect to various internal coordinates of a molecule such as bond length, bond angle etc.**
- **The PES is the energy of a molecule as a function of the positions (coordinates).**
- **This energy of a system of two atoms depends on the distance between them.**
- **At large distances the energy is zero, meaning "no interaction".**
- **The attractive and repulsive effects are balanced at the minimum point in the curve**

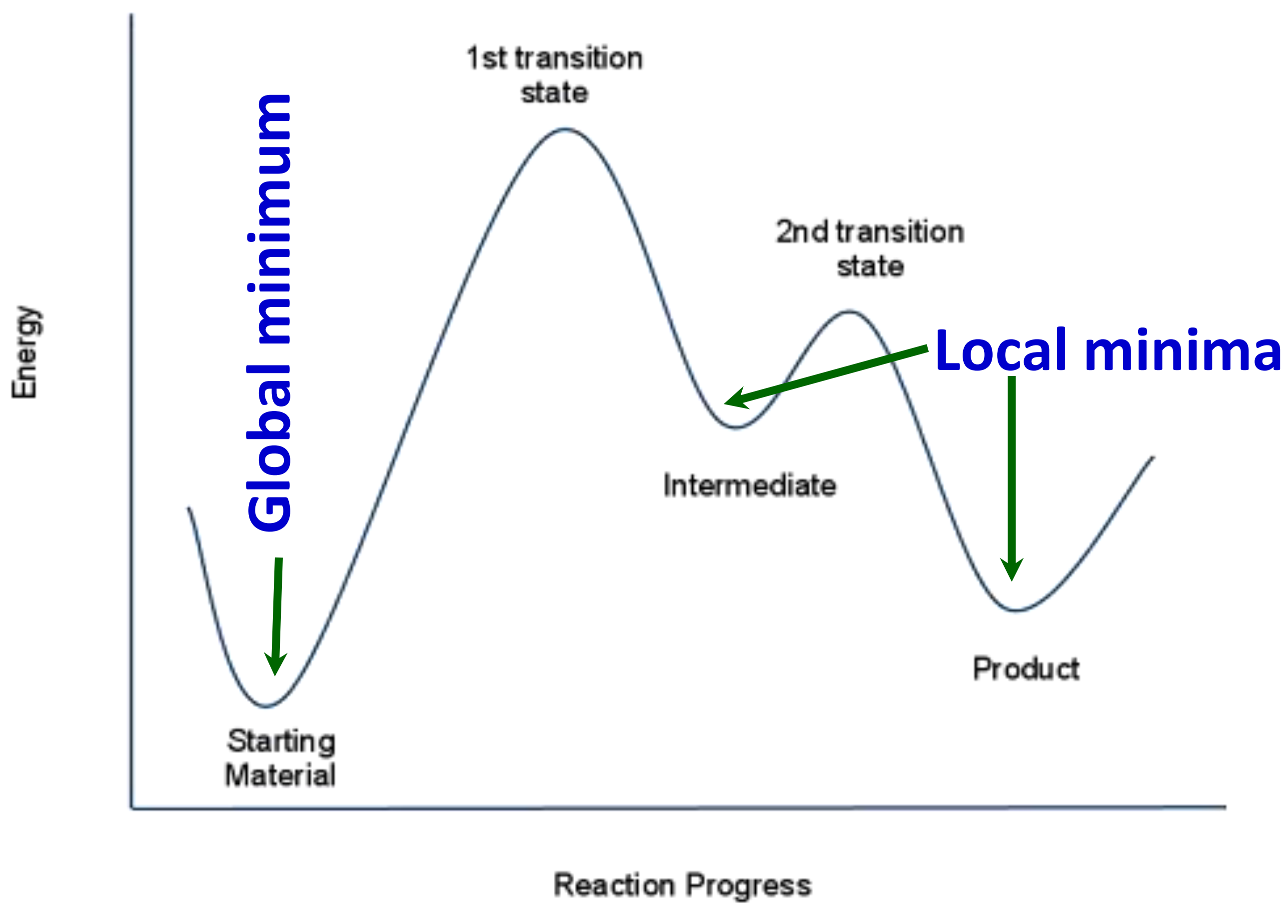


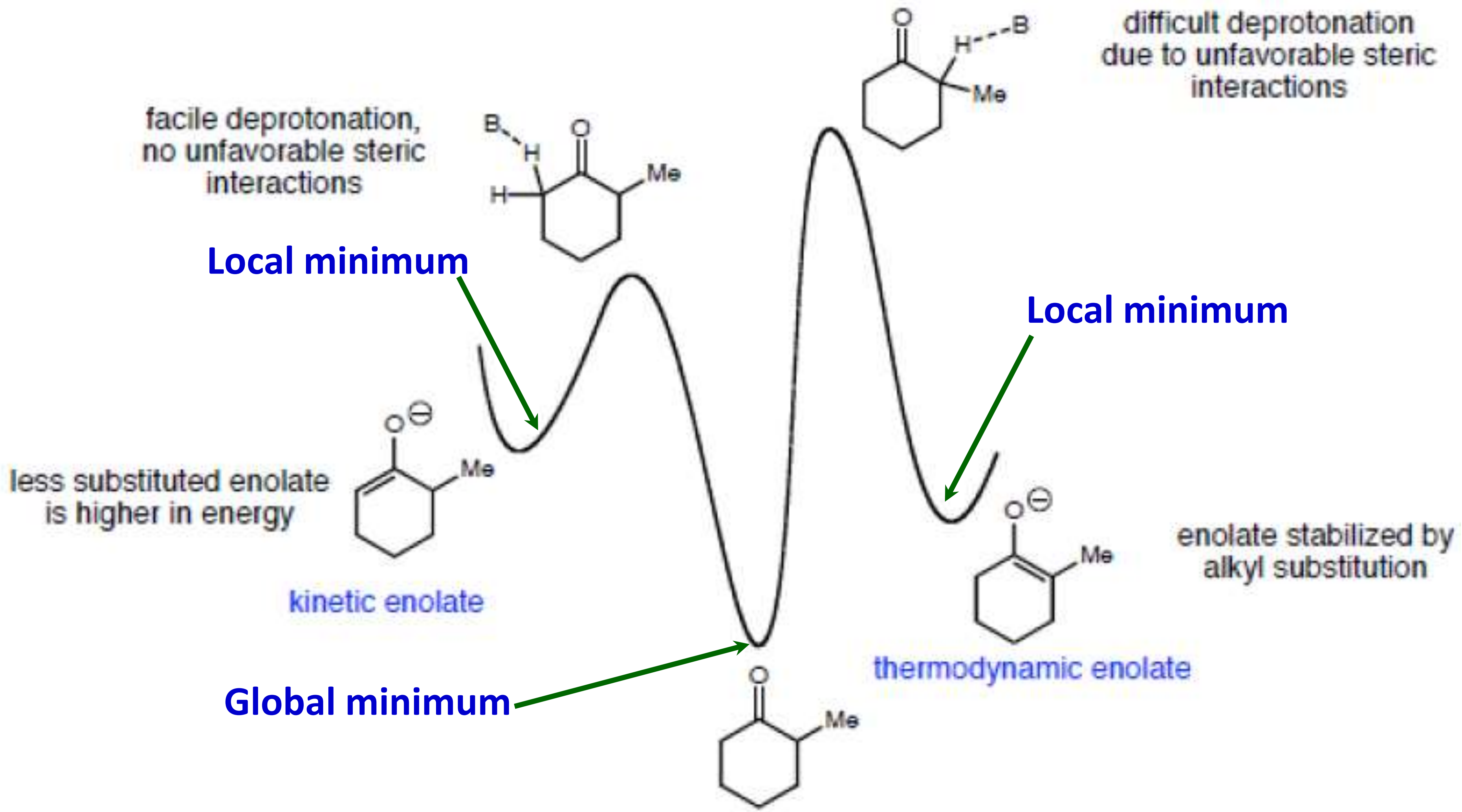
Potential Energy Surfaces and Mechanism



Conformational Analysis

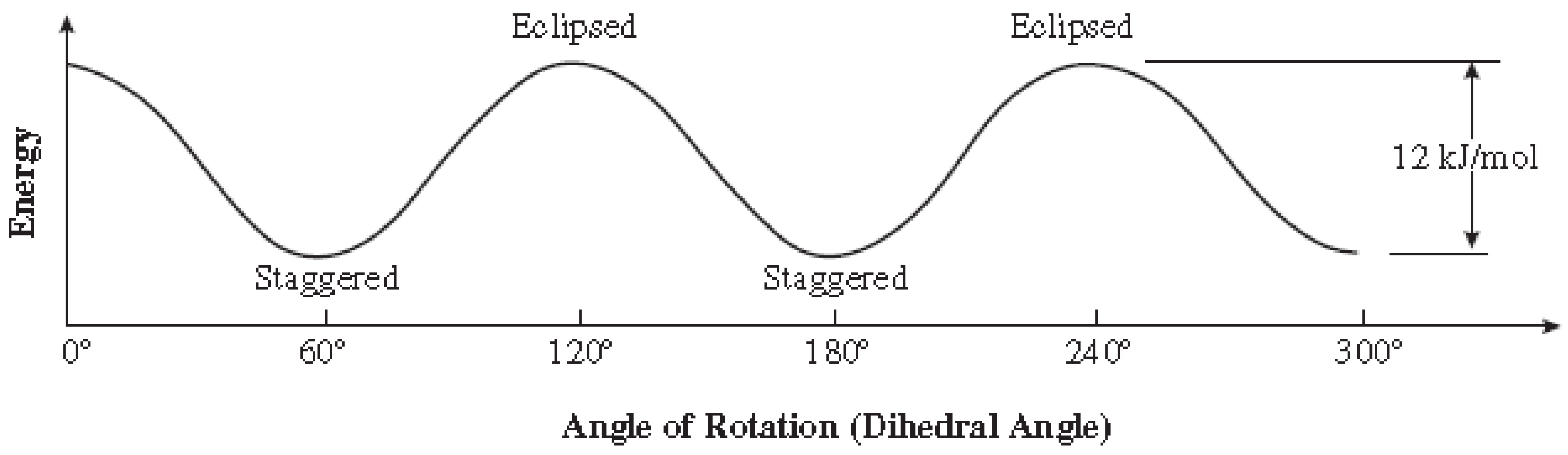
- Identification of all possible minimum energy structures (conformations) of a molecule is called conformational analysis.
- Conformational analysis is an important step in computational chemistry studies as it is necessary to reduce time spent in the screening of compounds for properties and activities.
- The identified conformation could be the local minimum, global minimum, or any transition state between the minima.
- Out of the several local minima on the potential energy surface of a molecule, the lowest energy conformation is known as the global minimum.



