VBS Purvanchal University Jaunpur (U.P)
[UNS Institute of Engineering & Technology]
Department of Chemistry

Molecular Orbital Theory

Unit I: Covalent Bonding & Molecular Geometry

Knowledge/Understanding Goals:

- Understand molecular theory
- Sigma & pi bonds

Skills:

- Calculate bond order using MO theory

What is Molecular Orbital Theory?

Molecular orbital (MO) theory, developed by Robert S.Mulliken and co-workers, constructs new orbitals that are *delocalized* (i.e., "spread out") across the entire molecule. The basic principle of MOT is as below:

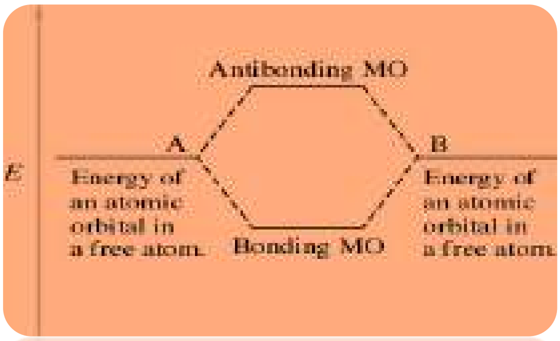
1. Total number of molecular orbits is equal to the total number of atomic orbitals from combining atoms.
2. Bonding molecular orbitals (BMO) have less energy than the constituent atomic orbitals before bonding. Antibonding molecular orbitals (ABMO) have more energy than the constituent atomic orbitals before bonding.
3. Following both the **Pauli exclusion principle** and **Hund's rule**, electrons fill in orbitals of increasing energy.
4. **Molecular orbitals (MO)** are best formed when composed of atomic orbitals of like energies.

How does it works?

Approximations are used Linear Combination of Atomic Orbital(LCAO): Mathematically combine (**add or subtract**) the atomic orbitals (specifically, the *atomic* wave functions) of nearby atoms to form MOs (*molecular* wave functions)

1. Addition of two wave functions gives a bonding MO (increases probability of finding electrons between the nuclei giving a bond)

2. Subtraction of two wave functions gives an antibonding MO (decreases probability of finding electrons between two nuclei to zero, a node)
3. Bonding and antibonding MOs most commonly combine in two types of symmetry, σ (sigma) and π (pi) bonds.
4. Antibonding orbitals are denoted by a superscript star (*)



Term to Know

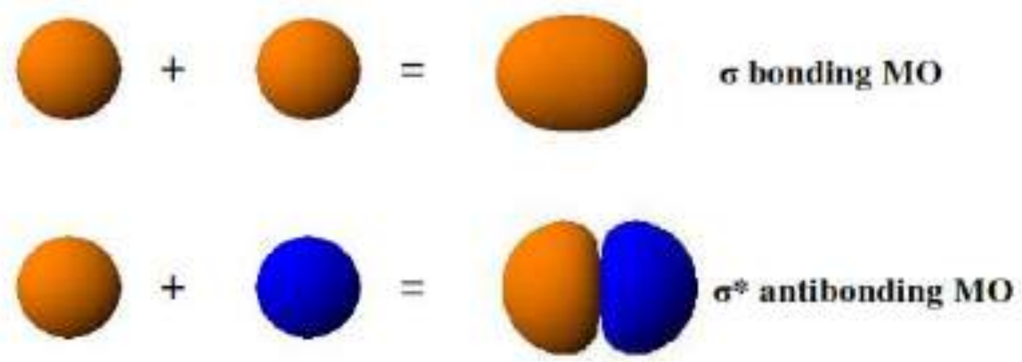
Bonding molecular orbital: *an orbital lower in energy than the atomic orbitals from which it is composed. (favours formation of molecule)*
Antibonding molecular orbital: *an orbital higher in energy than the atomic orbitals from which it is composed. (favours separated atoms) represented by a **
Bond order: *the difference between the number of bonding electrons and the number of antibonding electrons divided by two. Indicates bond strength.*
Homonuclear diatomic molecules: *those composed of two **identical** atoms.*
Heteronuclear diatomic molecules: *those composed of two **different** atoms **Para magnetism:** causes the substance to be drawn into a magnetic field; associated with unpaired electrons.*
Diamagnetic: *causes the substance to be repelled by the magnetic field; associated with paired electrons.*

General Energy Level Sequence for Filling Orbitals Using the MO Theory

$$\sigma 1s^2\ \sigma 1s^{2*}\ \sigma 2s^2\ \sigma 2s^{2*}\ (\pi 2p_x{}^2\ \pi 2p_y{}^2)\sigma 2p^2(\pi 2p_x{}^{2*}\ \pi 2p_y{}^{2*})\ \sigma 2p^{2*}$$

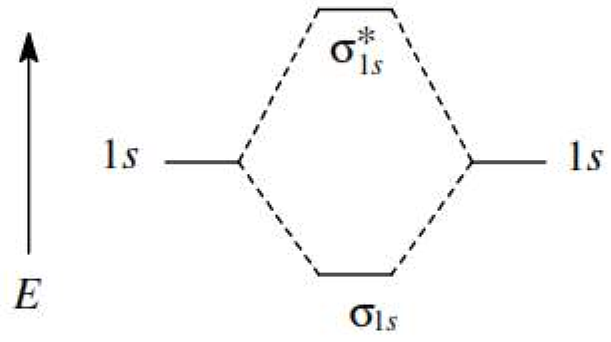
[*Valid for Atomic No = 7 or < 7]*

MOs from 1s Orbitals
Homonuclear Diatomic Molecules



- Positive combination causes a build-up of electron density between the nuclei, resulting in a **sigma bonding MO** (s).
- Negative combination results in a nodal plane between the nuclei, which works against bonding, resulting in a **sigma antibonding MO (s*)**
- In general, number of MOs formed as LCAOs equals numberof AOs used.

MO Energy Level Scheme
First Period Homonuclear Diatomic Cases

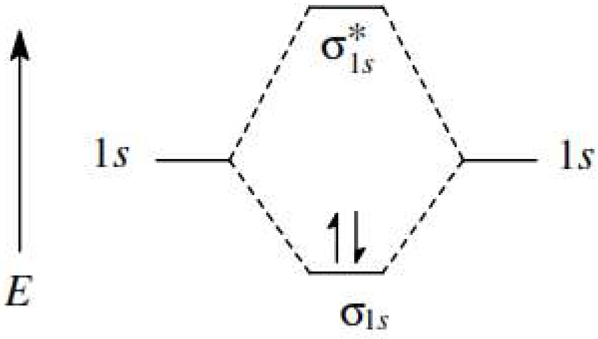


- Scheme is filled in the usual aufbau manner, following the Pauli exclusion principle and Hund's rule of maximum multiplicity (for the ground state).

- Bond order is defined as follows = ½ (# of bonding electrons - # of antibonding electrons)

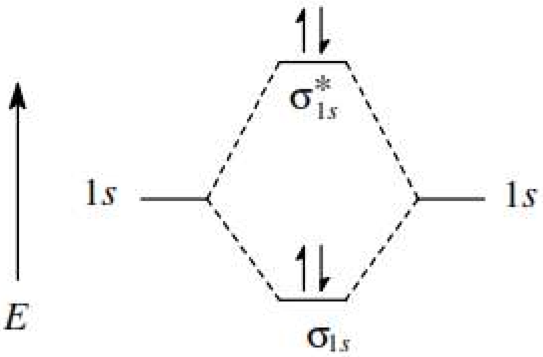
H_2 and He_2

H_2



bond order = ½(2 – 0) = 1

He_2



bond order = ½(2 – 2) = 0

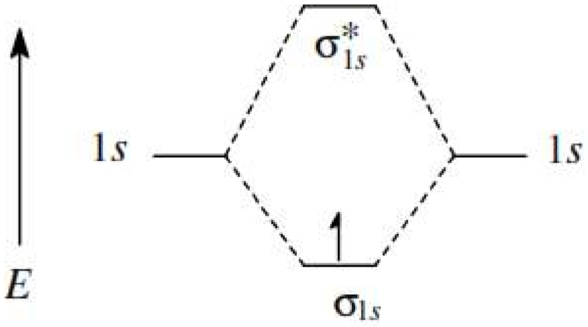
(He_2 does not exist.)

If the bond order is zero no bond!

H_2^+ and He_2^+

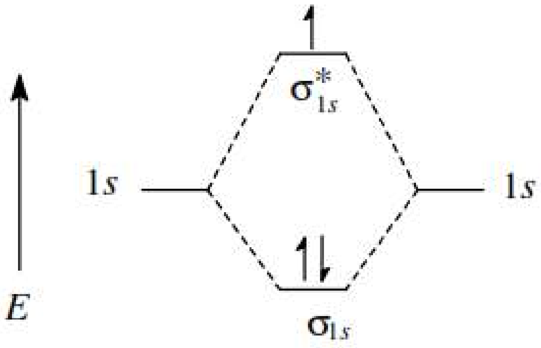
H_2^+ and He_2^+ Ions

H_2^+



bond order = ½(1 – 0) = ½

He_2^+



bond order = ½(2 – 1) = ½

Try This!!

