

Engineering Chemistry

BCHY101L



VIT[®]
Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)

Module 7

Industrial applications

Water purification methods - zeolites, ion-exchange resins and reverse osmosis; Fuels and combustion -LCV, HCV, Bomb calorimeter (numericals), anti-knocking agents); Protective coatings for corrosion control: cathodic and anodic protection - PVD technique; Chemical sensors for environmental monitoring - gas sensors; Overview of computational methodologies: energy minimization and conformational analysis.

Water purification methods

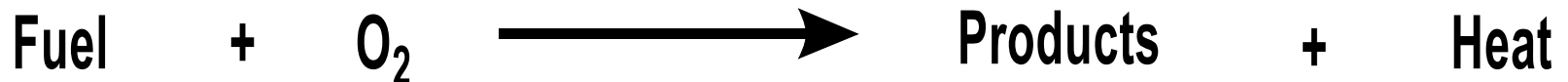
reverse osmosis

Protective coatings for corrosion control: cathodic
and anodic protection

PVD technique

Fuels

- Fuel – a combustible substance, upon burning in air or O_2 gives large amount of heat. Eg. wood, charcoal, kerosene, petrol, LPG, biogas, etc.
- Combustion – a process in which a substance burn in air or O_2 with evolution of heat. A substance which is burnt is called combustible substance.
- Fuels contain C and H as main constituent, during combustion C and H combine with O_2 and produce CO_2 and H_2O with simultaneous release of heat at rapid rate.
- CO_2 and H_2O has low energy than the compound from which it is formed.
- Thus energy released during the combustion process is the difference in the energy of the reactant and that of products formed.



more heat energy content

less heat energy content

Calorific Value (CV) of a fuel

- Efficiency of a fuel is judged based on their CV
- CV of fuel – quantity of heat evolved by complete combustion of unit quantity of fuel in air or O_2 .
- Units of heat is generally expressed in Calories (cal), Kilo calories (kcal), British Thermal Units (BTU), Centigrade Heat Unit (CHU)
- 1 Calorie (cal) – quantity of heat required to raise the temp. of 1 g of H_2O by $1^\circ C$

$$1 \text{ cal} = 4.185 \text{ Joules}$$

$$1 \text{ Kilocalorie} = 1000 \text{ cal.}$$

1 British Thermal Unit (BTU) – quantity of heat required to raise the temp. of 1 lb of H_2O by $1^\circ F$

$$1 \text{ BTU} = 252 \text{ cal} = 1054.6 \text{ Joules}$$

1 Centigrade Heat Unit – amount of heat required to raise the temperature of 1 lb of water through $1^\circ C$

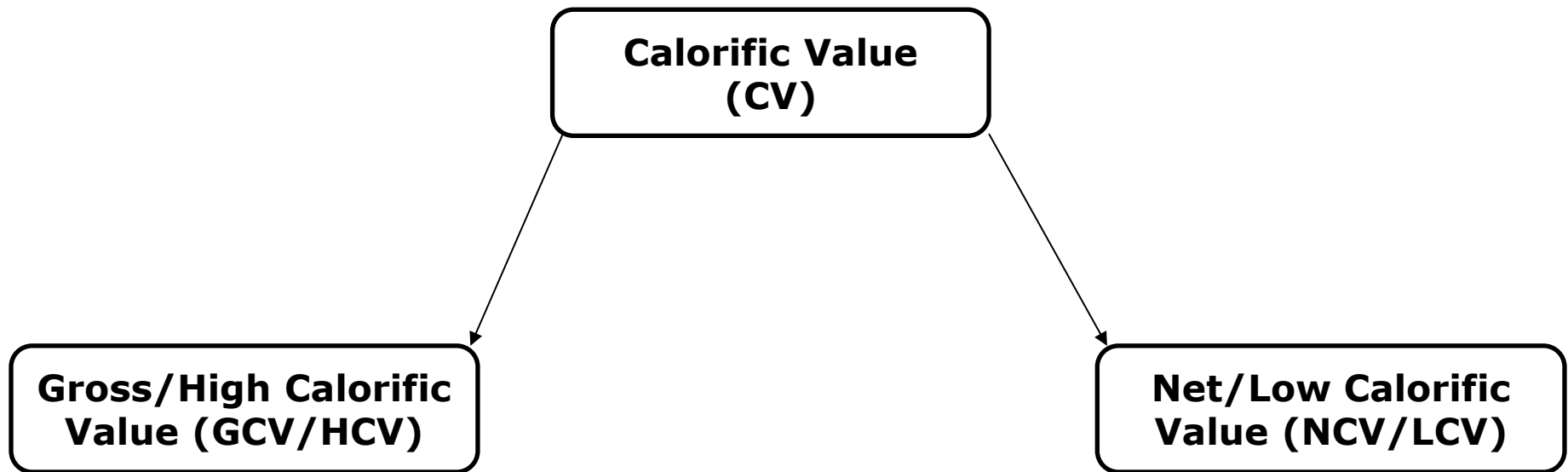
$$1 \text{ kg} = 2.2 \text{ lb}; 1^\circ C = 1.8^\circ F$$

Unit of CV of solids and liquids

- Generally expressed in calories/gram (cal/g) or kilocalories/gram (kcal/g) or BTU/lb or CHU/lb

Unit of CV of gas

- Expressed in kcal/m³ or cal/cm³ or BTU/ft³ at given T and P. Heat quantity per unit volume of gas is CV of gaseous fuel.
- Since volume of gas varies with T and P. CV of gaseous fuel includes T and P.
- CV of fuel generally expressed in two ways



Gross/High Calorific Value (GCV/HCV)

- Quantity of heat evolved by complete combustion of unit mass of fuel in air or O_2 and the products of combustion are brought down to normal temperature.
- Hydrocarbon fuel is mostly used. During combustion, carbon is oxidized to CO_2 and hydrogen to steam. When products of combustion are cooled to RT, latent heat of vaporization of steam released is added to heat of combustion of fuel.

Net/Low Calorific Value (NCV/LCV)

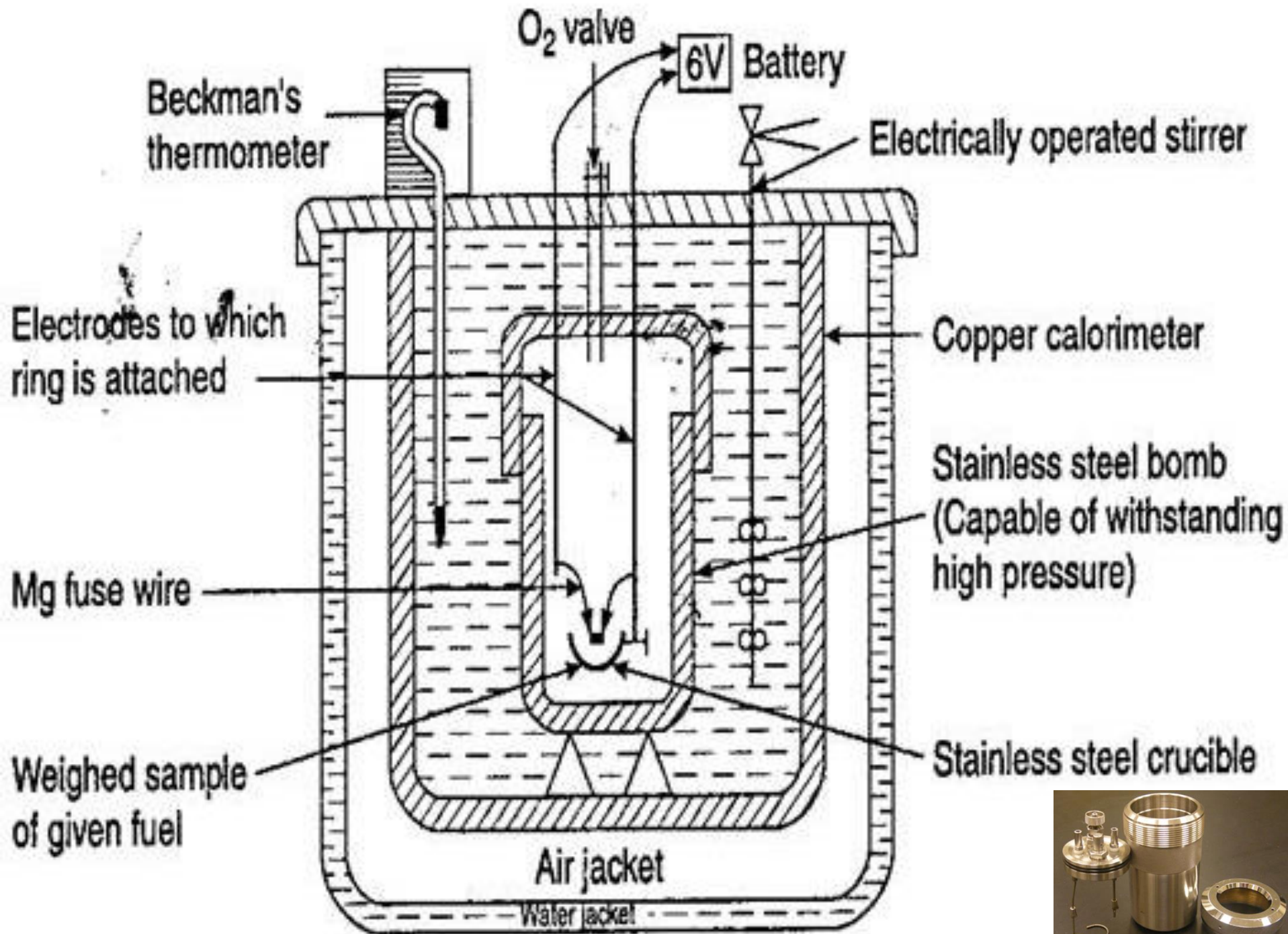
- Quantity of heat evolved when unit mass of fuel is burnt completely and the products are permitted to escape.
- In practice when fuel is burnt, the water vapor, and moisture are not condensed and they escape along-with hot combustion gases. Thus heat corresponds only to combustion and does not include latent heat of condensation of steam. The quantity of heat so measured is called net/low calorific value

$$GCV = \text{Heat of combustion of fuel} + \text{latent heat of condensation of steam}$$

$$NCV = GCV - \text{latent heat of steam}$$

Determination of Calorific Value

- CV of Non-volatile liquid fuel can be determined by Bomb Calorimeter
- Strong cylindrical stainless steel bomb inside which the combustion of fuel takes place.
- Bomb has a lid, which can be screwed to the body of bomb to make a perfect gas-tight seal.
- The lid is provided with two stainless steel electrodes and an oxygen inlet valve
- To one of the electrode a small ring is attached, which supports a nickel or stainless steel crucible, where the fuel is placed & burnt.
- Bomb is placed inside a copper calorimeter which is surrounded by an air-jacket and water-jacket to prevent heat loss due to radiation.
- Calorimeter provided with an electrically operated stirrer and Beckmann's thermometer, which can read accurately temperature difference up to $1/100^{\text{th}}$ of a degree



Working

- A known mass (0.5 to 1 g) of given fuel is taken in crucible.
- A fine Mg wire (0.75 mm) bent into loop and made to touch the fuel sample, is then stretched across the electrodes.
- Bomb lid is tightly screwed and bomb filled with O_2 to 25 atm.
- Bomb is lowered into copper calorimeter, containing a known mass of water.
- Calorimeter vessel is then placed in the insulating jacket.
- Stirrer is operated and initial temperature of the water is noted
- Electrodes are connected to 6V battery to ignite the sample. Sample burns and heat is liberated
- Heat liberated rises the temperature of water in the calorimeter. Uniform stirring of water is continued and maximum temp. attained is noted.

Heat Capacity

- Specific heat capacity (SHC): Amount of heat needed to increase the temperature of 1 g of a substance by 1 °C
- SHC of water = 1 cal/g for 1 °C rise.
- Heat capacity - amount of heat that W g of substance (which has certain SHC) absorbed to bring about 1 °C rise in temperature.
- Heat capacity = $W \times \text{SHC}$ W = mass of water

Calculation

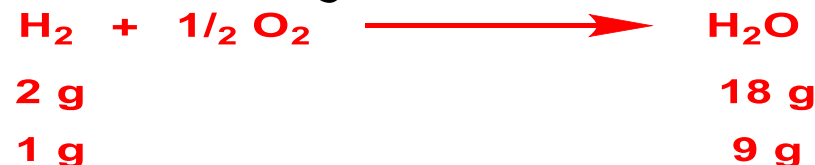
- Weight of the fuel sample taken = m g
- GCV of the fuel = θ cal/g
- Weight of the water taken in the calorimeter = W g
- Water equivalent of calorimeter, bomb, thermometer etc. = w g
- Initial temperature of water in calorimeter = t_1
- Final temperature of water in calorimeter = t_2
- Heat liberated by combustion of fuel = $m\theta$
- Heat absorbed by water and calorimeter etc. = $(W+w)(t_2-t_1)$

- Heat liberated by fuel = Heat absorbed by water, calorimeter etc.

$$m\theta = (W+w) (t_2-t_1) \times \text{SHC}$$

$$\text{g. cal/g} = \text{g. } ^\circ\text{C. cal/g } ^\circ\text{C}$$

- GCV of fuel (θ) = $[(W+w) (t_2-t_1) \times \text{SHC of H}_2\text{O}]/m$
- Note: Heat quantity calculated above is GCV because the products of combustion remain inside the calorimeter and brought down to ambient temperature.
- NCV can be calculated if the % of hydrogen in the fuel is known. Let the % of hydrogen be H
- 1 g of hydrogen produce 9 g of steam.
- So 1 g of fuel produce = $9H/100$ g steam
- Latent heat of condensation of steam = 587 cal/g
- Heat liberated by condensation of $9H/100$ g of steam = $9H/100 \text{ g} \times 587 \text{ cal/g}$



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

Corrections: For accurate results, the following correction applied.