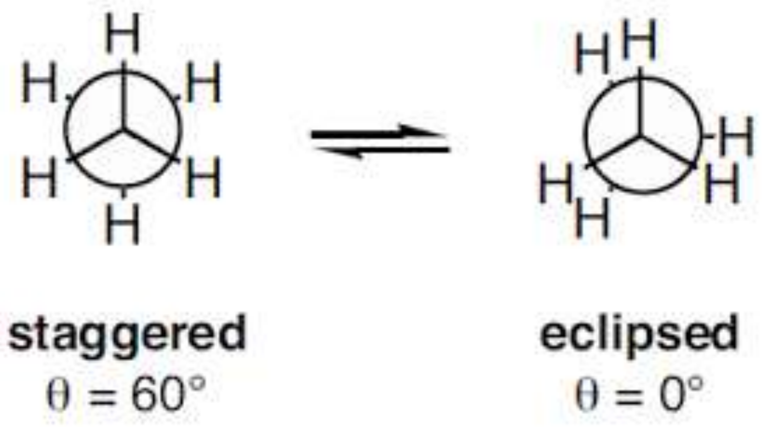


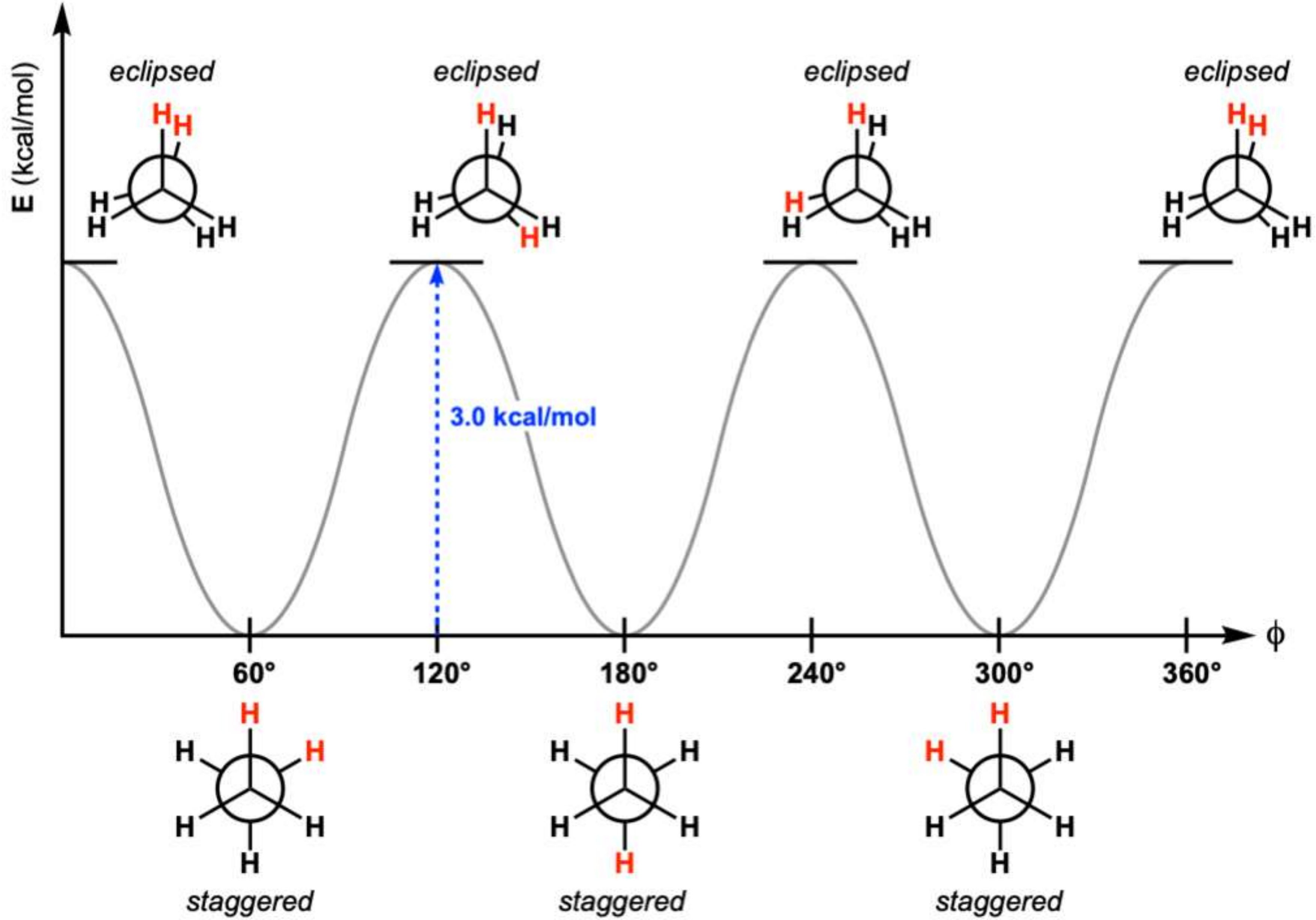
facile deprotonation, no unfavorable steric interactions
difficult deprotonation due to unfavorable steric interactions
Local minimum
Local minimum
less substituted enolate is higher in energy
kinetic enolate
enolate stabilized by alkyl substitution
thermodynamic enolate
Global minimum