Problem#1: Use MO diagrams to predict whether H_2^+ and H_2^- Exist. Determine their bond orders and electron configurations.

Problem#2: What is the molecular orbital diagram for the diatomic hydrogen molecule, H_2? How stable is the molecule? Is it diamagnetic or paramagnetic?

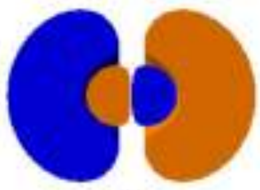
Problem#3: What is the molecular orbital diagram for the diatomic helium molecule, He_2? How stable is the molecule? Diamagnetic or paramagnetic?

MOs for Second Period Homonuclear Diatomic Molecules

- In general, atomic orbitals that are most similar in energy interact most effectively in forming MOs.
- MOs for second period diatomic molecules are combinations of the type 2*s*±2*s* and 2*p*±2*p*.

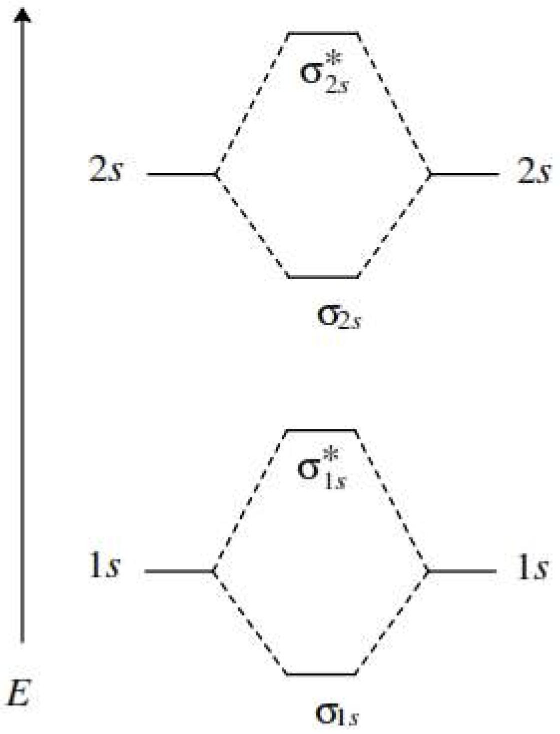
Sigma MOs from 2*s* ± 2*s*
(cutaway views)

σ_{2s}

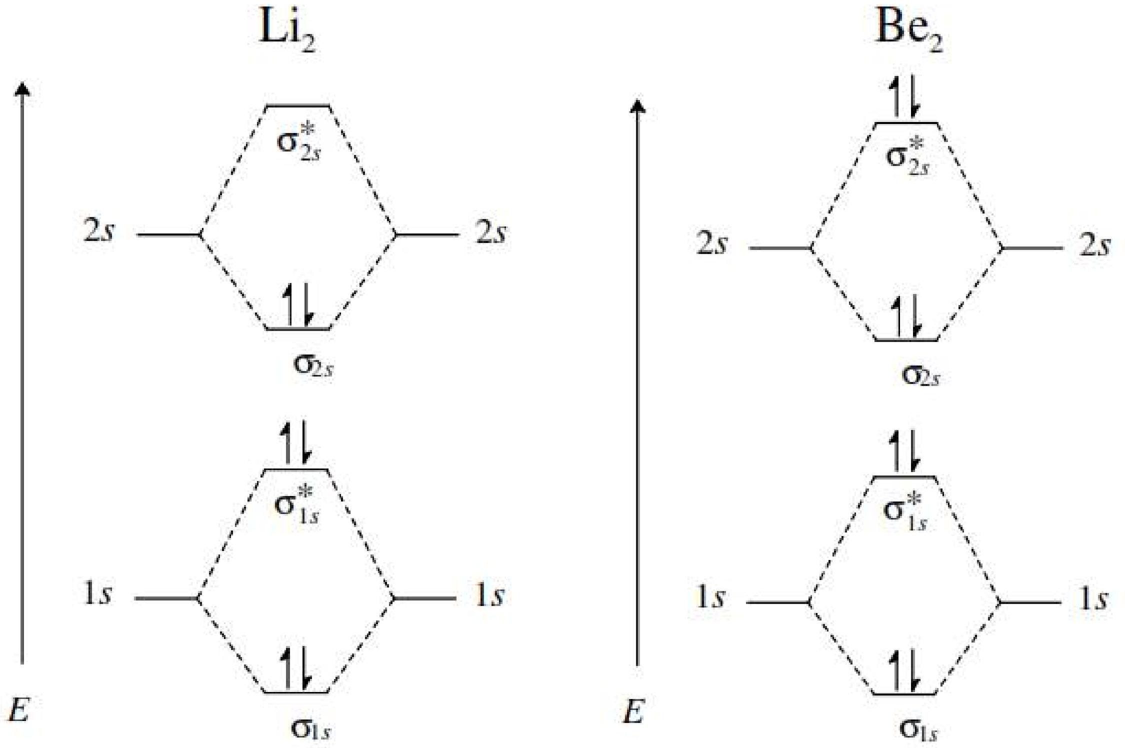


σ^*_{2s}

MO Energy Level Scheme
Li2, Be2, and Related Ions



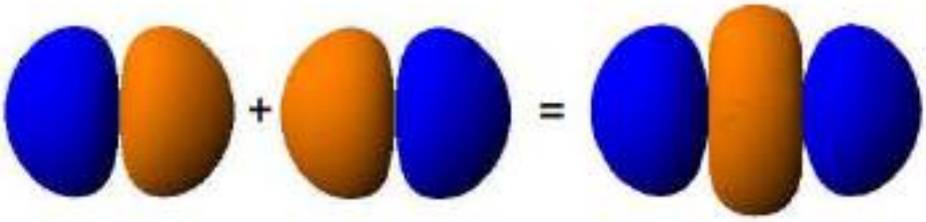
Configuration of Li_2 and Be_2



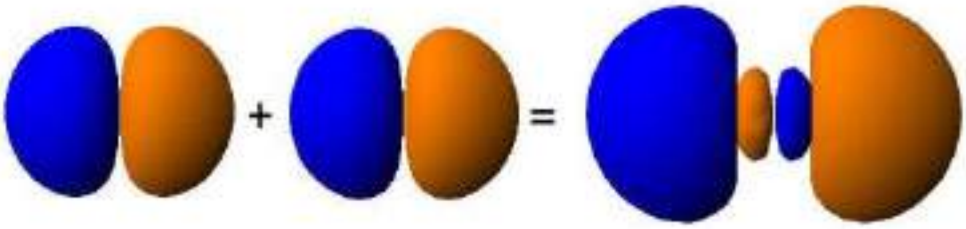
bond order = 1

bond order = 0

Sigma Orbitals from 2*p* ± 2*p*



σ_{2p}



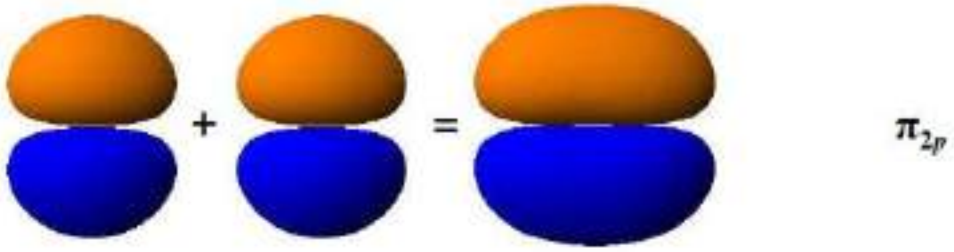
σ^*_{2p}

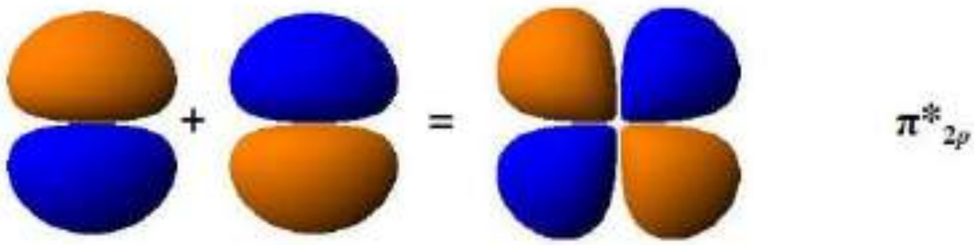
π MOs from 2p ± 2p

☞ Two degenerate π_{2p} bonding MOs, one from $2p_x + 2p_x$ and on from $2p_y + 2p_y$.

☞ Two degenerate π^*_{2p} antibonding MOs, one from $2p_x - 2p_x$ a one from $2p_y - 2p_y$.