- Fuse wire correction (t_F): Heat liberated, as measured above, includes the heat given out by ignition of the fuse wire used, which actually has to be excluded from GCV.
- Acid correction (t_A): Fuel containing S and N are oxidized to H_2SO_4 and HNO_3 , under high pressure and temperature of ignition.
- Formation of these acids are exothermic reactions. So, the measured heat also includes the heat given out during the acid formation.
- The amount of these acids is analyzed from washing of bomb by titration.
- For each ml of N/10 H_2SO_4 formed, 3.6 cal. should be subtracted
- For each ml of N/10 HNO_3 formed, 1.43 cal. should be subtracted
- Cooling correction (t_C): Time taken to cool the water in calorimeter from maximum temperature to room temperature is noted, let it be (u) and rate of cooling dt°/min , then cooling correction = $u \times dt^\circ$ This should be added to the observed raise in temperature.

$$\text{GCV of fuel } (\theta) = \frac{(W+w) (t_2 - t_1 + t_C) \times \text{SHC of } H_2O - (t_A + t_F)}{m}$$

cal/g (or kcal/kg)

Water Equivalent in Bomb Calorimeter (w)

- Water Equivalent - It is the amount of water which is thermally equivalent to the given body.
- In other words, the water equivalent of a body is that mass of water which has the same heat capacity that of the body itself.
- Eg. Heat required to bring about 1°C rise in temperature of calorimeter is 570 cal. So, this same amount heat (570 cal) can bring about 1°C rise in 570 g of water (we know that specific heat capacity of water is $1 \text{ cal/g }^{\circ}\text{C}$). Thus calorimeter is thermally equivalent to 570 g of water or simply its water equivalent is 570 g.
- Since water and bomb calorimeter are in thermal equilibrium during the experiment, the temperature noted in Beckmann's thermometer is also the temperature of bomb calorimeter.

Numerical

1) Calculate the CV of a fuel sample of coal 0.6 g. Water equivalent of calorimeter 2200 g. Increase in temperature = 6.52°C

Ans: GCV = 23906 cal/g

2) Calculate GCV and NCV of a fuel from the following data: Mass of fuel burnt = 0.75 g, water equivalent of calorimeter = 350 g, mass of water taken = 1150 g, rise in temperature = 3.02°C , % of hydrogen in fuel = 2.8.

Ans: GCV = 6040 cal/g ; NCV = 5892.1 cal/g

3) 0.6 g of a coal sample with 92% C, 5% hydrogen, and 3% ash, caused a rise in the temperature of 2000 g water by 3.2°C in a bomb calorimeter experiment. Calculate the GCV and NCV of coal, given. Water equivalent = 200 g.

Ans: GCV = 11733.3 cal/g; NCV = 11469.2 cal/g

4) On burning 0.75×10^{-3} kg of a solid fuel in a bomb calorimeter, the temperature of 2.5 kg water is increased from 24°C to 28°C . The water equivalent of calorimeter is 0.485 kg and the latent heat of steam is 587 kcal/kg. If the fuel contains 2.5% hydrogen, calculate its GCV and NCV.

Ans: GCV = 15920 kcal/kg ; NCV = 15787.9 kcal/kg

5) Determine the water equivalent of the bomb calorimeter apparatus which gave the following data in an experiment:

GCV of benzoic acid = 6324 cal/g

Wt. of benzoic acid taken = 1.364 g

Wt. of calorimeter = 1025 g

Wt. of calorimeter + water = 3025 g

Initial temperature = 11.872 °C

Final temperature = 14.625 °C

Cooling correction = 0.015 °C

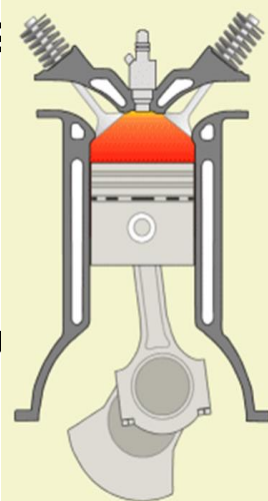
Heat from fuses = 22 cal

Washing of the bomb on analysis indicate the presence of 3.5 ml of N/10 HNO_3 and there is no H_2SO_4 formed.

Ans: Water equivalent of calorimeter = 1126 g

Knocking

- Gasoline – a complex mixture of hydrocarbons (100 different compounds) ranging from C_5 to C_9 . Most of these are branched-chain alkanes and some are aromatic compounds. Its boiling range is $40-120\text{ }^{\circ}\text{C}$.
- Diesel is a mixture of hydrocarbons ranging from C_{10} to C_{18} and boiling range is $250-320\text{ }^{\circ}\text{C}$
- Diesel is hard to vaporize than petrol. This is why the two are not interchangeable in car engines.
- Gasoline (petrol) is main source of fuel in motors. In the internal combustion engine (ICE) of motors the following occurs
 - Compression of gasoline generates fine droplets of gas vapor
 - Gasoline vapor is mixed with air and transfer to ICE
 - Petrol-air (fuel) mixture is compressed
 - Mixture is ignited by spark from spark plug and burn
 - Gases produced by combustion reaction expands
 - Expansion causes piston to move i.e K.E is produced



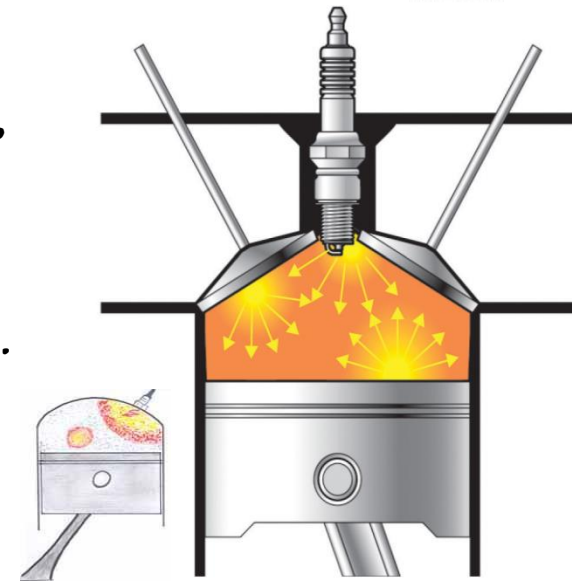
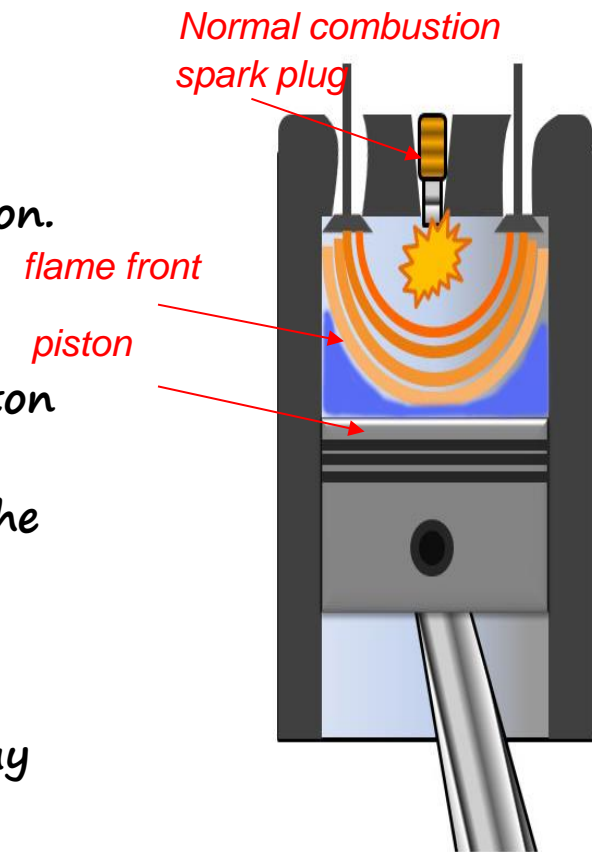
- To run the engine smoothly combustion of fuel-air mixture inside ICE should proceed in a controlled fashion.

Normal combustion

- After ignition flame spread rapidly and smoothly through gas mixture. The expanding gas drives the piston down the cylinder.
- In a properly functioning engine, the fuel burns with the flame front progressing smoothly from the point of ignition across the combustion chamber.

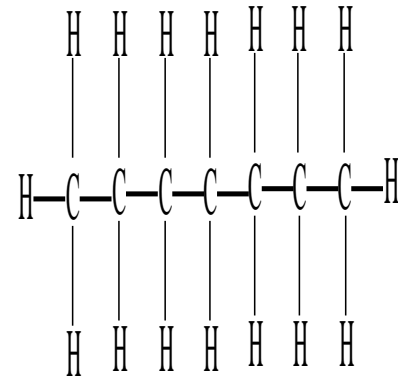
Abnormal combustion

- Last unburned fuel-air mixture outside flame front may get spontaneously ignited and combusted, rate of oxidation is so great producing an explosive violence sound - 'knocking'. It results in loss of efficiency
- Knocking causes damage to engine parts and spark plug, decrease in efficiency, increase in fuel consumption, undesirable rattling sound etc.
- It can be avoided by adjusting CR, burning time, using high octane number fuel and using anti-knocking agents. The most common method to avoid knocking is to burn gasoline of higher octane number.



Octane number

➤ Octane number is equal to the percentage by volume of iso-octane (2,2,4-trimethyl pentane) in a mixture of n-heptane and iso-octane having the same knocking tendency compared to the sample of gasoline being tested

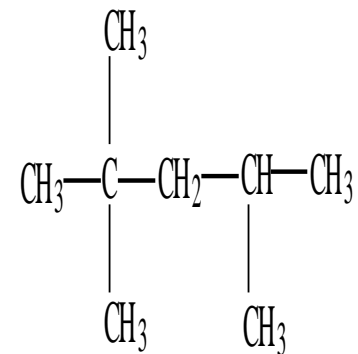


n-heptane

➤ Iso-octane has the best antiknocking properties and assigned an octane number of 100 whereas n-heptane has poor antiknocking property and assigned an octane number of zero.

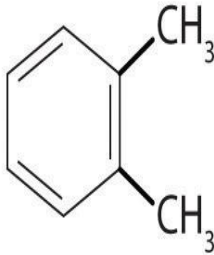
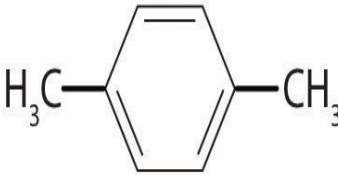
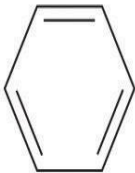
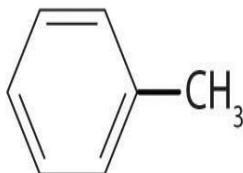
➤ The hydrocarbons present influence the knocking properties of gasoline which vary according to the series

Straight chain paraffin > branched chain paraffin > olefin > cycloparaffin > aromatics.



Isooctane

➤ The fuel which has same knocking tendency with the mixture having 80% iso-octane has octane number 80.

Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
<i>n</i> -heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0	<i>o</i> -xylene		107
<i>n</i> -hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	25	ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	108
<i>n</i> -pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	62	<i>t</i> -butyl alcohol	$(\text{CH}_3)_3\text{COH}$	113
isooctane	$(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)_2$	100	<i>p</i> -xylene		116
benzene		106	methyl <i>t</i> -butyl ether	$\text{H}_3\text{COC}(\text{CH}_3)_3$	116
methanol	CH_3OH	107	toluene		118

➤ Knocking tendency of gasoline

**straight-chain paraffins > branched-chain paraffins (iso-paraffins)
> olefins > cyclo-paraffins (naphthenes) > aromatics**

- Hydrocarbons with branched-chains are more resistant to knocking than the corresponding straight-chain paraffins.
- Olefins of same carbon-chain length possess better anti-knocking property than the corresponding paraffins. Anti-knocking tendency increases as the position of double bond approaches the center of chain.
- Knocking tendency decreases with presence of double bonds and cyclic structure.
- Aromatic hydrocarbons (eg. benzene, toluene, xylene) have high octane number.
- Alcohols have high octane number.
- Naphthenes have high octane number than normal paraffins.
- Gasolines obtained by cracking have higher octane number than straight run gasolines.
- Alternately octane number of fuel can be increased by adding anti-knocking agents.

Anti-knocking agents

- Substances added to control knocking are called anti-knocking agents eg. tetra ethyl lead (TEL, $(C_2H_5)_4Pb$), tetra methyl lead (TML, $(CH_3)_4Pb$), diethyl telluride $(C_2H_5)_2Te$.
- They are added to motor fuel eg. about 0.5 ml of TEL is added to gasoline as anti-knocking agent.

Mechanistic action of TEL

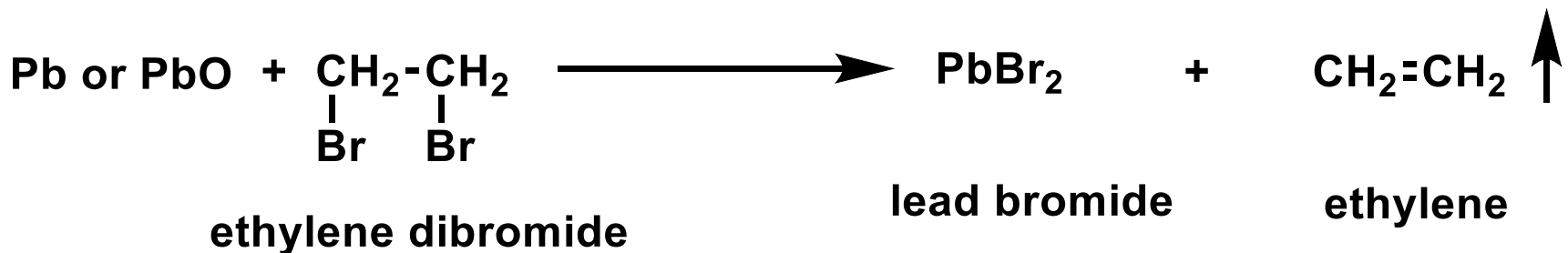
- TEL converted into cloud of finely divided PbO particles, which reacts with any hydrocarbon peroxides formed, thereby slowing down the chain oxidation and decreasing the chances of any early detonation.