Ethane Conformations

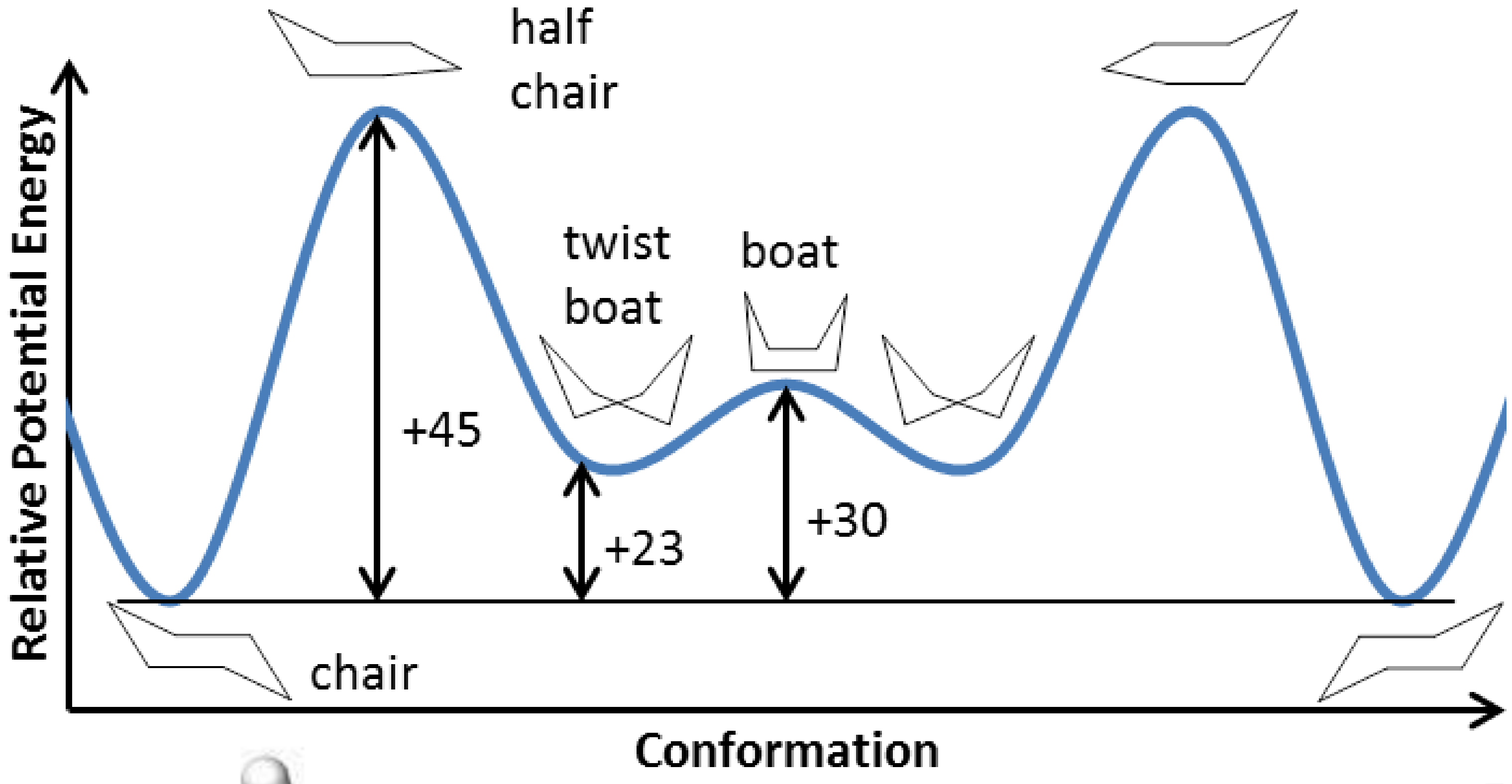


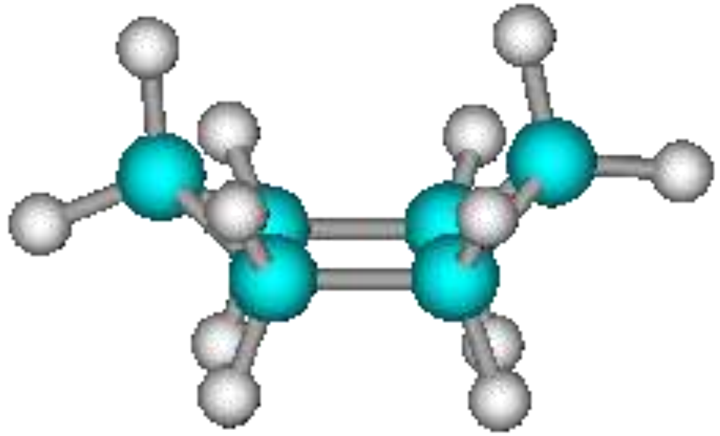
The torsional energy of ethane is lowest in the staggered conformation. The eclipsed conformation is about 3.0 kcal/mol (12.6 kJ/mol) higher in energy. At room temperature, this barrier is easily overcome, and the molecules rotate constantly.