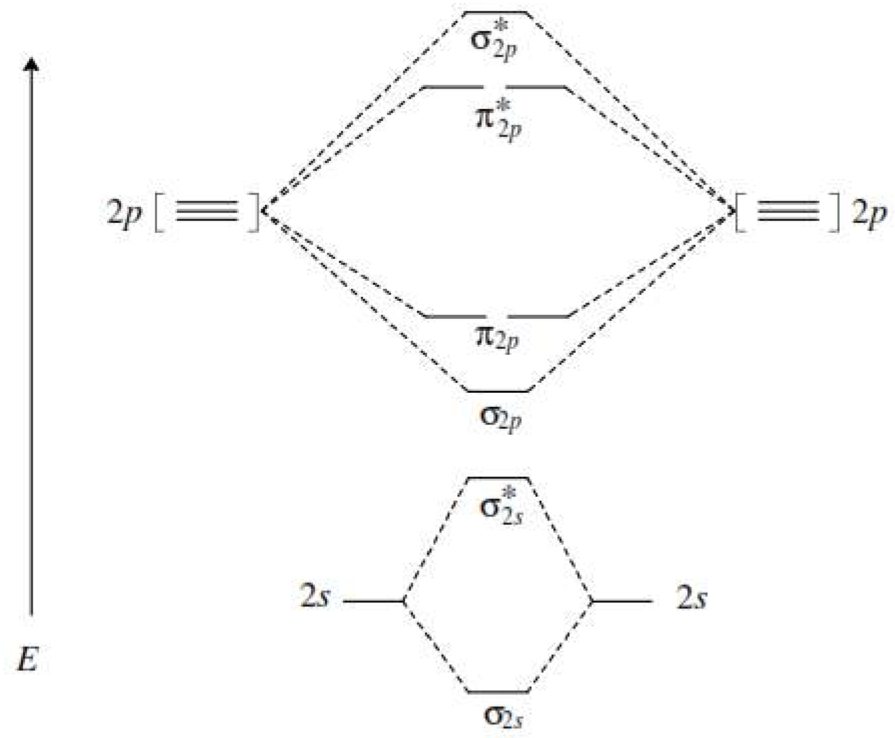
$2p_y \pm 2p_y$ Combinations



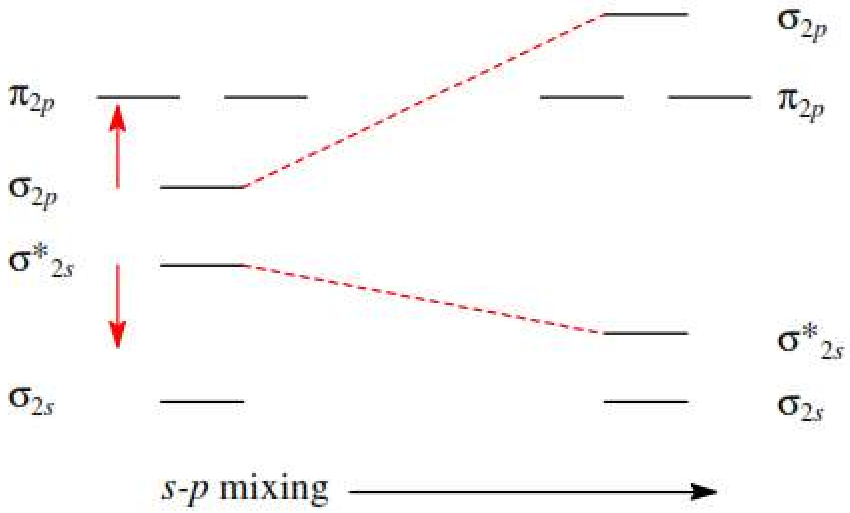


MO Scheme for O_2 through Ne_2 and Related Ions

☞ The core configuration levels σ1S and σ*1S are omitted.

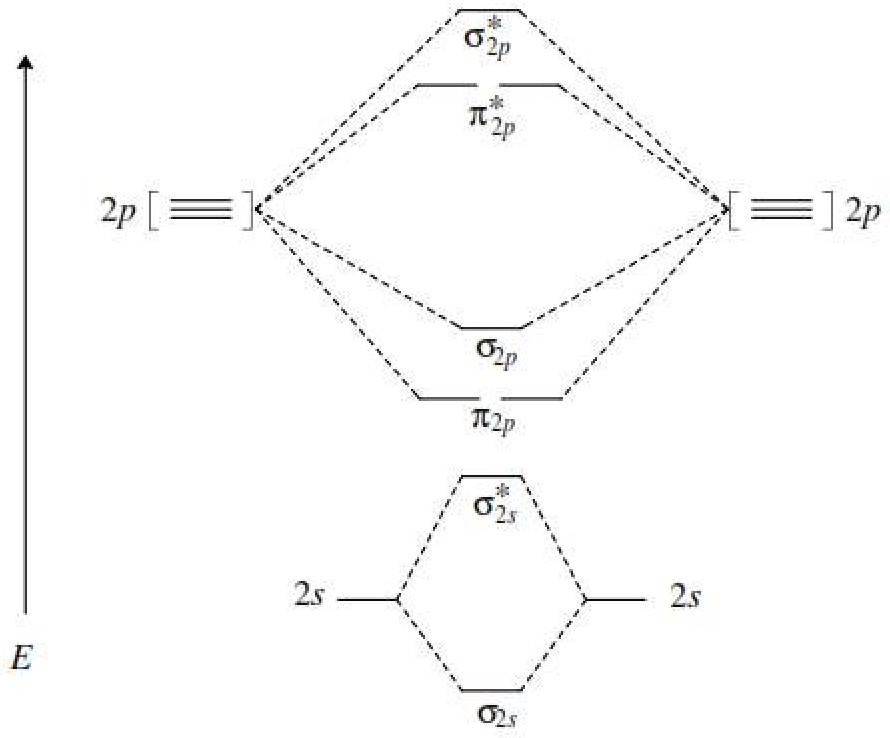


- ☞ In diatomic molecules of the lighter elements **B2, C2** and **N2,** mixing between sigma-type MOs causes the σ*2S level to move down and the σ 2p level to move up in energy.

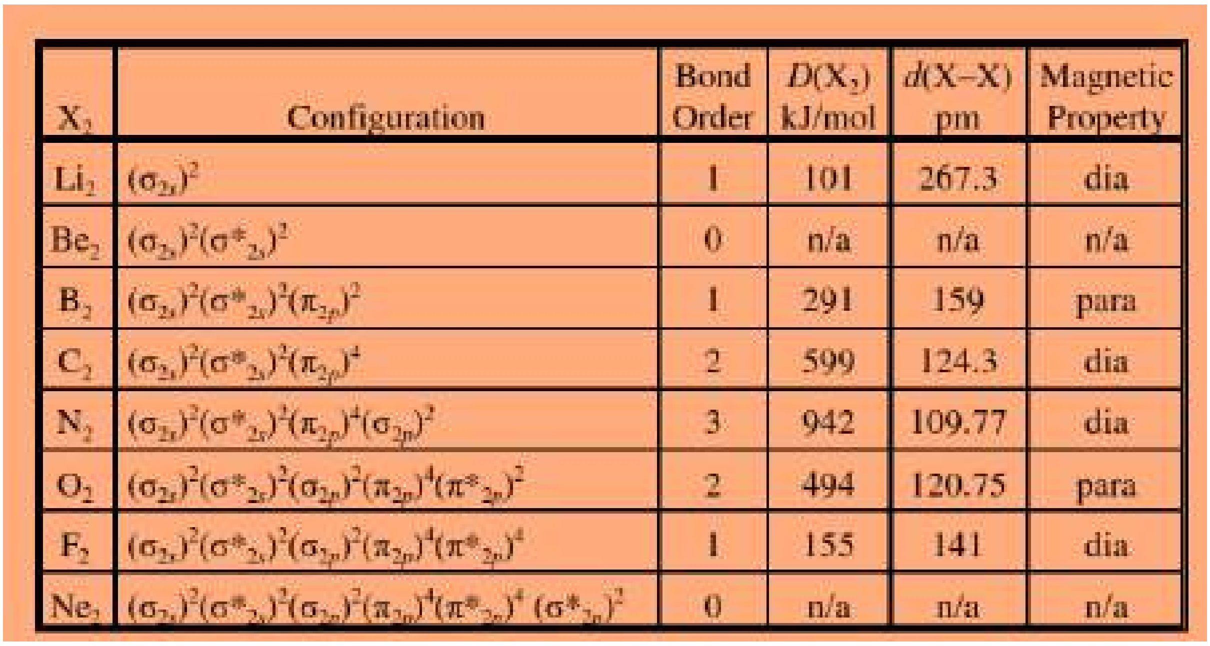


- ☞ The σ2p level rise above that of π2*p*.
- ☞ This results in the following scheme, in which the relative ordering π2*p*< σ2p occurs.