Disadvantage of TEL

- PbO formed is harmful to engine life. In order to eliminate PbO from the engine a small amount of $C_2H_4Br_2$ is also added with TEL in gasoline.
- $C_2H_4Br_2$ removes PbO as volatile $PbBr_2$ with the exhaust gases. These lead halides are poisonous to human beings and animals.
- Also leaded gasoline cannot be used in automobiles equipped with catalytic convertor - Pb present in exhaust gas poisons the catalyst.

Unleaded gasoline

- Alternative methods of increasing octane number of gasoline is to add high octane compounds like iso-pentane, iso-octane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether (MTBE).
- MTBE is preferred over the others because it contains oxygen in the form of ether and supplies oxygen during combustion thereby reducing the extent of peroxy compound formation.
- Major advantage of unleaded gasoline is that it permits the use of catalytic converter attach to the exhaust in automobiles.

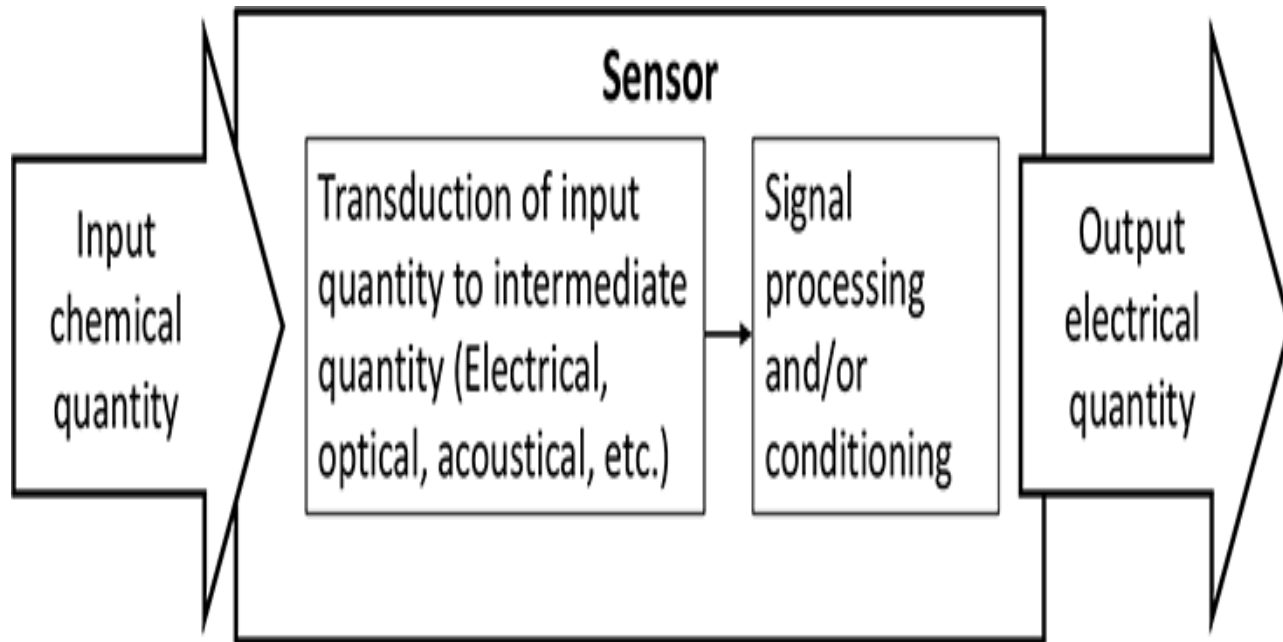


Chemical sensors for environmental monitoring - gas sensors

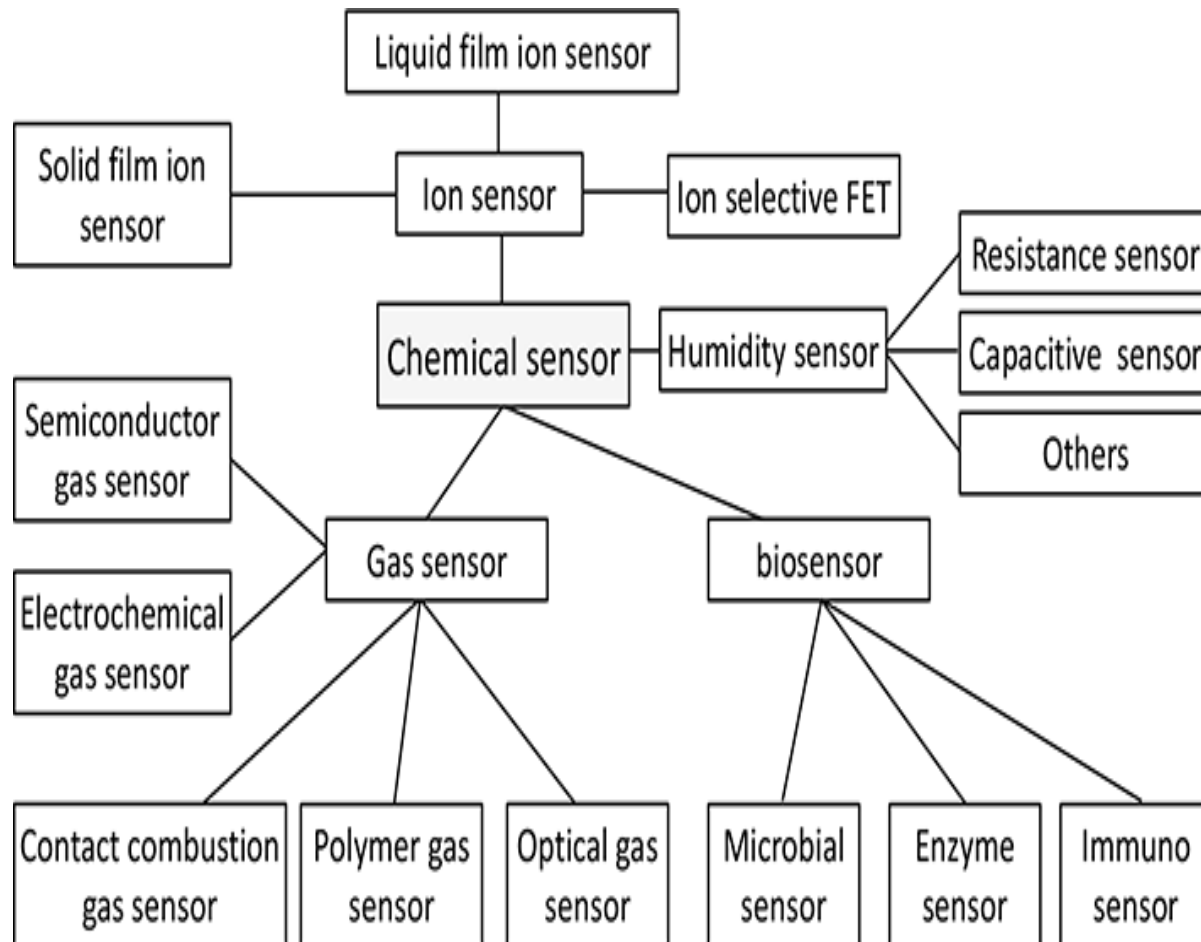
Introduction

- *Chemical sensors are measurement devices that convert a chemical or physical property of a specific analyte into a measurable signal, whose magnitude is normally proportional to the concentration of the analyte.*
- *A chemical sensor typically contains two main components: a receptor and a transducer. The receptor transforms chemical information about a sample into a form of energy. The transducer then transforms the energy into some form of analytical signal.*
- *The chemical sensor is an analyser that responds to a particular analyte in a selective and reversible way and transforms input chemical quantity, ranging from the concentration of a specific sample component to a total composition analysis, into an analytically electrical signal.*

How it works?



Classification of Chemical Sensors



Gas sensors

- Gas sensor is a subclass of chemical sensors.
- Gas sensor measures the concentration of gas in its vicinity.
- Gas sensor interacts with a gas to measure its concentration.
- Each gas has a unique breakdown voltage i.e. the electric field at which it is ionized. Sensor identifies gases by measuring these voltages.
- The concentration of the gas can be determined by measuring the current discharge in the device.
- Types of gas sensors:
 - Electrochemical gas sensor
 - Contact combustion gas sensor
 - Optical gas sensor
 - Polymer gas sensor
 - Semiconductor gas sensor

IR absorption type CO₂ gas sensor

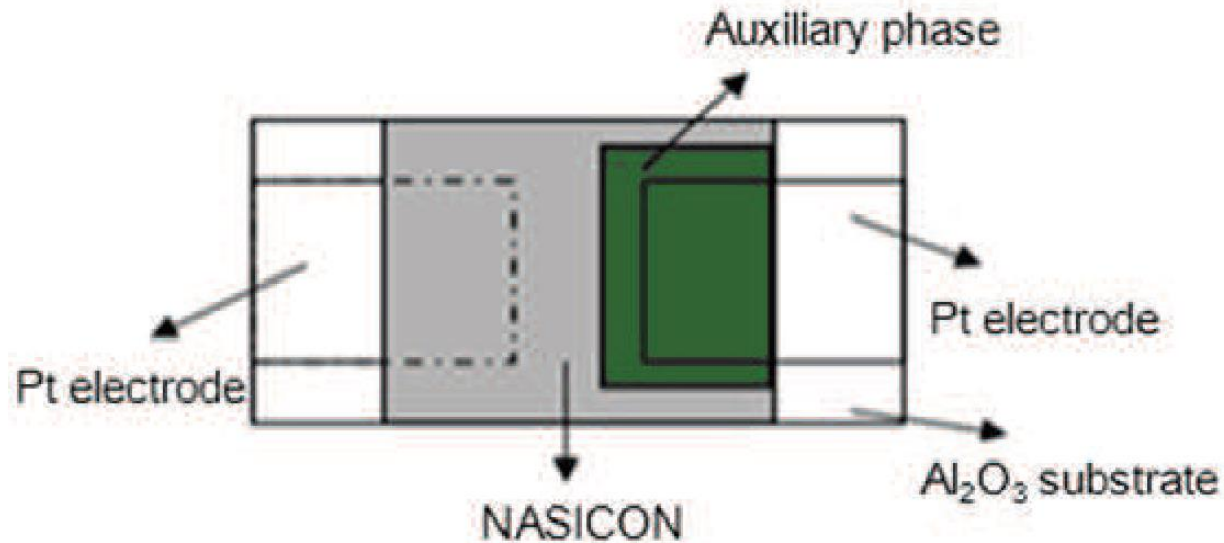
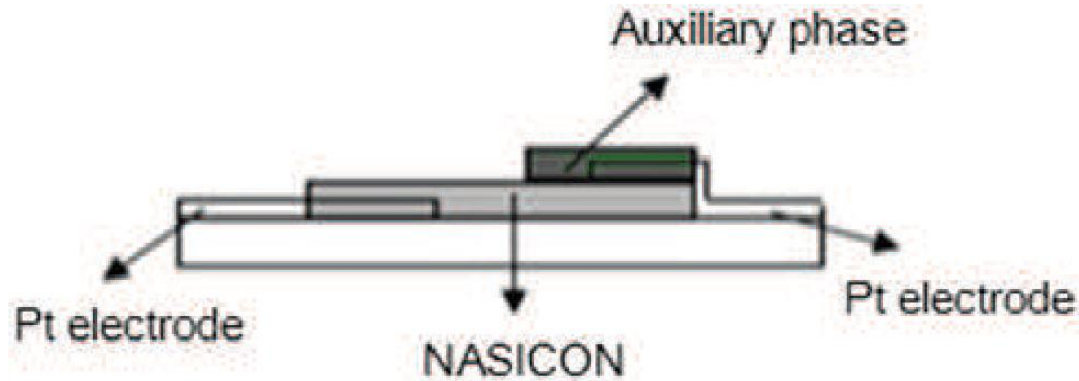
- CO₂ absorbs infrared light therefore CO₂ sensor consists of a tube containing an infrared source at one end and an infrared detector at the other end.
- The infrared detector detects the infrared light which is not absorbed by CO₂ between source and detector.
- Infrared radiation which is not being absorbed by CO₂ produces heat so the temperature will increase.
- The infrared detector measures the temperature.
- A voltage is produced due to the temperature increase in the infrared sensor.
- We can read amplified voltage into the data logger.



Solid electrolyte-type CO₂ sensors

- Low-cost, high-sensitivity, high-selectivity and simple-element structure.
- **NASICON** is the active element. Formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($1.8 < x < 2.4$)
- A commercial NASICON with a nominal-composition is $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$
- Binary carbonate systems such as Na_2CO_3 - BaCO_3 , Na_2CO_3 - CaCO_3 , Li_2CO_3 - BaCO_3 , and Li_2CO_3 - CaCO_3 are also used as active elements (as auxiliary constituents).
- The NASICON layer was screen-printed with a paste on the alumina substrate. The Pt electrodes were also screen-printed on the designated regions before and after the deposition of the NASICON layer.
- The assembly was sintered at 900°C, 1000°C, and 1100°C for 4 hours in air, respectively. After this, a series of auxiliary phases (Na_2CO_3 - CaCO_3) was screen-printed on the Pt sensing electrode.
- The EMF response to CO₂ content as a function of the CO₂ concentration is calculated. Greater the CO₂ concentration greater the EMF recorded.