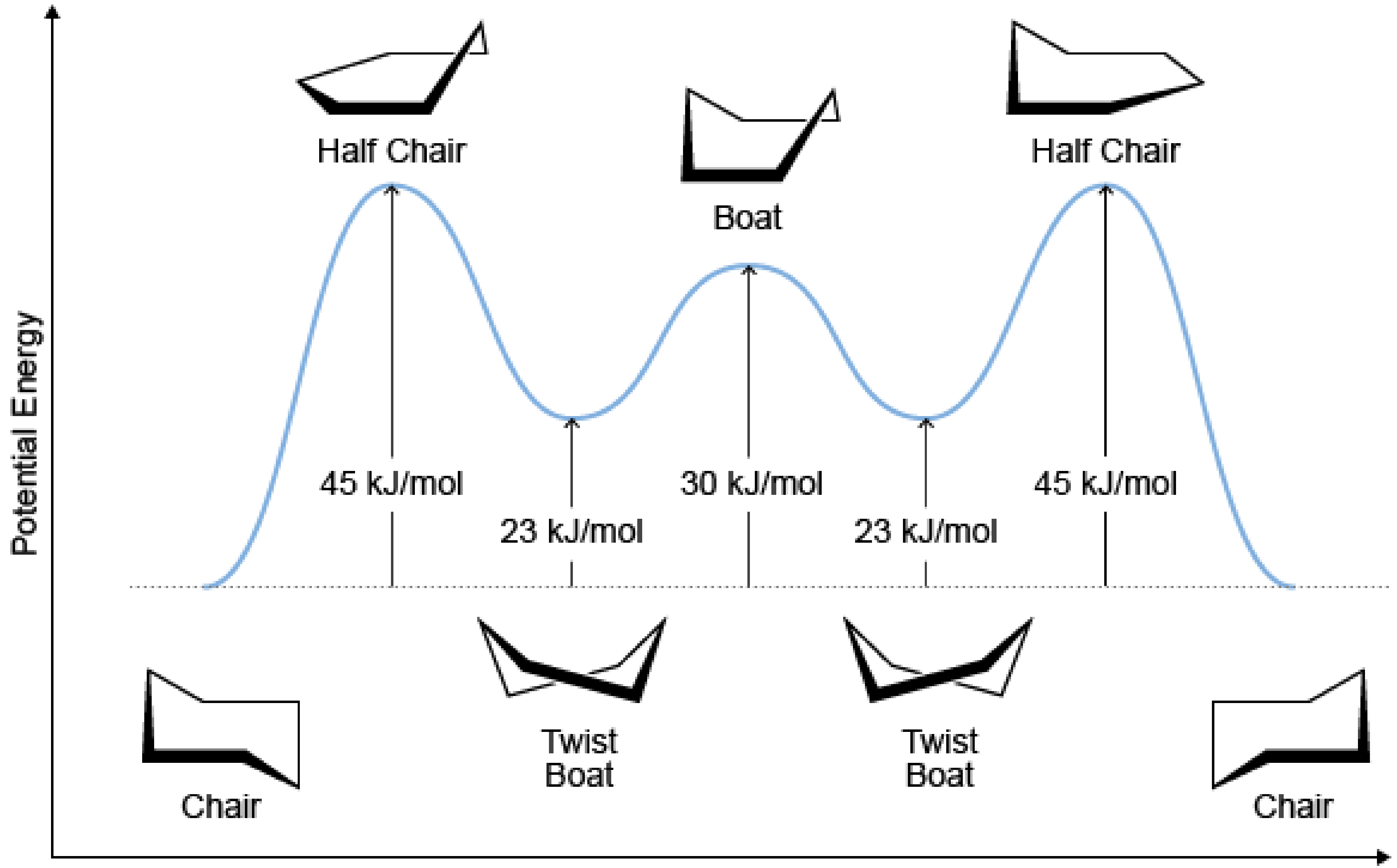



E (kcal/mol)
eclipsed
eclipsed
eclipsed
eclipsed
3.0 kcal/mol
60°
120°
180°
240°
300°
360°
ϕ
staggered
staggered
staggered