MO Scheme for B2 through N_2 and Related Ions



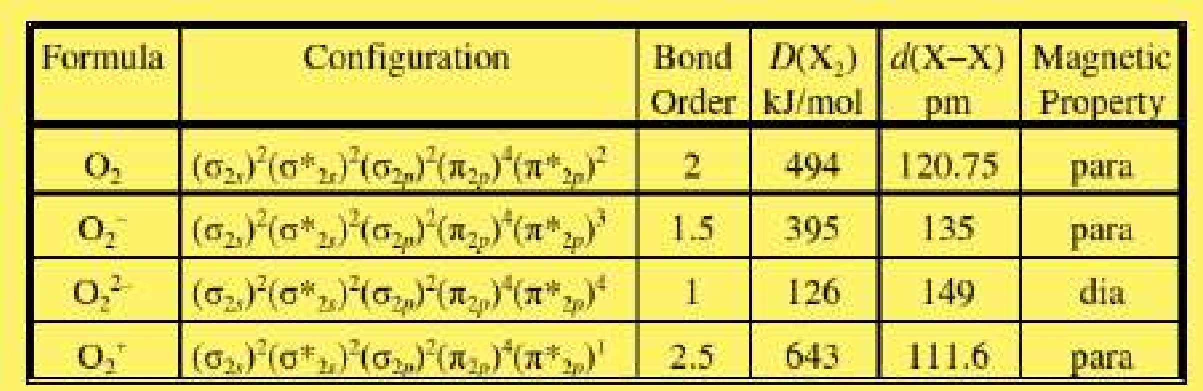
Configurations of Second Period Homonuclear Diatomic Molecules



X_2	Configuration	Bond Order	$D(X_2)$ kJ/mol	$d(X–X)$ pm	Magnetic Property
Li_2	$(\sigma_{2s})^2$	1	101	267.3	dia
Be_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0	n/a	n/a	n/a
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^2$	1	291	159	para
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4$	2	599	124.3	dia
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$	3	942	109.77	dia
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494	120.75	para
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	155	141	dia
Ne_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4 (\sigma^*_{2p})^2$	0	n/a	n/a	n/a

MO Description of O2 And Its Ion

- MO model predicts the observed paramagnetism, which VB theory cannot explain easily.



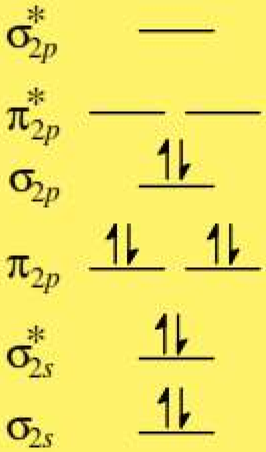
Formula	Configuration	Bond Order	$D(X_2)$ kJ/mol	$d(X–X)$ pm	Magnetic Property
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494	120.75	para
O_2^-	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^3$	1.5	395	135	para
O_2^{2-}	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	126	149	dia
O_2^+	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^1$	2.5	643	111.6	para

Second Period Heteronuclear Diatomic Molecules

- ☞ MO scheme for homonuclear diatomic molecules can be adapted to describe bonding in heteronuclear diatomic molecules.
- ☞ The two atoms do not contribute equally to each MO.
    - More electronegative element has lower energy AOs and makes a greater contribution to bonding MOs.
    - Less electronegative atom makes a greater contribution to antibonding MOs.
- ☞ Ordering of MOs energies in heteronuclear cases tends to be like lighter homonuclear cases: i.e. $\pi 2p < \sigma 2p$

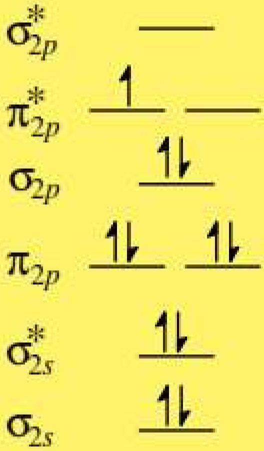
Heteronuclear Diatomic Molecules Examples

CO, CN^-, NO^+ (10 valence electrons, like N_2



bond order = 3

NO (11-electron free radical, like O_2^+)



bond order = 2.5

PHYSICAL CHEMISTRY
Electrochemistry

Syllabus & Study Material

Course Content:

1. **Electrochemical Cell(i.e. Galvanic Cell)**
2. **Equilibrium Potential**
3. **Concentration Cell**
4. **Fuel Cell**
5. **Electrochemical Theory of Corrosion and Protection**

Terms to Know:

Electrochemistry: The study of the interchange of chemical and electrical energy.

OIL RIG: Oxidation is loss, reduction is gain (of electrons)

Oxidation: The loss of electrons, increase in charge

Reduction: The gain of electrons, reduction of charge

Oxidation number: The assigned charge on an atom

Oxidizing agent (OA): The species that is reduced and thus *causes* oxidation

Reducing agent (RA): The species that is oxidized and thus *causes* reduction

Electrochemical Cell

The devices used for converting chemical energy to electrical energy & electrical energy into chemical energy are known as electrochemical cells they contain two electrodes in contact with an electrolyte, they are mainly of two types.

A. **Galvanic cells/Voltaic Cell**
B. **Electrolytic cell**

GALVANIC CELL

A *galvanic cell* or *voltaic cell* is a device in which a redox reaction, spontaneously occurs and produces an electric current. i.e. DANIAL CELL. There are following things here *in Galvanic Cell.*

- ☞ It consists of Zn rod and Cu rod; Zn rod and Cu rod dipped in $ZnSO_4$ solution and $CuSO_4$ solution respectively.
- ☞ Each electrode in its electrolytic solution is known as half-cell.
- ☞ The two solutions are connected by a salt bridge, and thus two electrolytic solutions are in contact with each other, in order to complete the circuit.

ANATOMY [Parts of Voltaic/Galvanic Cell]:

There are following parts in the cell.

- **ANODE**: the electrode where oxidation occurs. After a period of time, the anode may appear to become smaller as it falls into solution (decrease in concentration).
- **CATHODE:** the anode where reduction occurs. After a period of time it may appear larger, due to ions from solution plating onto it (increase in concentration).

- **SALT BRIDGE:** A device used to maintain electrical neutrality in a galvanic cell. This may be filled with agar which contains a neutral salt or it may be replaced with a porous cup.
- **ELECTRON FLOW**: Always from anode to cathode. (through the wire)
- **VOLTMETER**: measures the cell potential (*emf*) . Usually is measured in volts.

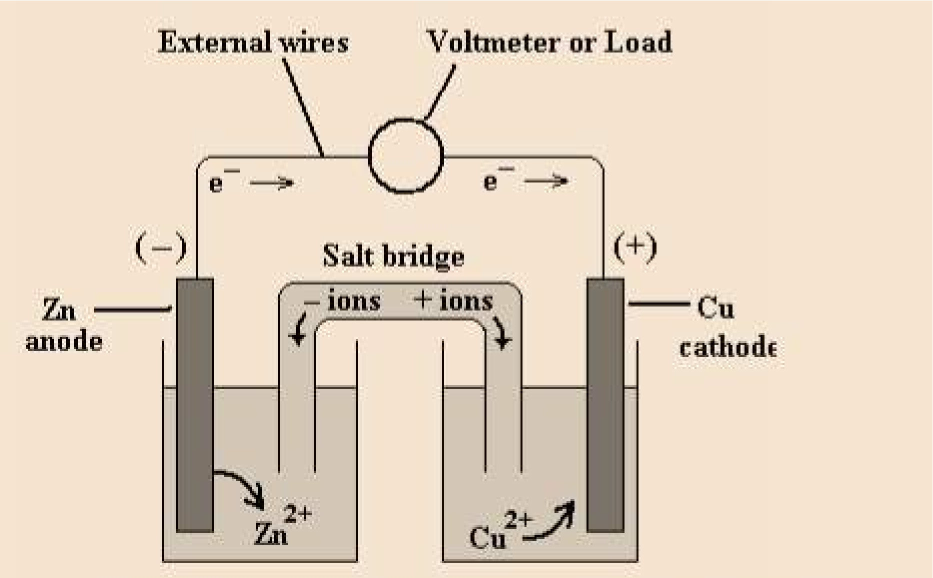


Figure 1. Galvanic cell (or battery) based on the redox reaction i

CELL REACTION

The Electrode Reaction of Galvanic Cell:

At Anode: $Zn \longrightarrow Zn^{+2}(aq)$ [OXIDATION]

At Cathode: $Cu^{+2}(aq) + 2e \longrightarrow Cu(s)$ [REDUCTION]

Net Reaction: $Zn + Cu^{+2}(aq) \longrightarrow Zn^{+2}(aq) + Cu(s)$

CELL REPERSENTATION

An electrochemical cell or galvanic cell is obtained by coupling two half cells. From IUPAC Convention the designed in the following ways:

- **ANODE** | ANODE SOLUTION ‖ CATHODE SOLUTION | **CATHODE**
  EX: $Zn \mid Zn^{+2}(1.0M) \parallel Cu^{+2}(1.0\ M) \mid Cu(s)$
  [Negative Terminal, OXIDATION] [Positive Terminal, REDUCTION]
- Cell is generally written with the negative electrode [ANODE] on the left hand side and the positive electrode [CATHODE] on the right side.
- [|] Single line represents phase separation.
- [‖] Double line represent(s) **SALT BRIDGE.**

***Pease refer the* Fig 1 *For* GALVANIC CELL**

STANDARD REDUCTION POTENTIALS

- Each half-reaction (OX/RED) has a cell potential.
- Each potential is measured against a standard which is the standard hydrogen electrode [consists of a piece of inert Platinum that is bathed by hydrogen gas at 1 atm]. **The hydrogen electrode is assigned a value of ZERO volts.**

- **Standard conditions: 1 atm for gases, 1.0*M* for solutions and 25°C for all (298 K).** We use **NAUGHT^0** to symbolize standard condition. That means E_{cell}, emf or Ecell, become E^0_{cell}……..when measurements are taken at standard conditions.
- when a Galvanic cell is constructed from zinc sulphate and copper(II) sulphate using the respective metals as electrodes at Standard condition.