Solid electrolyte-type CO_2 sensors

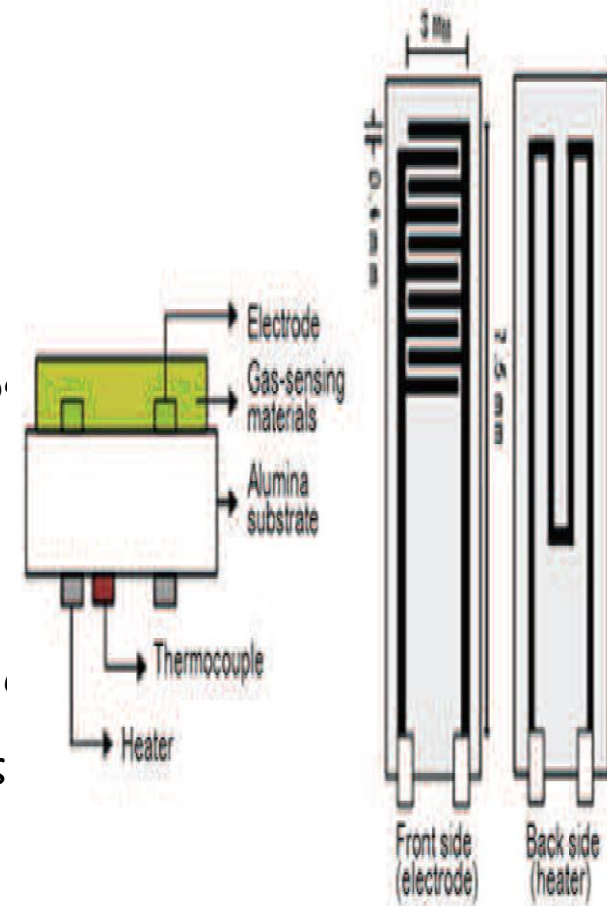
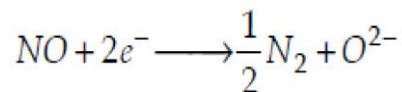


Hydrogen gas sensor

- Mostly palladium is used to detect hydrogen because palladium selectively absorbs hydrogen gas and forms the chemical palladium hydride.
- Types of hydrogen gas sensor:
 - Electrochemical
 - Thin film sensor
 - Thick film sensor
 - Chemochromic hydrogen sensors
 - Diode based Schottky sensor
 - Optical fiber hydrogen sensors
 - Nanoparticle-based hydrogen micro sensors

NO_x gas sensor - Metal oxide type

- WO₃ is known as the most promising NO_x gas-sensing material
- Other materials: ZnO, SnO₂, In₂O₃, TiO₂, etc.
- These sensing materials are oxygen-deficient nonstoichiometric compounds
- The conductivity of these n-type semiconductors, such as WO₃ and In₂O₃, is estimated based on the electron created by the surplus metal.
- When sensing materials are exposed to oxidizing gases at temperature ranging from 200°C to 300°C, the concentration of electrons is decreased due to the reaction between the electron and the gas.
- Consequently, the conductivity decreases and the resistance increases.
- As NO_x is also an oxidizing gas, the concentration of electrons is decreased due to the reaction between the electrons in the sensing materials and NO_x gas as shown in the following equations:



Carbon monoxide gas sensor

- CO is a colourless, tasteless and odourless gas produced by incomplete combustion of carbon-containing materials. It is often referred to as the "silent killer" because it is virtually undetectable by humans.
- Types of CO sensors:
 - Semiconductor sensor
 - Electrochemical sensor
 - Biomimetic type
 - Opto-chemical type (Widely used)

Opto-chemical type CO sensor

- The detector consists of a pad of a coloured chemical which changes colour upon reaction with carbon monoxide. They only provide a qualitative warning of the gas however. The main advantage of these detectors is that they are the lowest cost, but the downside is that they also offer the lowest level of protection.
- One reaction used for carbon monoxide detection is potassium disulphitopalladate (II) catalytic oxidation.



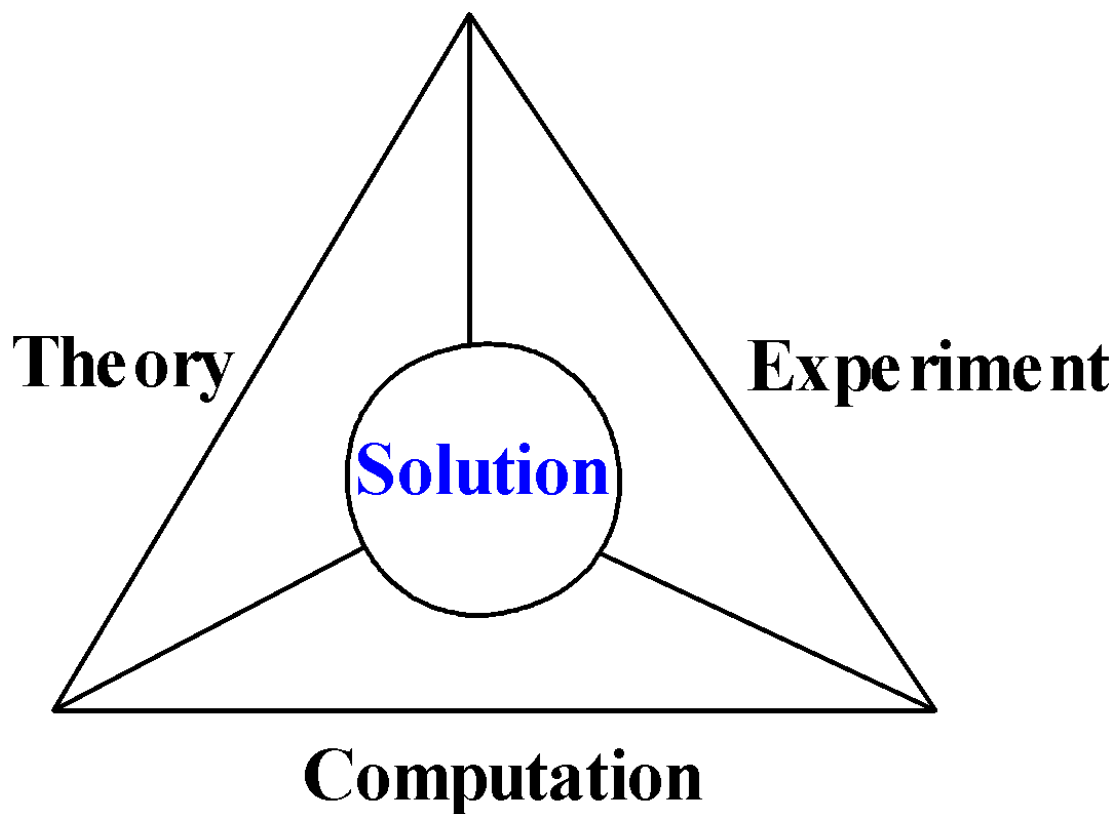
- As reaction progresses, atomic palladium release causes the color to change from yellow to brown to black.

Biomimetic and electrochemical type CO sensor

- A biomimetic sensor works in a fashion similar to haemoglobin which darkens in the presence of CO proportional to the amount of carbon monoxide in the surrounding environment.
- It uses cyclodextrins, a chromophore, and a number of metal salts. This can either be seen directly or connected to an infrared source of photons such as an IR LED and then monitored using a photodiode.
- The electrochemical detector uses the principle of a fuel cell to generate an electrical current when the gas to be detected undergoes a chemical reaction.
- The generated current is precisely related to the amount of carbon monoxide in the immediate environment close to the sensor.
- Essentially, the electrochemical cell consists of a container, two electrodes, connection wires and an electrolyte, typically sulfuric acid. Carbon monoxide is oxidized at one electrode to carbon dioxide while oxygen is consumed at the other electrode.
- Advantages of electrochemical cell over other technologies: highly accurate and linear output to carbon monoxide concentration, requires minimal power as it is operated at room temperature, and has a long lifetime.

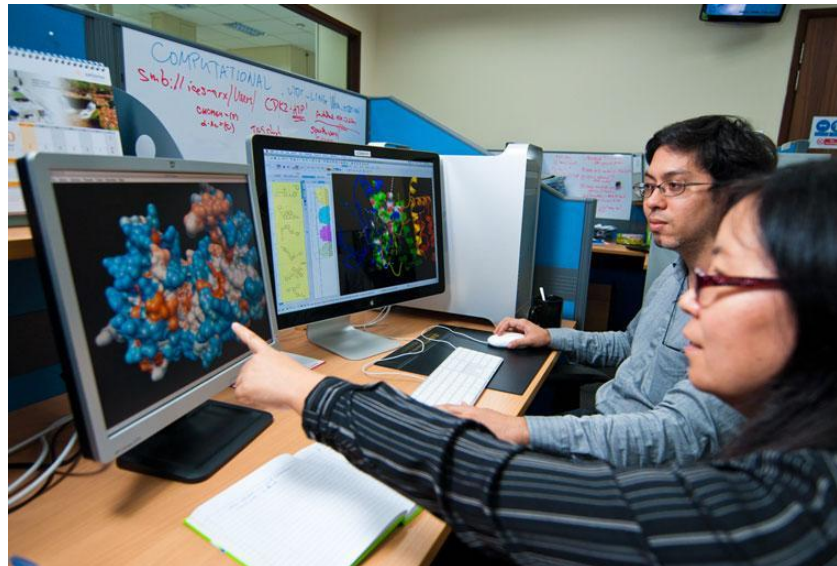
Overview of computational methodologies: energy minimization and conformational analysis.

Computational chemistry is the use of computers to solve the equations of a theory or model for the properties of a chemical system.



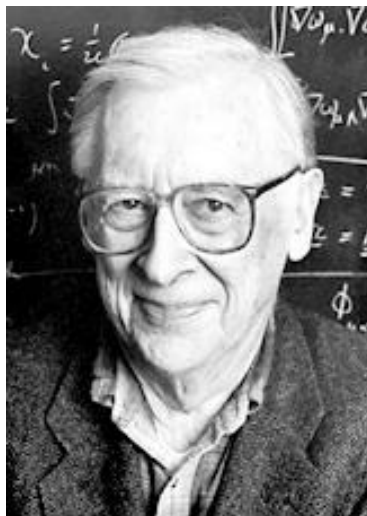
Three “Pillars” of Scientific Investigation

- Experiment
- Theory (analytical equations)
- Computational Simulation
- (“theoretical experiments”)



- Simulation is becoming a **third pillar of science**, along with theory and experiment.
- Using theory, we develop models: **simplified representations of physical systems**.
- We test the accuracy of these models in experiment, and use simulation to help refine this feedback loop.
- **Anything that can be measured can be simulated**, including properties related to energetics, structures, and spectra of chemical systems.

The Nobel Prize in Chemistry 1998



John A. Pople



Walter
Kohn

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "*for his development of the **density-functional theory***" and John A. Pople "*for his development of **computational methods in quantum chemistry***".

2013 Nobel Prize In Chemistry



© Nobel Media AB. Photo: A. Mahmoud
Martin Karplus



© Nobel Media AB. Photo: A. Mahmoud
Michael Levitt



© Nobel Media AB. Photo: A. Mahmoud
Arieh Warshel

"for the development of multiscale models for complex chemical systems"

- Martin Karplus, Université de Strasbourg, France, and Harvard University, Cambridge, MA, USA
- Michael Levitt, Stanford University, Los Angeles, CA, USA
- Arieh Warshel, University of Southern California (USC), CA, USA

Computational Chemistry

WHY

do theoretical calculations?

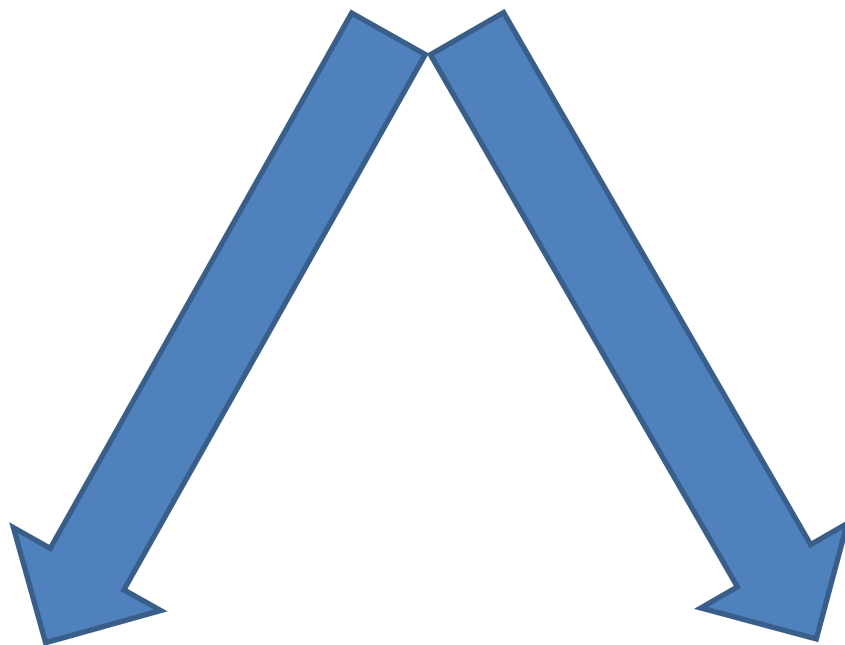
WHAT

do we calculate?

HOW

are the calculations carried out?