Conformations of Cyclohexane

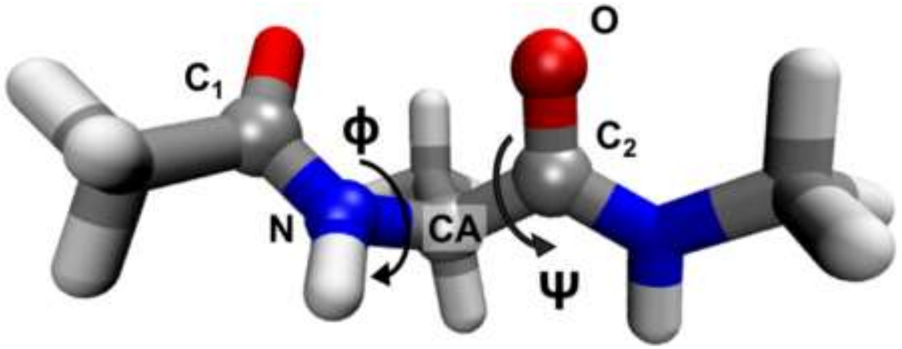


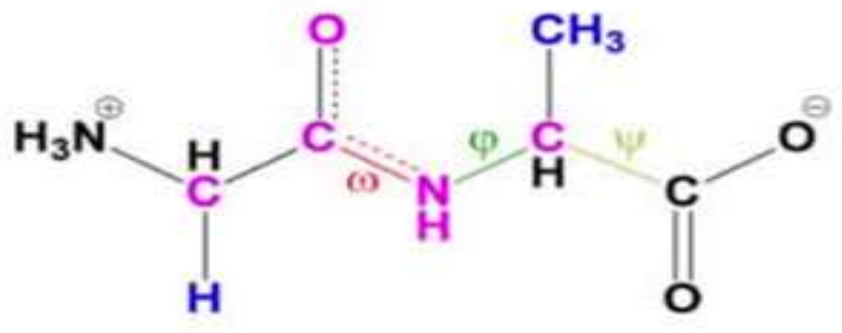


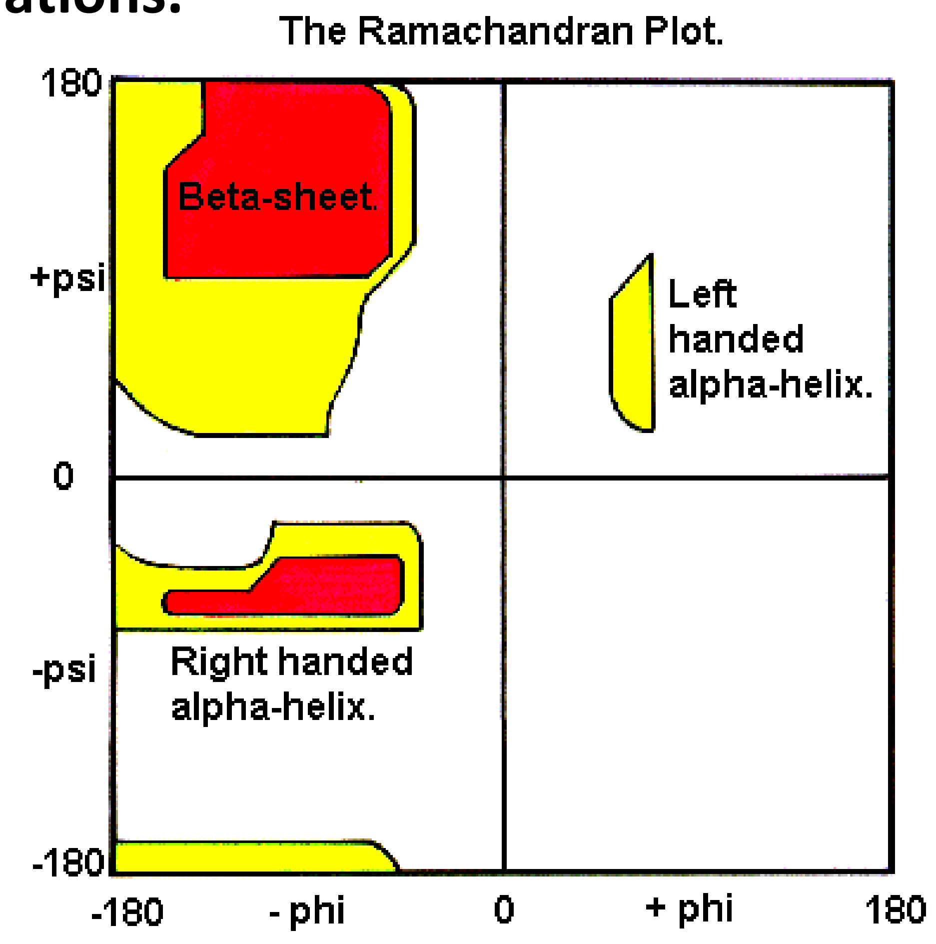

Half Chair
Boat
Half Chair
Potential Energy
45 kJ/mol
23 kJ/mol
30 kJ/mol
23 kJ/mol
45 kJ/mol
Chair
Twist Boat
Twist Boat
Chair

Ramachandran plot: Peptide and Protein systems

- In a polypeptide, the main chain N – C and C – C bonds relatively are free to rotate. These rotations are represented by the torsion angles *phi and psi*, respectively.
- G N Ramachandran used computer models of small polypeptides to systematically vary phi and psi with the objective of finding stable conformations.







Geometry optimization Or Energy Minimization

To Find

- Minimum energy geometry
- Lowest energy structure
- Most stable conformation

- Many problems in computational chemistry (and scientific computing in general!) are optimization problems
- Finding the "stationary points" in multidimensional system – Difficult Job

Why do we need the stable geometry?

- The **most stable geometry** is the one which yields minimum energy
- Objective of geometry optimization is to find an atomic arrangement(geometry) which makes the molecule most stable

Methods of Optimization

Energy only:

- Simple methods

Energy and first derivatives (forces)

- Steepest descents (poor convergence)
- Conjugate gradients (retains information)
- Approximate Hessian update

Energy, first and second derivatives

- Newton-Raphson
- Broyden (BFGS) updating of Hessian (reduces inversions)
- Rational Function Optimization (for transition states)