  - 1.0 *M* solutions of each salt are used
  - overall voltage of 1.10 V for the process

Calculating Standard Cell Potential

Remember the following point at the time of calculating the standard potential:

1. Decide which element is oxidized or reduced using the table of reduction potentials. Remember: **THE MORE POSITIVE REDUCTION POTENITAL GETS TO BE REDUCED.**
2. Write both equations along with their voltages.
3. Balance the two half reaction with suitable number * ***Do not multiply the voltage value****
4. Set the formula to get the potential value.

$$E^o_{cell} = E^o_{right} - E^o_{left}$$

or

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

Based on the values for the standard reduction potentials for the two half-cells in Galvanic Cell [–0.76 V for zinc anode and +0.34 V for copper cathode], the *standard cell potentia* **E^o_{cell}.**

$$E^o_{cell} = +0.34V - (-0.76V) = +1.10V$$

The positive voltage for E^o_{cell} indicate that at standard condition the reaction is spontaneous/feasible.

[*Recall that* $\Delta G° = -nFE°cell$, *so that positive* $E°cell$ *result in a negative* $\Delta G°$]**.Thus Galvanic cell produce an Electric Current.**

NERNST EQUATION

When conditions are not standard, the *Nernst equation*, is used to calculate the potential of a cell. The Nernst Equation is:

$$E_{cell} = E^0_{cell} - \left(\frac{RT}{nF}\right)(\ln Q)$$

Where **R** = Universal Gas Constant (8.314 $JK^{-1}mol^{-1}$)

T = is the temperature in kelvin, K

n = # of electron transferred in the REDOX reaction

Q= is the reaction Quotient for ion product/ion reactant of the cell.

N.B: The solid electrode [Zn(s)/Cu(s)] have the constant “concentration” and so do not appear in Q.

F = is the Faraday constant with a known value of **96,500 J/ (V.mol).**

For a Galvanic cell: $Zn + Cu^{+2}(aq) \rightarrow Zn^{+2}(aq) + Cu(s)$ so Q and lnQ

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad \text{and} \quad \ln Q = \ln [Zn^{2+}] - \ln [Cu^{2+}]$$

Since for equation n = 2. The Nernst equation for redox reaction:

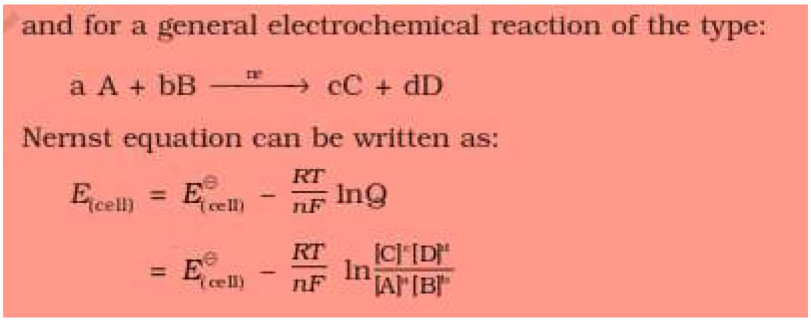
$$E_{cell} = E^0_{cell} - \left(\frac{RT}{2F}\right)\ln[Zn^{2+}] + \left(\frac{RT}{2F}\right)\ln[Cu^{2+}]$$

Or

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

By converting the natural logarithm in above equaton to the base 10 and substituting the values of ***R***, ***F*** and ***T*** = 298 K, it reduces to:

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$



and for a general electrochemical reaction of the type:

$$aA + bB \xrightarrow{ne} cC + dD$$

Nernst equation can be written as:

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{nF}\ln Q$$

$$= E^{\ominus}_{(cell)} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

EQULIBRIUM CONSTANT

As E_{cell} decline with reactant converting to products, E_{cell} , eventually reaches **ZERO.**

ZERO potential means reaction is at Equilibrium [DEAD BATTERY]. Also Q = K and $\Delta G° = 0$ as well.

At equilibrium:

$$\frac{[Zn^{+2}]}{[Cu^{+2}]} = \text{Kc, at T} = 298\text{K}$$

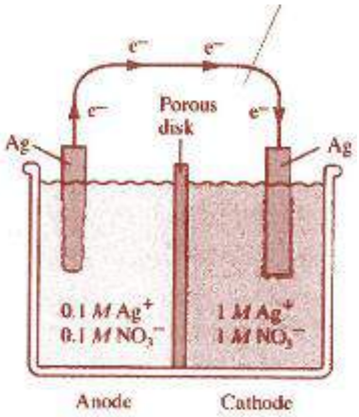
$$E^0_{cell} = \frac{0.0591}{2}\log Kc$$

For general equation:

$$E^{\ominus}_{(cell)} = \frac{2.303RT}{nF} \log K_C$$

CONCENTRATION CELL

We can construct a cell where both compartments (half-cell) contain the same components BUT at different concentrations.



Notice the difference in the concentrations pictured at left. Because the right compartment contains 1.0 *M* Ag^+ and the left compartment contains 0.10 *M* Ag^+, there will be a driving force to transfer electrons from left to right. Silver will be deposited on the right electrode, thus lowering the concentration of Ag^+ in the right compartment. In the left compartment the Silver electrode dissolves [producing Ag^+ ions] to raise the concentration of Ag^+ in solution.

Characteristics:

- The electrical energy in a concentration cell arises from the transfer of a substance from the solution of lower concentration (around the other electrode) a concentration cell is made up of two half cells having identical electrodes, except that the concentration of the reactive ions at the two electrodes are different
  - The emf arises due to the change in the concentration of either the electrolytes or the electrode.

CELL PRESENTATION

Ex: Siver rod(s) immersed two different concentration of **SILVER NITRATE** ($AgNO_3$). According to cell convention.

Ag | $AgNO_3$ (C_1) ‖ $AgNO_3$ (C_2) | Ag
[DILUTE] [CONCENTRATED]
(-ve Electrode, Anode) (+ve Electrode, Cathode)

AN OX : an oxidation occur at ANONDE
RED CAT: reduction occur at CATHODE

FAT CAT : The electrons in a voltaic or galvanic cell ALWAYS flow **F**rom the **A**node **T**o the **CAT**hode

Ca+hode : the cathode is + in Concentration cells

THEORY:

when a metal(M) electrode is dipped in a solution containing its own ions (M^{n+}) , then a potential (E) is developed at the electrode, the value of which varies with the concentration(C) of the ions in accordance with the Nernst's equation.

$$\mathbf{E = E^o - 2.303\frac{RT}{nF}\log C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)}$$

Let us consider a general reaction:

$$[\text{ANODE}]\quad M \,|\, M^{n+}(C_1M) \;\|\; M^{n+}(C_2M) \,|\, M \quad [\text{CATHODE}]$$

(Oxidation) (Reduction)

C_1 and **C_2** are the concentrations of the active metal ions (M) in contact with the 2 electrodes Respectively and **C_2** > **C_1**emf of cell is:

$$= E^o_{right} - E^o_{left}$$

$$= E^o + \frac{0,0591}{n}\log C2 - E^\circ + \frac{0.0591}{n}\log C1$$

$$E_{cell} = \frac{0.0591}{n}\log(C_2/C_1) \quad \text{at } 25^0\text{ C}$$

And at any temp., the general equation is

$$E_{cell} = \frac{2.303\times R\times T}{nF}\log(C_2/C_1)$$

CELL REACTION

At anode : $M \dashrightarrow M_{(C1)} + n\,e^-$

At cathode : $M^{n+}(C_2) + n\;e^- \dashrightarrow M$

On cell reaction : $M^{n+}(C_2) + n\,e^- \dashrightarrow M^{n+}(C_1)$

Applications of Galvanic Cells

Batteries: cells connected in series; potentials add together to give a total voltage.