**Theoretical/Computational
Chemistry**



Classical Mechanics

**Quantum
Mechanics**

**Sir Isaac Newton
(1642 - 1727)**



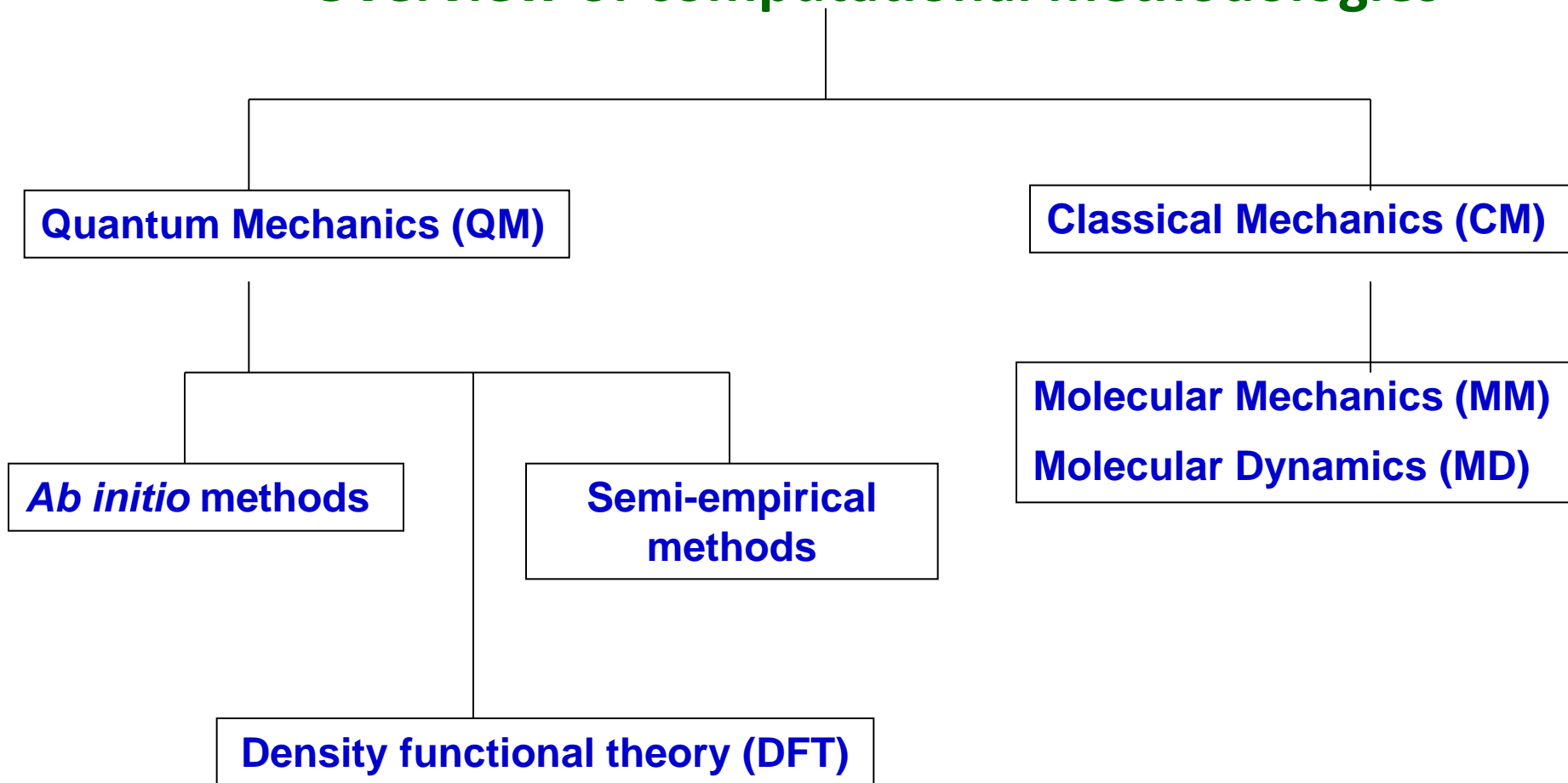
$$F = ma$$

**Erwin Schrödinger
(1887 - 1961)**



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

Overview of computational methodologies



Schrödinger Equation

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

- **H** is the quantum mechanical Hamiltonian for the system (an operator containing derivatives)
- **E** is the energy of the system
- **Ψ** is the wave function (contains everything we are allowed to know about the system)
- $|\Psi|^2$ is the **probability distribution of the particles**

Ab-initio methods

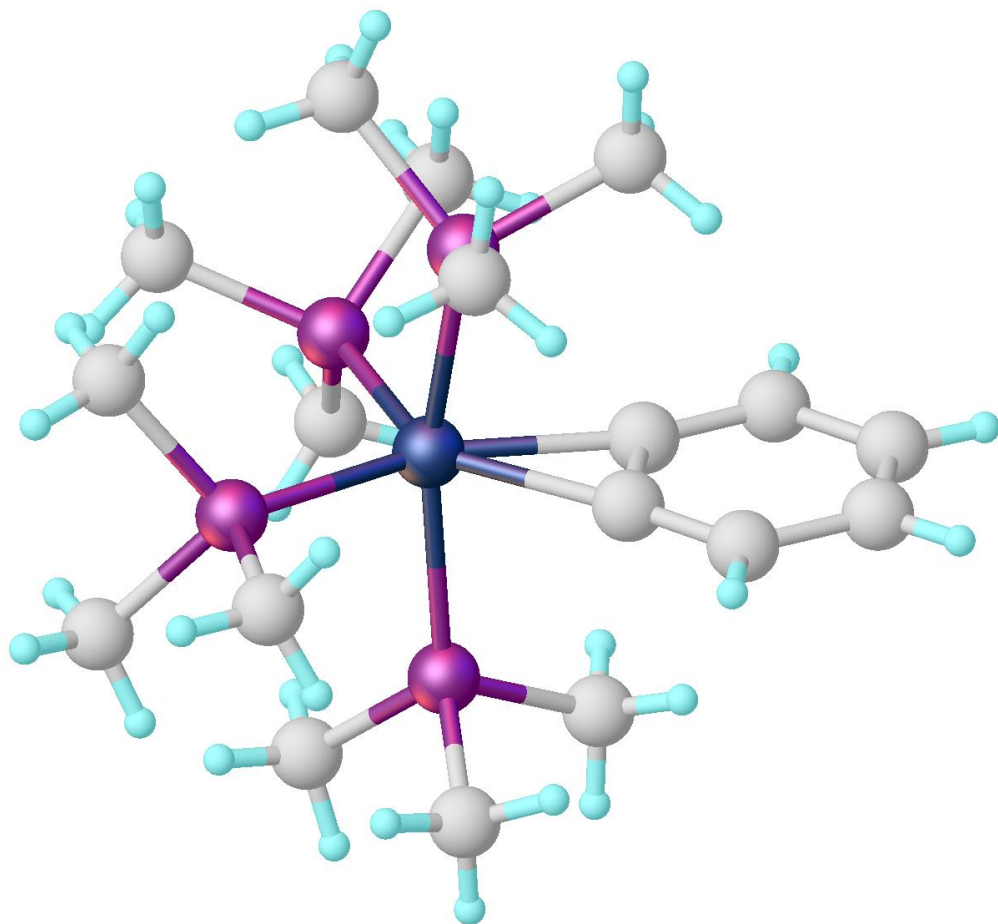
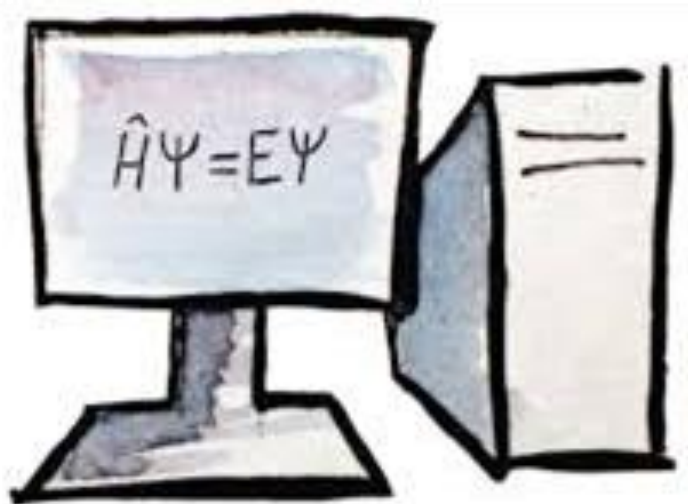
- The term "*Ab Initio*" is Latin for "from the beginning". Computations of this type are derived directly from theoretical principles, with no inclusion of experimental data.
- Mathematical approximations are usually a simple functional form for an approximate solution to A wave function! (The Schrödinger Equation).
- These methods try to compute an accurate as possible many electron wavefunction which then automatically leads to an accurate total energy.
- Accuracy can be systematically improved.

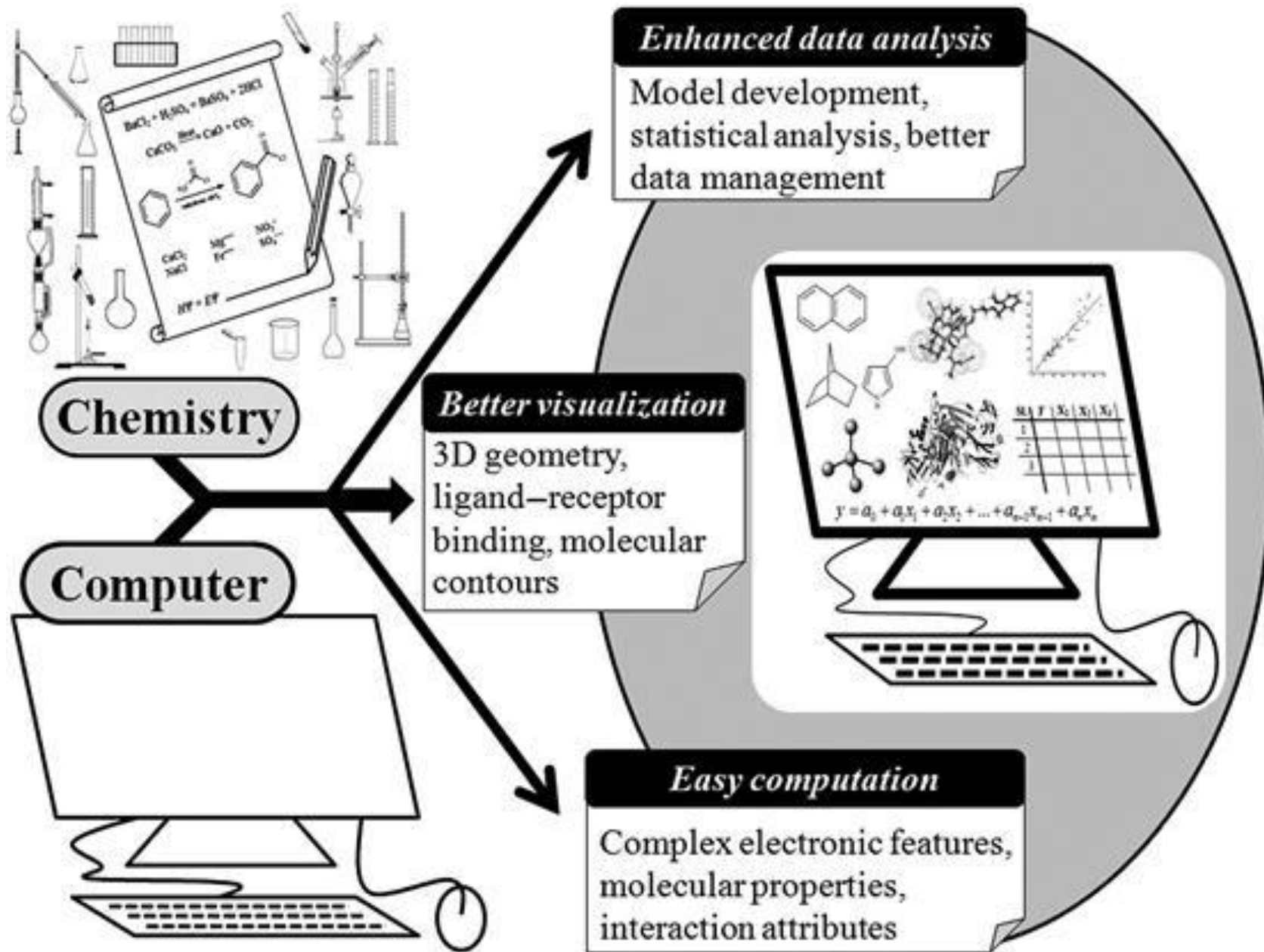
Semi-empirical methods

- It uses approximations from empirical (experimental) data to provide the input into the quantum chemical models.
- Accuracy depends on parameterization.

- **DFT** allows getting information about the energy, the structure and the molecular properties of molecules at lower costs. It goes with electron density instead of wave function. **Accuracy varies with functionals, however, there is no systematical way to improve the accuracy.**
- **Molecular mechanics** uses classical physics and empirical or semi-empirical (predetermined) force fields to explain and interpret the behavior of atoms and molecules. **Generally not very accurate.**
- **Molecular dynamics** is a computer simulation technique that **allows one to predict the time evolution of a system of interacting particles** (atoms, molecules, etc.)