Examples:

Lead-storage batteries (car)--Pb anode, PbO_2 cathode, H_2SO_4 electrolyte

Dry cell batteries

Acid versions: Zn anode, C cathode; MnO_2 and NH4Cl paste

Alkaline versions: some type of basic paste, ex. KOH

Nickel-cadmium – anode and cathode can be recharged

Fuel cells

Reactants continuously supplied (spacecraft –hydrogen and oxygen)

FUEL CELL

Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells.**

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (**Fig. 3.12**)

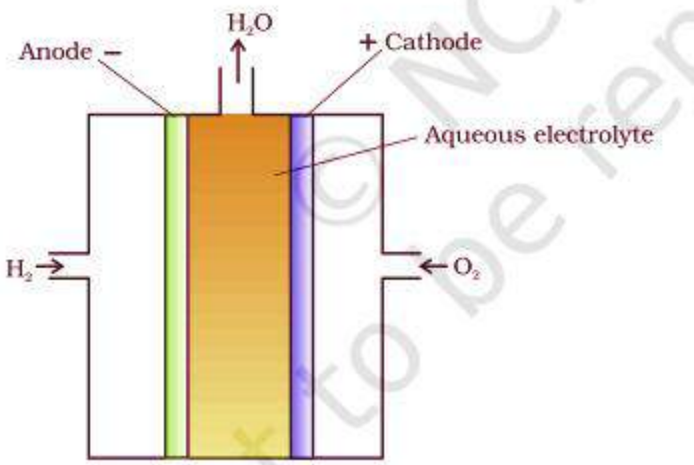
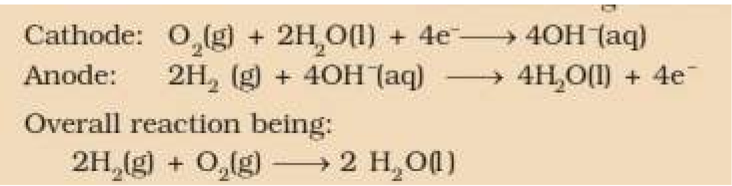


Fig. 3.12: *Fuel cell using H_2 and O_2 produces electricity.*

The cell was used for providing electrical power in the **Apollo space programme**.

The water vapours produced during the reaction were condensed and added to the drinking water supply for the **astronauts.** In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for **increasing the rate of electrode reactions**.

The Electrode reaction:



Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Overall reaction being:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an **efficiency of about 70 %** compared to thermal plants whose **efficiency is about 40%.**

Advantages of fuel cells

1. No emission of toxic gases. Chemical wastes are in safe limits. The reactants and products are environmental friendly.
2. High efficiency of conversion of chemical energy to electrical energy. So can be used as an excellent renewable energy resource.
3. No noise pollution like generators.

Limitations of fuel cells

1. The main limitation of fuel cells lie in high initial costs associated with electrode material and design costs.
2. High cost of H_2 gas.
3. Lack of infrastructure for distributions and marketing of hydrogen gas.

CORROSION AND ITS CONTROL

Process of deterioration or destruction and consequent loss of a solid metallic material through an unwanted chemical or electrochemical attack by its environment at its surface is called corrosion. Thus corrosion is a reverse process of extraction of metals. For Ex:

a. Rusting of Iron
b. Formation of green film of basic carbonate.

THEORIES OF CORROSION

Corrosion can be explained by the following two theories.

1. Dry or chemical corrosion.
2. Wet or electrochemical corrosion.

ELECTROCHEMICAL CORROSSION

Electrochemical corrosion involves:

- The formation of **Anodic** and **Cathodic** Areas.
- Electrical contact between the **Cathodic** and **Anodic** parts to enable the conduction of electrons.
- An electrolyte through which the ions can diffuse or migrate this is usually provided by moisture (*behave as Electrolyte*).
- Corrosion of anode only.
- Formation of corrosion product is somewhere in between cathode and anode.

Chemistry of Corrosion: Corrosion of iron (**RUSTING**) generally takes place in presence of water and air. A particular spot which made up with iron, where OXIDATION takes place called ANODE. The electrochemical reaction is:

$$\text{ANODE: } 2Fe(s) \longrightarrow 2Fe^{2+} + 4\,e^{-} \quad E^{o}_{Fe^{2+}/Fe(s)} = -0.44V$$

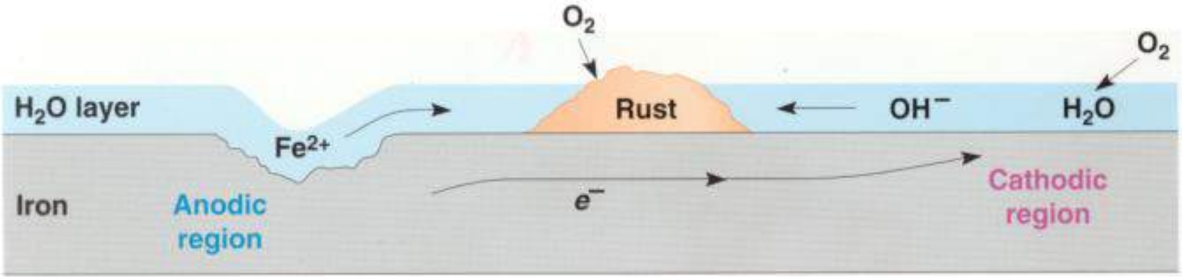
The electron release from ANODE move through metal and reach to another particular part of the iron and reduce the OXYGEN in presence of H^+(believe to be from carbonic acid which formed by the dissolution of carbon dioxide from air in to water). This spot behave as CATHODE.

CATHODE: O_2 (g) + $4H^+$ (aq) + $4e^- \longrightarrow$ $2H_2O$ (l) $E^o_{H^+}|O_2|H_2O$ = 1.23V

The net reaction being:

$2Fe(s) + O_2\,(g) + 4H^+(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2H_2O(l)$ E^o_{cell} = 1.67 V

The Fe^{2+} (ferrous ions) are further oxidised to Fe^{3+}(ferric ion) by atmospheric oxygen. Which come out as RUST in the form of **HYDRATED FERRIC OXIDE** ($Fe_2O_3.xH_2O$) along with HYDROGEN ION which again participate in the reaction cycle resulting in continuous corrosion (see Fig below)



The rate of corrosion is measured by the current of metal ions leaving the metal surface in the anodic region. This flux of ions gives rise to the **CORROSION CURRENT**,*I*, which can be identified with the anodic current, I_a.

CORROSION CONTROL

Several techniques for inhibiting corrosion are available. There are most efficient way of corrosion protection is **CATHODIC protection**.

In catodic protection the object is connected to a metal having more –ve standard REDUCTION potential (such as magnesium metal E^o = -2.36V). This magnesium acts as **SACRIFICIAL ANODE, supplying its own electrons to the IRON (Fe) and become oxidised to Mg^{2+} in this processes (refer the fig 1 below).**

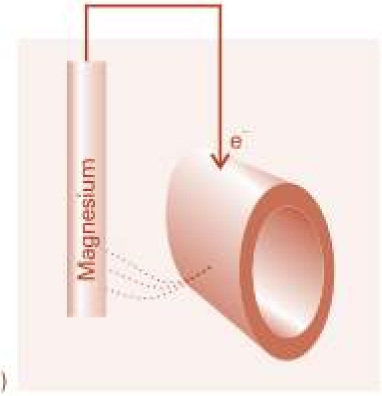


Fig1: Cathodic protection an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (For example, a pipeline, bridge, or boat).

A block of magnesium replaced occasionally is much cheaper than the ship, building, or pipeline for which it is being sacrificed.

In **impressed-current cathodic protection** an external cell supplies the electrons and eliminates the need for iron to transfer its own (**refer below fig 2**)

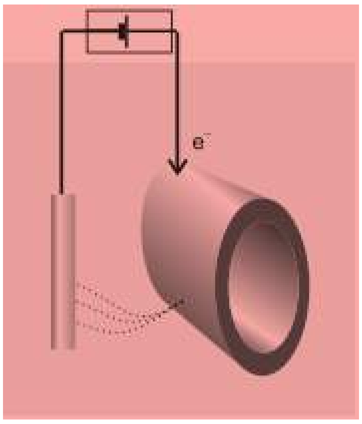


Fig 2: **In impressed-current cathodic protection electrons are supplied from an external cell so that the object itself is not oxidized. The broken lines depict the completed circuit through the soil**.

QUESTION FOR REVIEW

Q#1: Calculate the emf of the **DANIAL CELL.**

$\mathbf{Zn \,|\, Zn^{+2}(0.1M) \;\|\; Cu^{+2}(0.1) \,|\, Cu}$

At 298 K . $E^o_{cell} = 1.10V$

Q#2: Calculate the Electrode potential of copper rod dipped in 0.01M solution of copper sulphate at 298K. $E^o_{Cu^{2+}/Cu} = 0.34$ V.

Q#3: What is salt bridge?

Q#4: Draw the label diagram of the **GALVANIC** cell.

Q#5: For cell,

$\mathbf{Mg(s) \,|\, Mg^{2+}\,(aq) \;\|\; Zn^{2+}(aq) \,|\, Zn(s)}$

- **a.** Draw the complete cell diagram
- **b.** Identify the Cathode and Anode
- **c.** Write the complete cell reaction.
- **d.** Write the NERNST equation for this cell.
- **e.** Calculate the E^o_{cell} (*take the help of Electrochemical Series*)

Q#6: Calculate the emf of the following cell:

$\mathbf{Zn \,|\, Zn^{2+}(aq)(0.001M) \;\|\; Ag^{+}(aq)(0.1M) \,|\, Ag(s)}$

Given: $E^o_{Ag^+/Ag}$ = +0.80 V and $E^o_{Zn^{+2}/Zn}$ = -0.76V

Q# 7: What is sacrificial anode? Mention its role in corrosion control.