Doing Chemistry with Computers

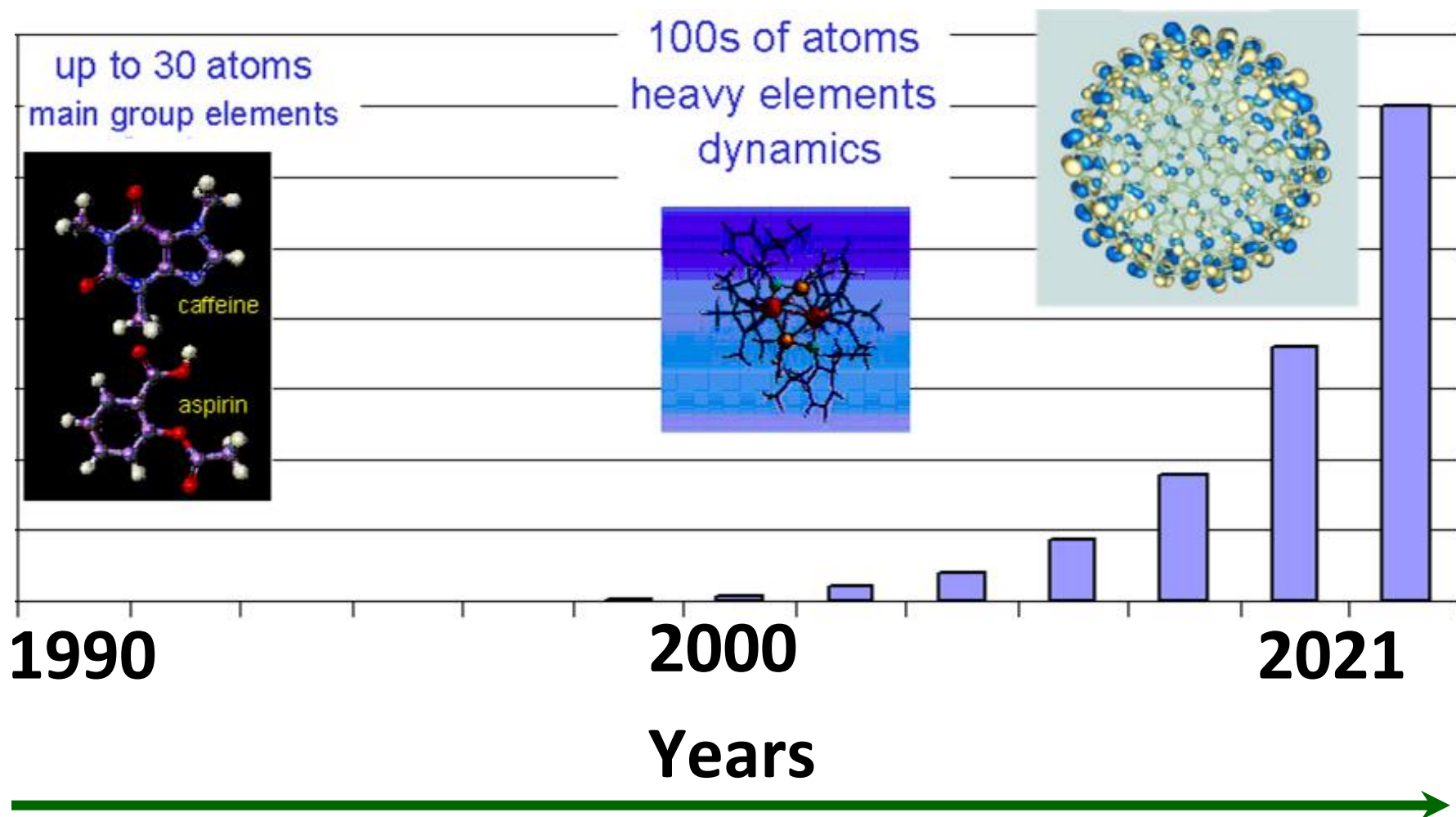




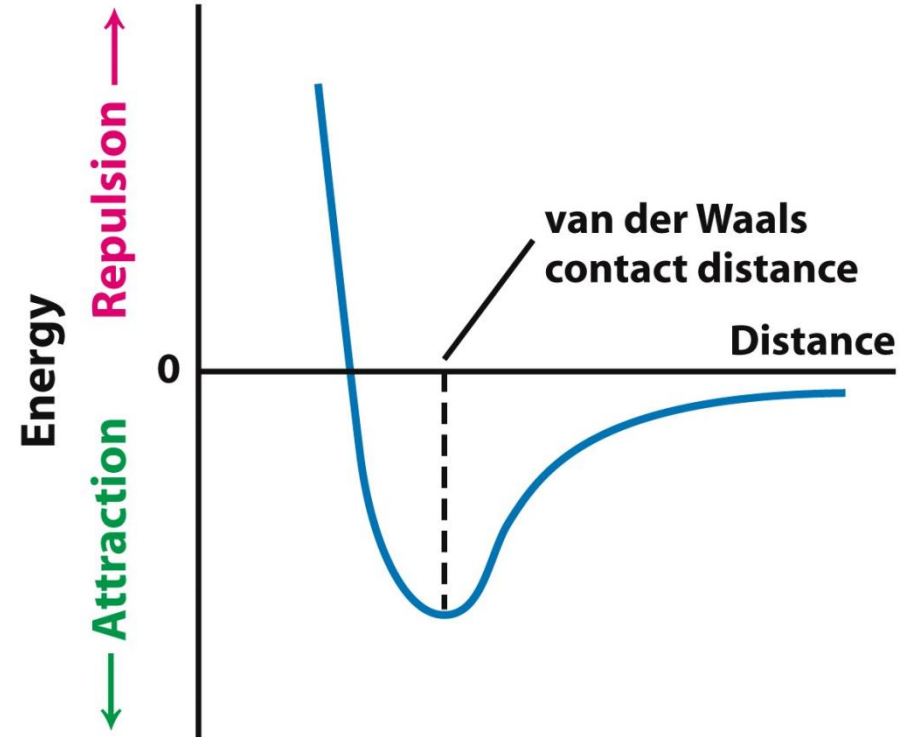
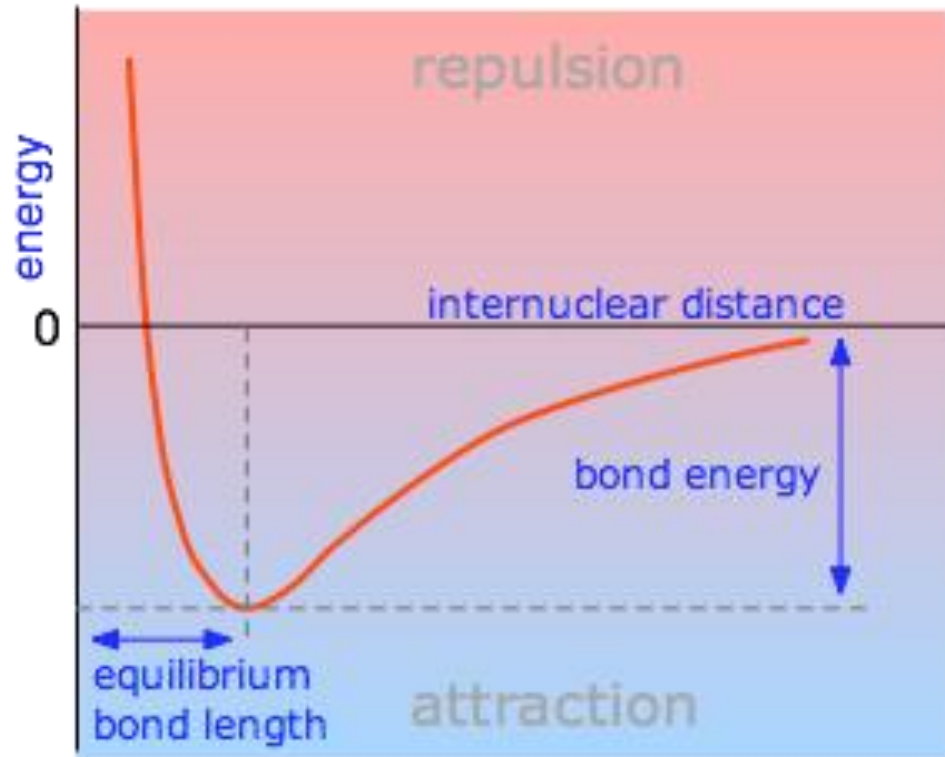
Using computational chemistry software you can in particular perform:

- **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**
- **Calculations of rate constants for chemical reactions: Chemical kinetics**
- **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

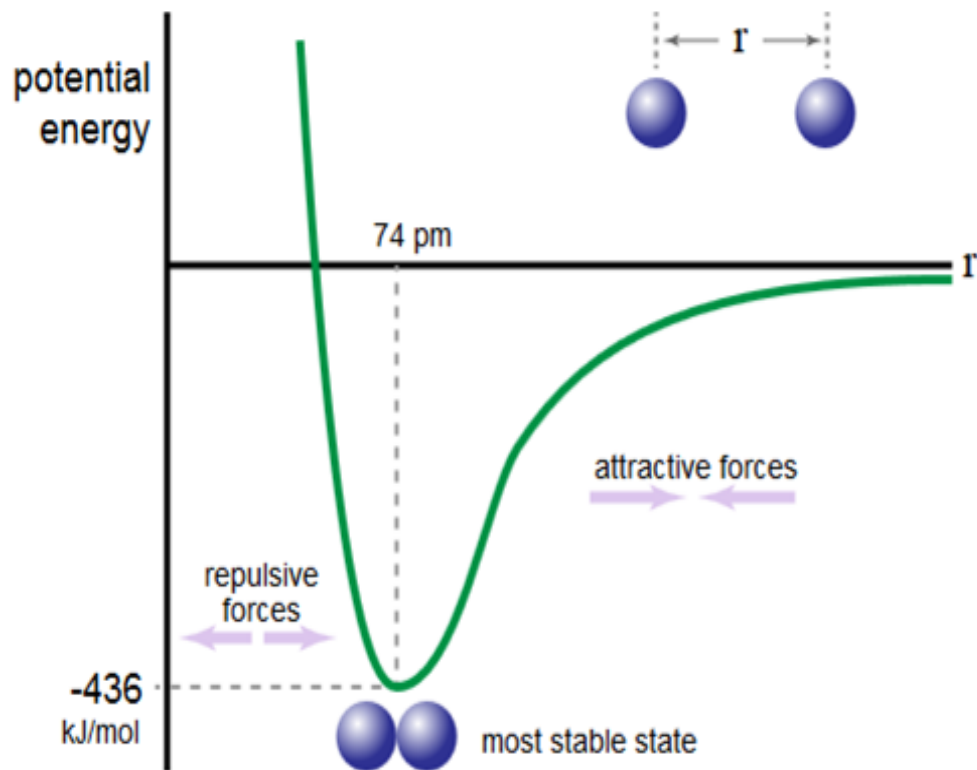
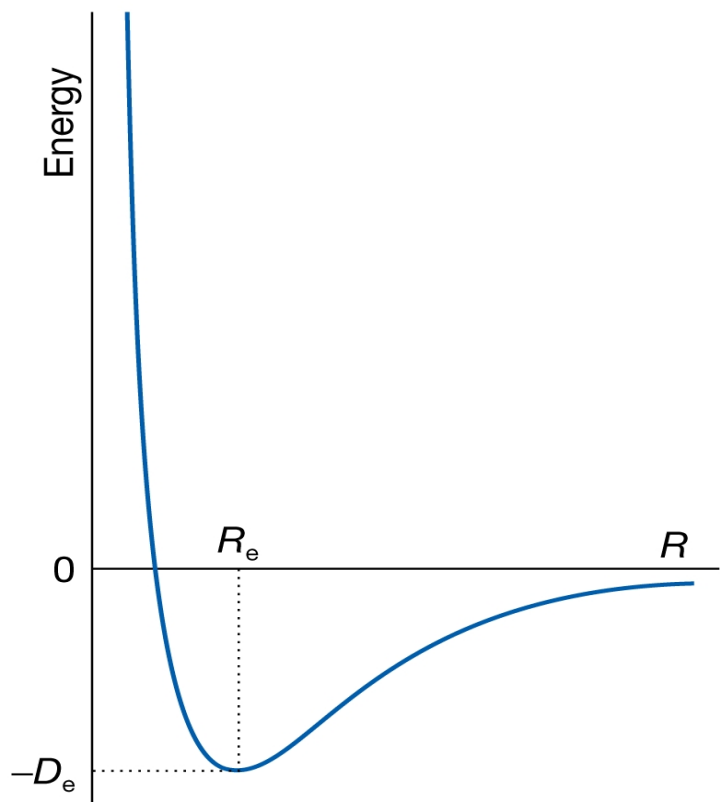


- Structure of a molecule in general is how atoms are arranged in the molecule in the three dimensional space.
- **Potential energy surface (PES)** is a plot of energy with respect to various internal coordinates of a molecule such as bond length, bond angle etc.

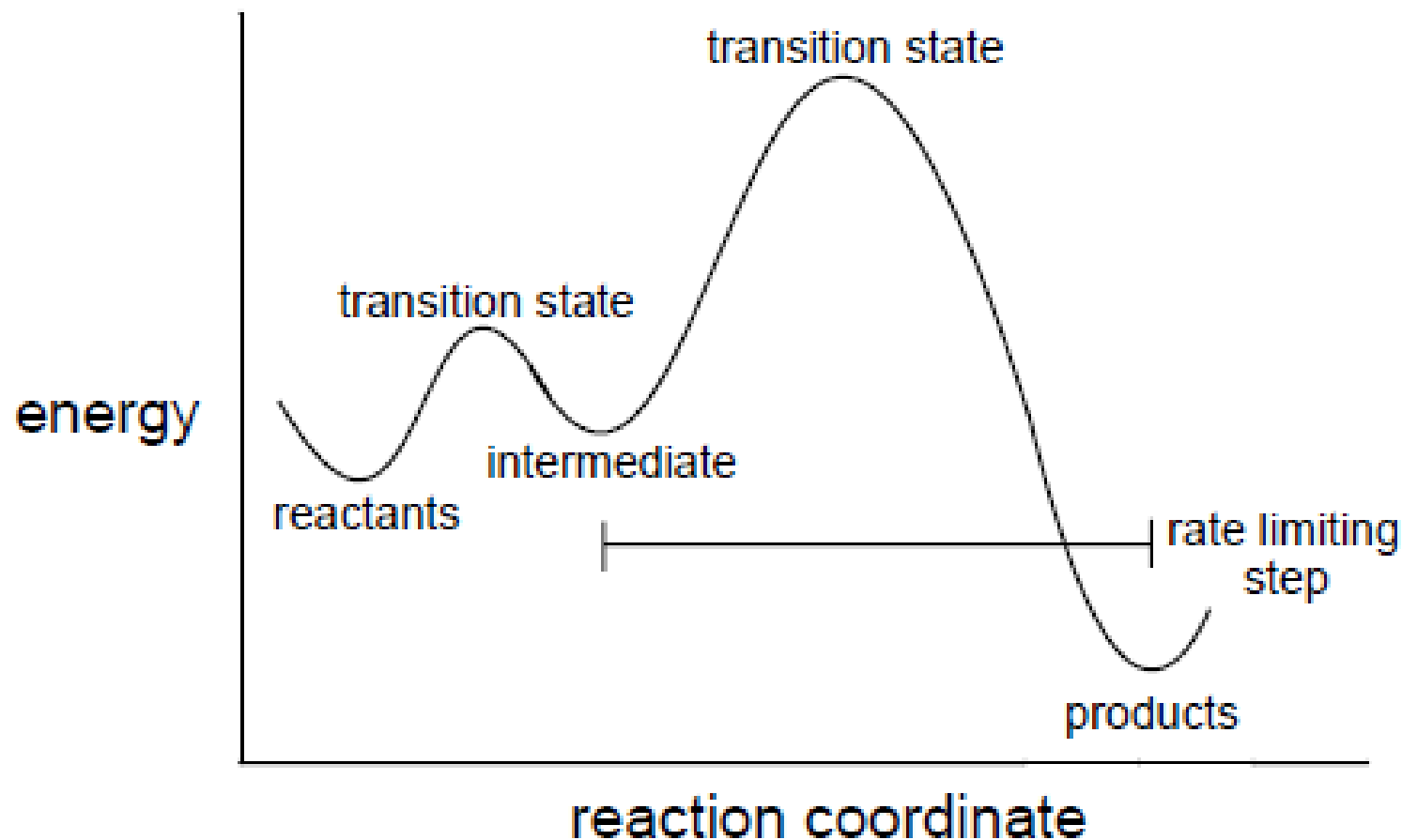


- **The PES is the energy of a molecule as a function of the positions (coordinates).**
- **This energy of a system of two atoms depends on the distance between them.**
- **At large distances the energy is zero, meaning “no interaction”.**
- **The attractive and repulsive effects are balanced at the minimum point in the curve**

Potential energy for nuclear motion in a diatomic molecule

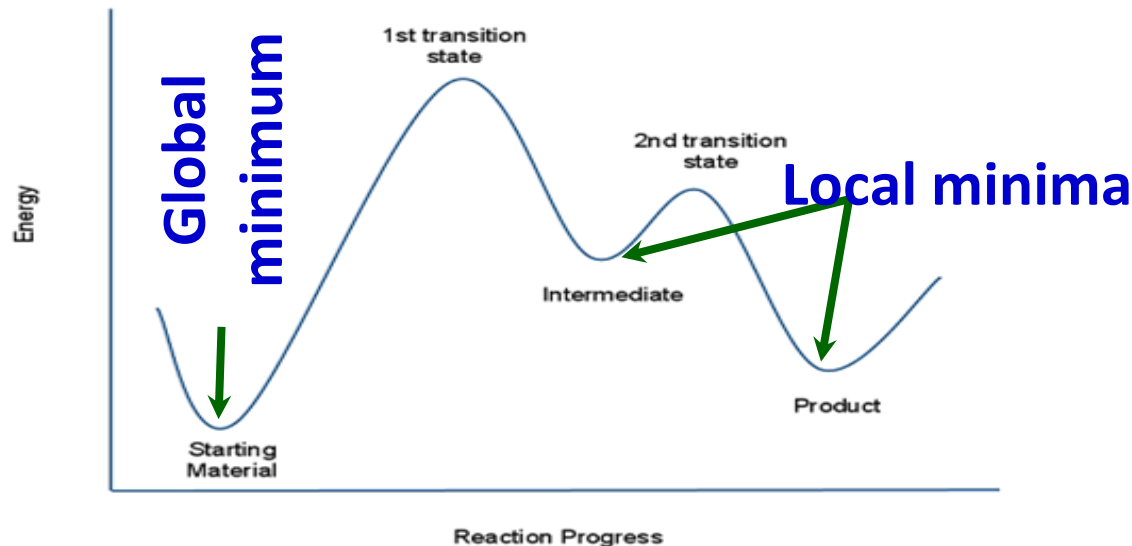


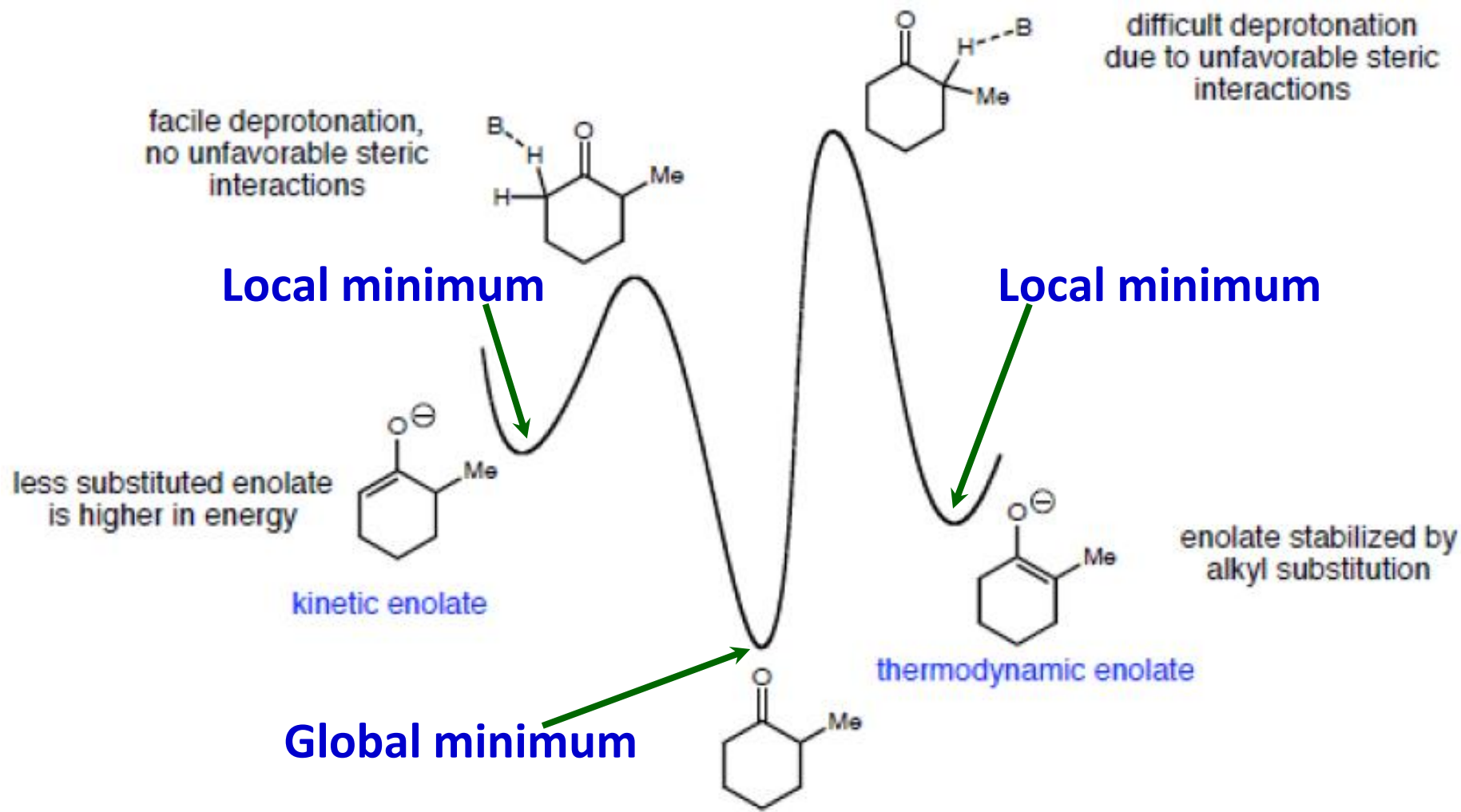
Potential Energy Surfaces and Mechanism



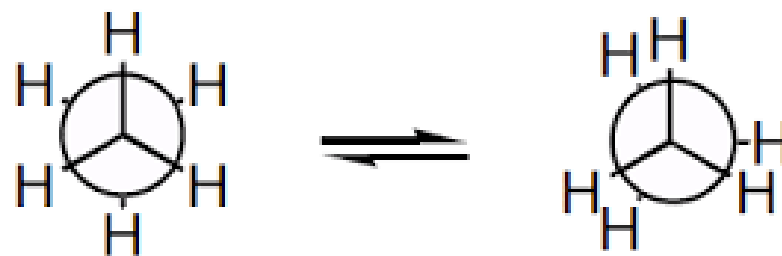
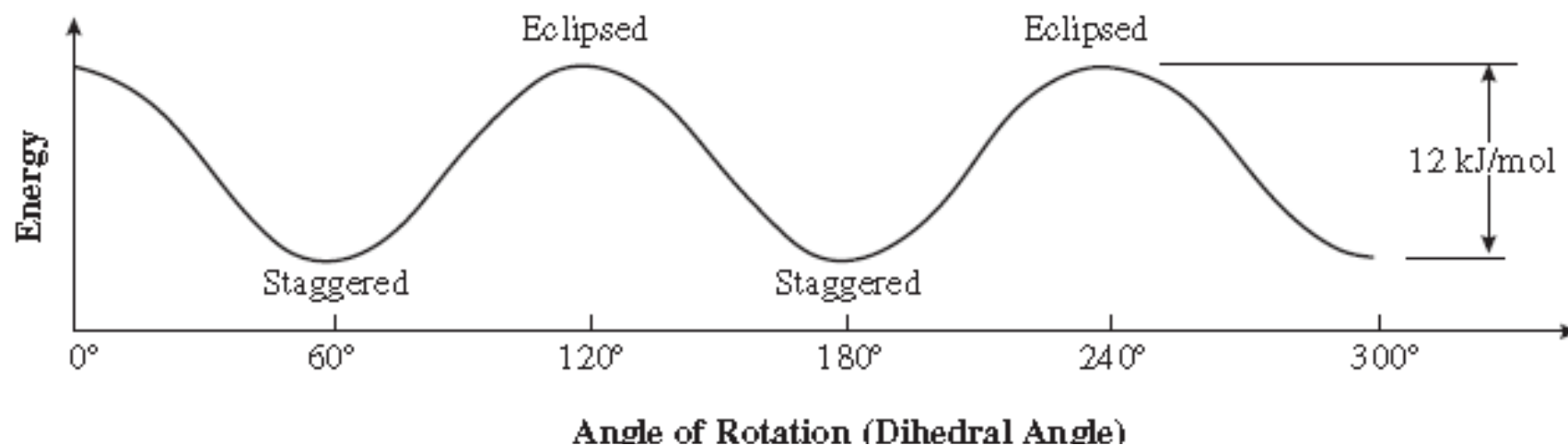
Conformational Analysis

- 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.