THE PHASE RULE

COURSE CONTENT:

- **Phase Rule**
- **Component(s)**
- **Degree of Freedom**
- **One component System**
- **The Water System**

PHASE RULE

This rule was deduced on the basis of thermodynamic principles by J. Willard Gibbs. This rule Predicts qualitatively the effect of temperature, pressure and concentration on a heterogeneous equilibrium. Gibbs phase rule may be stated as follows:

"In a heterogeneous system in equilibrium, the number of degrees of freedom plus the number of phases is equal to the number of components plus two"

Mathematically: **$F + P = C + 2$**

Or **$F = C - P + 2$**

Where:

F = No of Degree of Freedom
C = No Of Component
P = Number of Phase
2 = Additional variables of temperature and pressure besides the concentration variables

PHASE

A phase is defined as any homogeneous (identical physical and comical composition, throughout the system) and physically distinct part of a system which is separated from other parts of the system by interfaces (junction of two phase).

For EX: **SINGLE PHASE [Air is a mixture of O_2, N_2, CO_2 & water vapour]**

Thermal decomposition of calcium Carbonate having 3 phase [2 solid & 1 gas]

COMPONENT

The number of component of a system at equilibrium is defined as the minimum number of independently variable constituents which are required to express the composition of each phase in the system. **Ex: Sulphur System & Water System**

Degrees of Freedom

The degree of freedom or variance of a system is defined as the minimum number of variable factors such as temperature, pressure and concentration which should be arbitrarily fixed in order to define the system completely.

Example:

1. For a given sample of any gas PV = nRT. Any two of the three variables P, V, T define the system completely. Hence the system is **bivariant** or it has two degrees of freedom.
2. A gaseous mixture say N2 and O2 gases (mixed 50% each), is completely defined when three variables temperature, pressure and concentration are specified. thus, the degrees of freedom is three or the system is **trivariant.**

It is concluded that:

1. The greater the number of components in a system, the greater is the degree of freedom for a given number of phases.
2. The greater the number of phases, the smaller is the number of degrees of freedom.
3. The number of phases is maximum when the number of degrees of freedom = Zero, for a given number of components.

Advantages of Phase' Rule:

1. It provides a simple method of classifying equilibrium states of systems.
2. It predicts the behaviour of systems with changes in the variables that govern the system in equilibrium.
3. It finds extensive use in the study of many heterogeneous systems. In particular it has been found extremely useful in the extraction of metals.

LIMITATION OF PHASE RULE:

1. The phase rule is applicable to heterogeneous systems in equilibrium, so, it is therefore of no use for such systems which are slow in attaining the equilibrium state.
2. It is applicable to a single equilibrium state.

PHASE DIAGRAM

A phase diagram is the sum total of the description of the behaviour of the phases under equilibrium.

APPLICATION OF GIBBS PHASE RULE TO ONE COMPONENT SYSTEM

From the mathematical expression,

$$F = C - P + 2$$

When C =1 and P = 1

F = 1-1+2

= 2

Hence, all one component systems can be completely described graphically by stating only two variables, pressure and temperature on appropriate axis.

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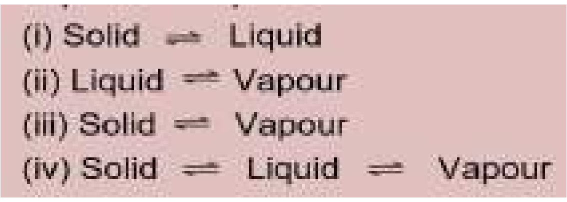
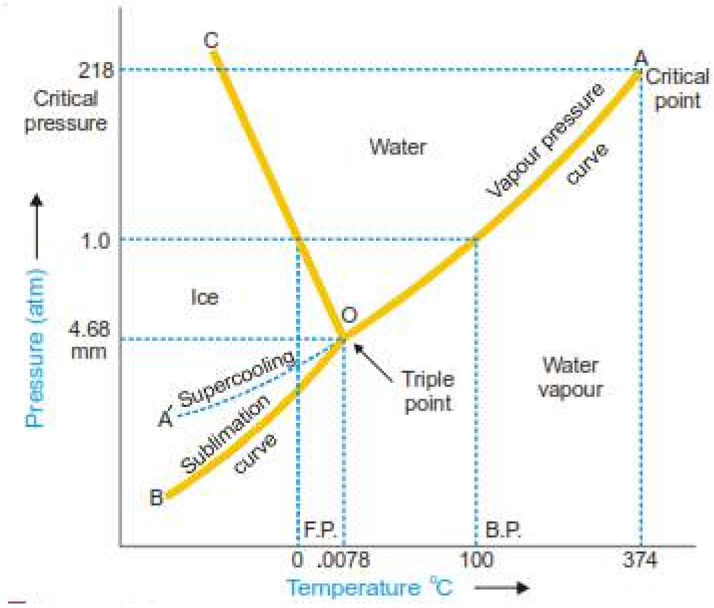
WATER SYSTEM

It is a one component system. Water exists in three possible phases viz. ice (solid) , water (liquid), and vapour (gas). These three single phases may form four possible equilibria.



(i) Solid $\rightleftharpoons$ Liquid
(ii) Liquid $\rightleftharpoons$ Vapour
(iii) Solid $\rightleftharpoons$ Vapour
(iv) Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

The phase diagram of water is given as:



DISCRIPTION OF PHASE DIAGRAM

The phase diagram of water consist of:

1. Stable Curves: **THREE** OA, OB and OC
2. Metastable Curve: **ONE**, OA’
3. Areas: THREE, AOB, COB & AOC

S.NO	CURVES	NAME OF CURVE	PROPERTISE
1	OA	Vapour pressure Curve	☞ The vapour pressure of water increases with increase in temperature ☞ The water vapour system is univariant. F = C-P +2 = 1-2+2 = 1 ☞ Above critical temp. on the vapour phase exists whatever may be the value of pressure.
2	OB	Sublimation Curve of Ice	☞ Along this curve solid ice in equilibrium with its vapour. ☞ F = C-P +2 = 1-2+2 = 1, univarient system.

3	OC	Fusion Curve of Ice	☞ Along this curve, two phases, ice and water are in equilibrium. ☞ F = C-P +2 = 1-2+2 = 1, univarient system. This means that for any given pressure, melting point must have one fixed value.
AREAS			
1	BOC AOC AOB	ICE WATER VAPOUR	☞ In these areas, the degrees of freedom for the system is two or they are bivariant

TRIPLE POINT

The point O at which the curves AO, BO and CO meet is called the triple point. At this point all the three phases viz , ice, water and vapour co-exist. Thus, P =3.

According to phase rule, at triple point O,

F = C –P + 2, =1-3+2 , F = 0

Thus, the degree of freedom at triple point is zero, which indicates that there is only one set of variables P, T at which all the three phases coexist.

QUESTION FOR REVIEW

1. Define or explain the following term(s):
   - A. Phase Rule
   - B. Degree of Freedom
   - C. Phase
   - D. Component
   - E. Triple Point
2. Draw the complete phase diagram for water system and discus in the regards to the following terms:
   - a. CURVES
   - b. AREAS
   - c. TRIPLE POINT
3. Define the following system:
   - a. Bi-varient System
   - b. Univarient System
4. Apply Phase rule to the water system?

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CHEMICAL KINETICS

COURSE CONTENT:

- **Order & Molecularity of reactions**
- **Zero Order and Second Order reaction**
- **Integrated rate law**
- **Theory of reaction rate**

Rate Law & Reaction Order

The reaction ***rate law expression*** relates the rate of a reaction to the concentrations of the reactants. Each concentration is expressed with an order (**exponent**).

For a general reaction:

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

Reaction rate law is:

$$v = K\,[A]^m\,[B]^n$$

m and **n** are the reactant orders and determined from **EXPEREMENTS. m and n are not STOICHIOMETRIC coefficient of the reaction.**

The reaction order with respect to A is m and with respect to B is n. The overall order of the reaction (m+n) may range from 1 to 3 and can be fractional (1/2, 3/2, 5/2….).

Sr.No	Reactions	Molecularity	Rate law	Order
1	$A \longrightarrow P$	1	$v = K[A]$	1
2	$A+B \longrightarrow P$	2	$v = K[A][B]$	2
3	$A+A \longrightarrow P$	2	$v = K[A]^2$	2
4	$A+B+C \longrightarrow P$	3	$v = K[A][B][C]$	3
5	$A+A+A+A \longrightarrow P$	3	$v = K[A]^3$	3

K = rate constant

Note: When order of reaction is 1 (first order) no exponent is written. If exponent is zero order of reaction is ZERO

The Overall Order of a reaction is the sum of the individual orders:

Q#1: The reaction $A + B + C \longrightarrow$ Products, is found to obey the rate law

$$v = \frac{-d[A]}{dt} = K\,[A][B]^{1/2}[C]^2$$

What is the overall order of reaction?

Solution:

……………………………………………………………………………………………

……………………………………………………………………………………………

UNIT OF RATE CONSTANT

The units of a rate constant (**k**) will change depending upon the overall order. Unit of rate (*v*) is always Ms^{-1}**[M= Molar concentration, mol L^{-1}]**.