Ethane Conformations



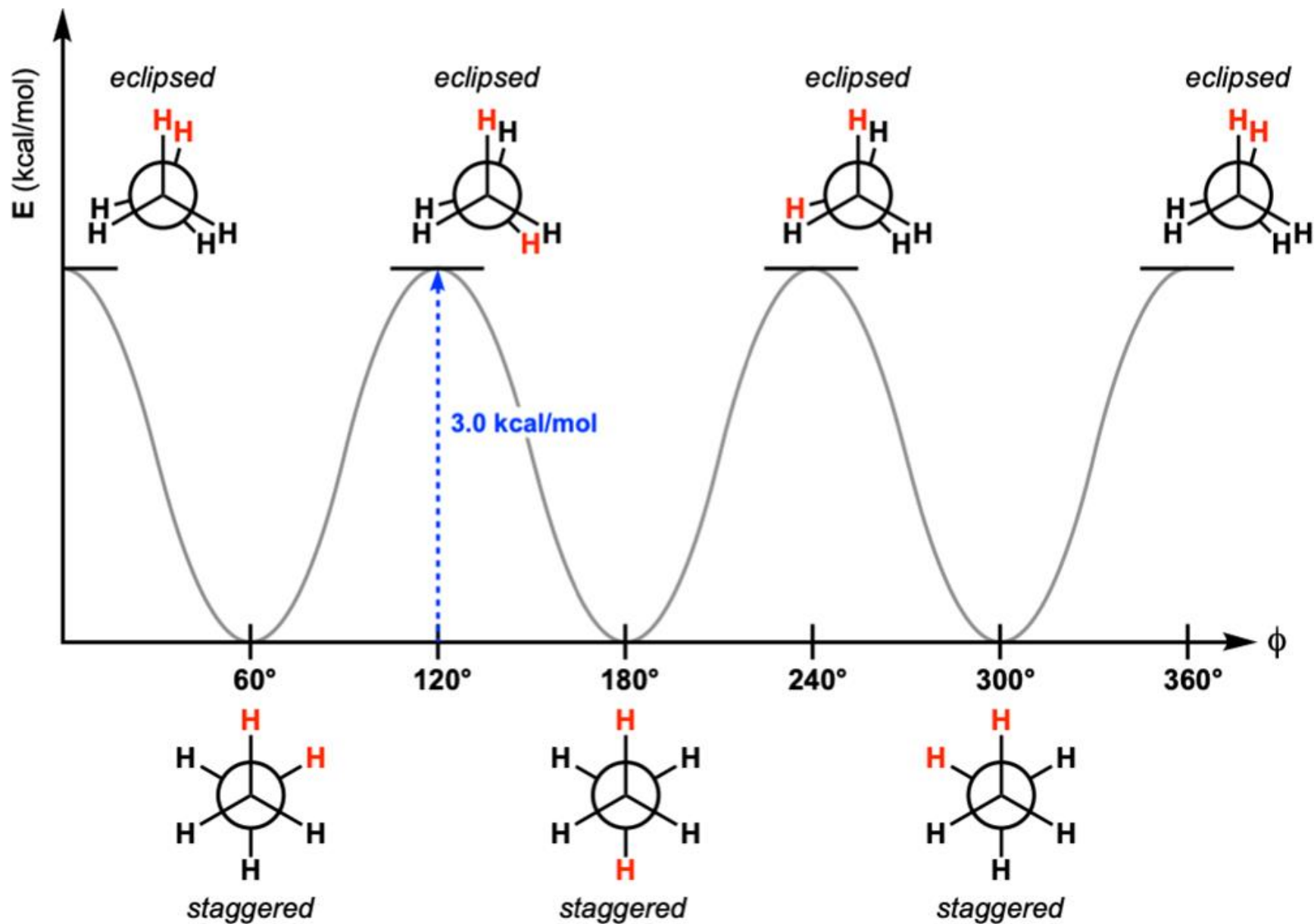
staggered

$$\theta = 60^\circ$$

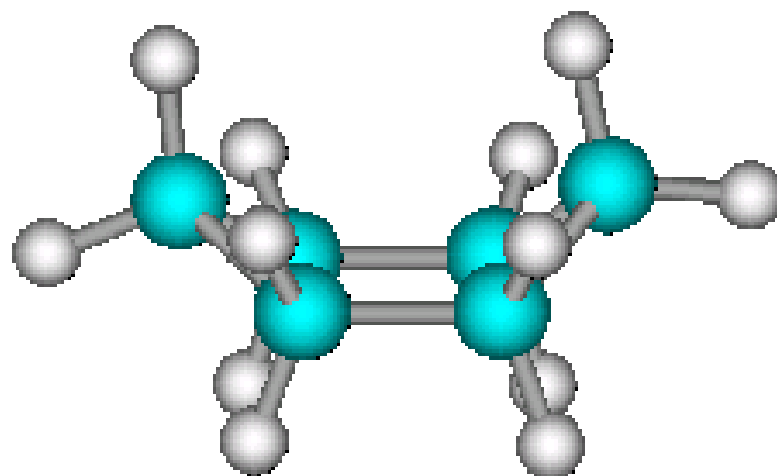
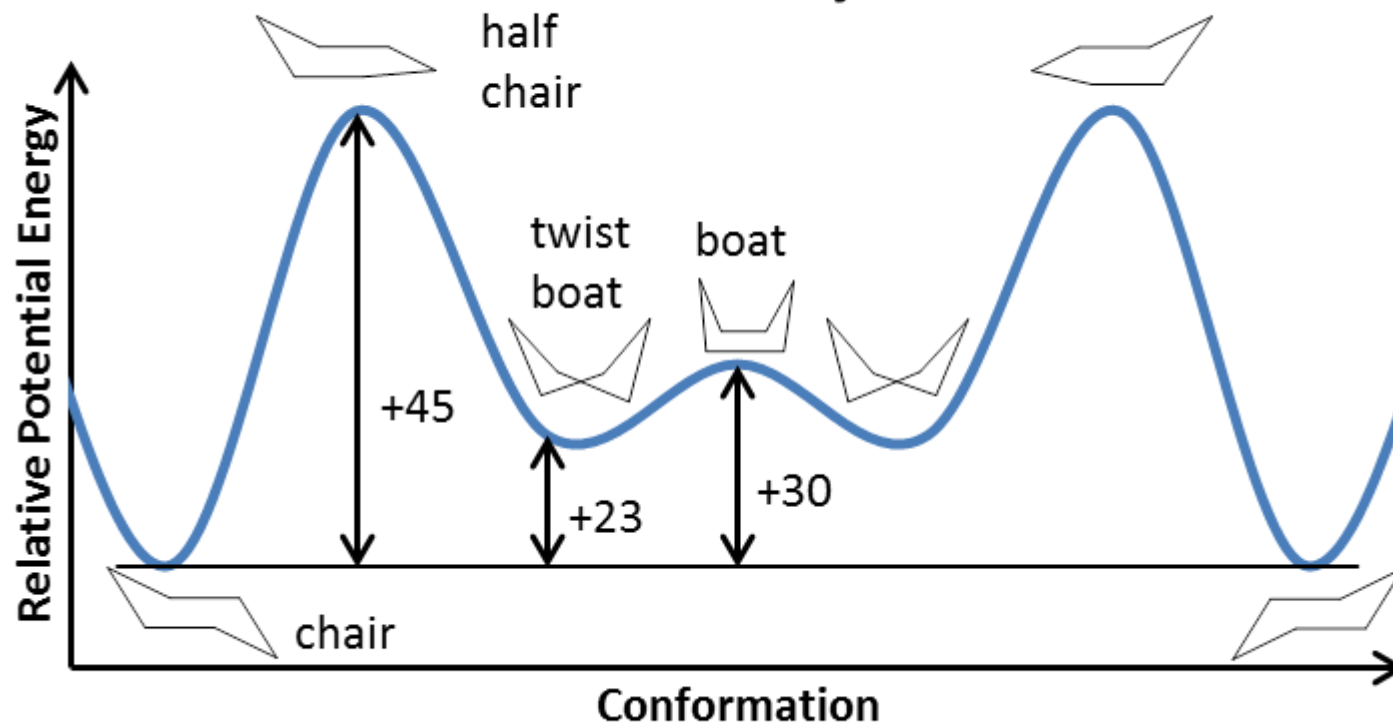
eclipsed

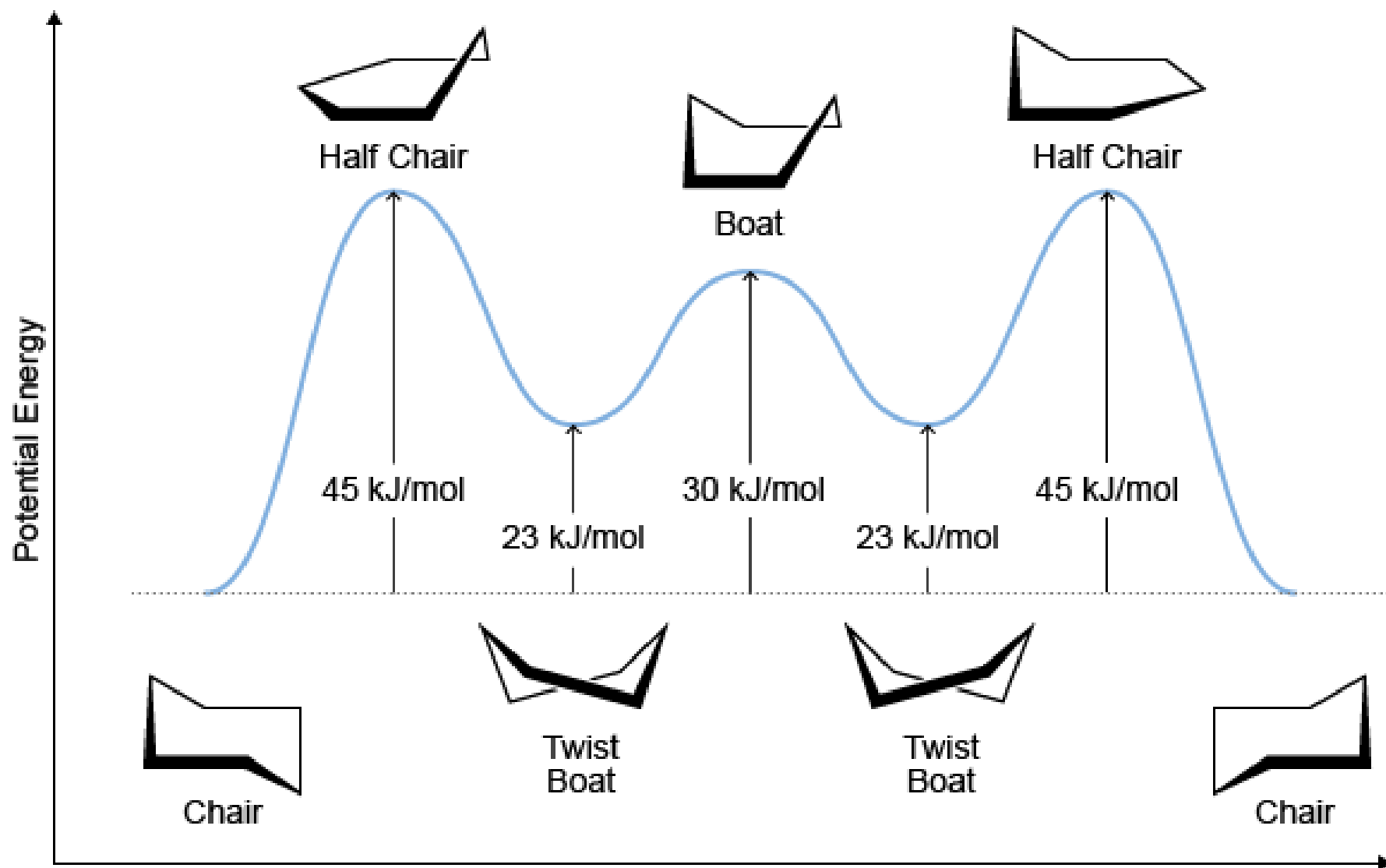
$$\theta = 0^\circ$$

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.



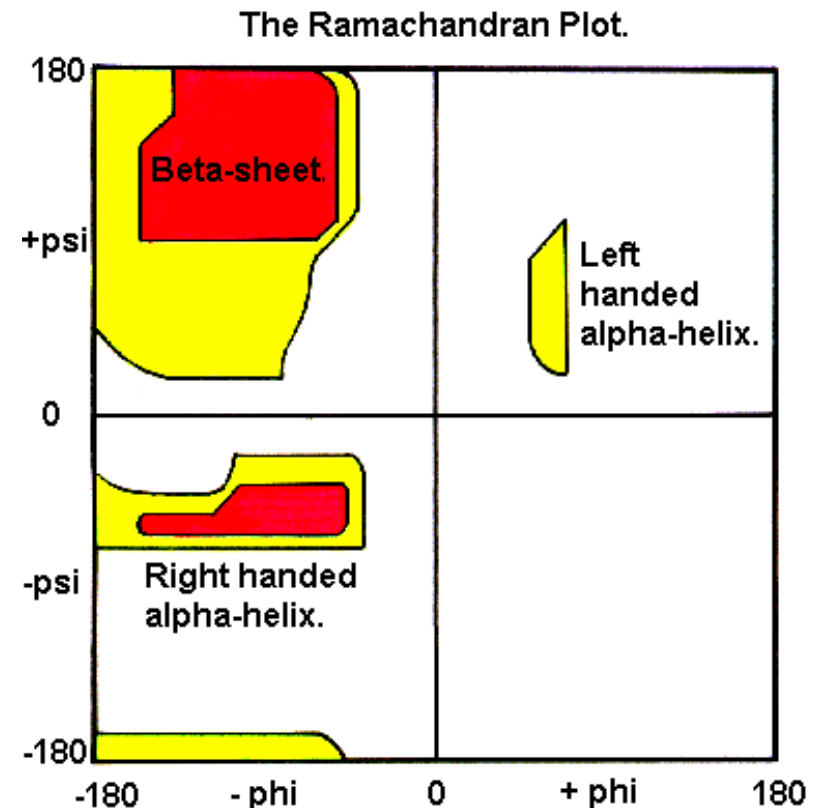
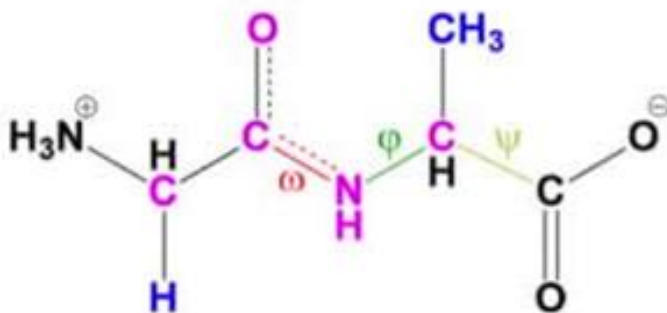
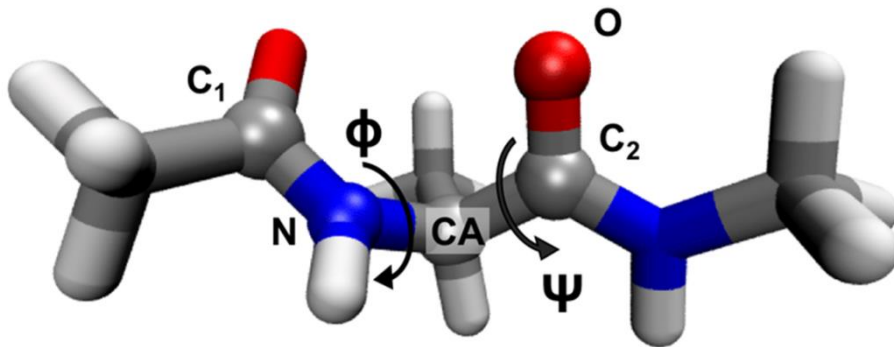
Conformations of Cyclohexane





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?

Geometry optimization

- 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)

End of Module 7