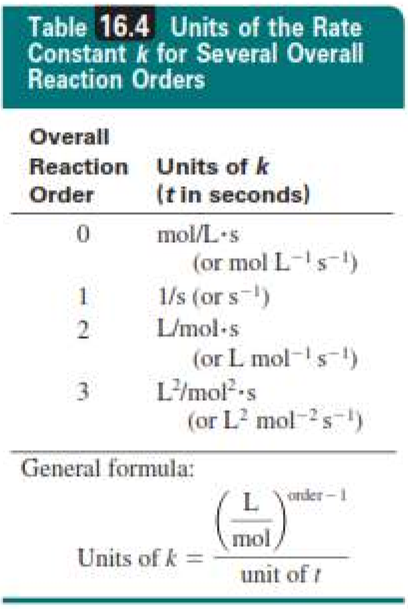


Table 16.4 Units of the Rate Constant *k* for Several Overall Reaction Orders

Overall Reaction Order	Units of *k* (*t* in seconds)
0	mol/L·s (or mol L^{-1} s^{-1})
1	1/s (or s^{-1})
2	L/mol·s (or L mol^{-1} s^{-1})
3	L^2/mol^2·s (or L^2 mol^{-2} s^{-1})

General formula:

$$\text{Units of } k = \frac{\left(\dfrac{\text{L}}{\text{mol}}\right)^{\text{order}-1}}{\text{unit of } t}$$

INTEGRATED RATE LAW: Concentration Change over Time

[Characteristics of ZERO & Second Order Reaction]

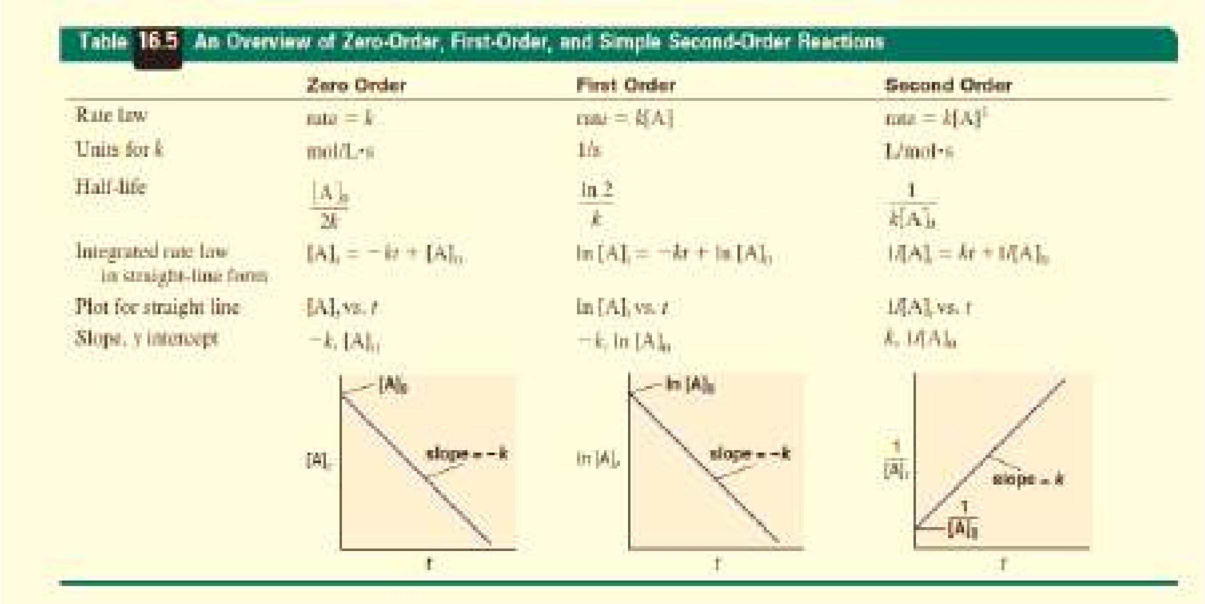
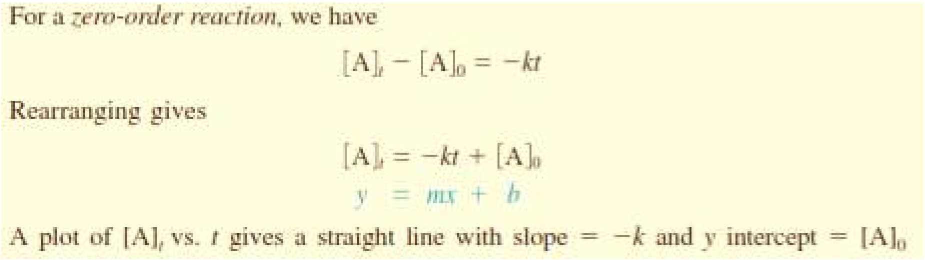


Table 16.5 An Overview of Zero-Order, First-Order, and Simple Second-Order Reactions

	Zero Order	First Order	Second Order
Rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
Units for k	mol/L·s	1/s	L/mol·s
Half-life	$\frac{[A]_0}{2k}$	$\frac{\ln 2}{k}$	$\frac{1}{k[A]_0}$
Integrated rate law in straight-line form	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$1/[A]_t = kt + 1/[A]_0$
Plot for straight line	$[A]_t$ vs. t	$\ln [A]_t$ vs. t	$1/[A]_t$ vs. t
Slope, y intercept	$-k$, $[A]_0$	$-k$, $\ln [A]_0$	k, $1/[A]_0$



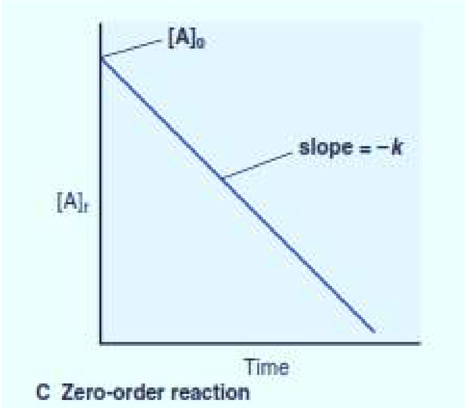
For a *zero-order reaction*, we have

$$[\mathrm{A}]_t - [\mathrm{A}]_0 = -kt$$

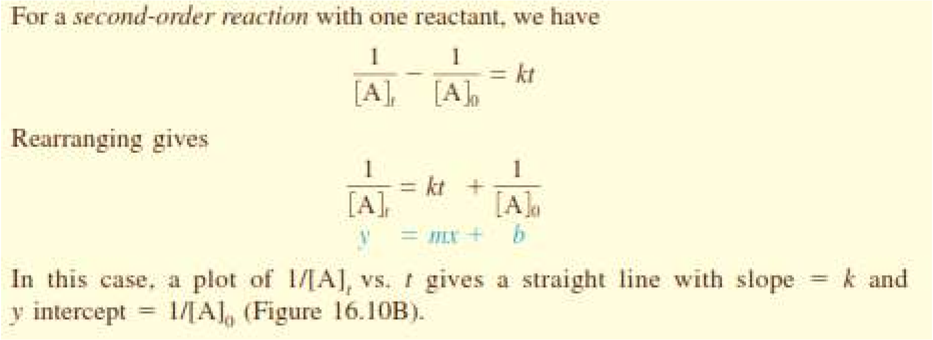
Rearranging gives

$$\begin{aligned}[\mathrm{A}]_t &= -kt + [\mathrm{A}]_0\\ y &= mx + b\end{aligned}$$

A plot of $[\mathrm{A}]_t$ vs. t gives a straight line with slope $= -k$ and y intercept $= [\mathrm{A}]_0$



C Zero-order reaction



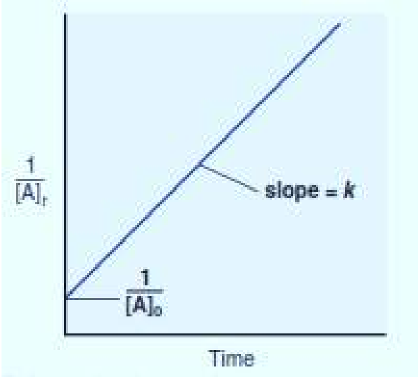
For a *second-order reaction* with one reactant, we have

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt$$

Rearranging gives

$$\begin{aligned}\frac{1}{[\mathrm{A}]_t} &= kt + \frac{1}{[\mathrm{A}]_0}\\ y &= mx + b\end{aligned}$$

In this case, a plot of $1/[\mathrm{A}]_t$ vs. t gives a straight line with slope $= k$ and y intercept $= 1/[\mathrm{A}]_0$ (Figure 16.10B).



Determining Reaction Orders by Changing Reactant Concentrations

For a general reaction:

$$A + 2B \longrightarrow C + D$$

The rate law, expressed in general terms, is

$$v = K\,[A]^m\,[B]^n$$

To find the values of **m** and **n,** we run a series of experiments in which one reactant concentration changes while the other is kept constant, and we measure the effect on the initial rate in each case.

$$\left[\frac{\text{Concentration 2}}{\text{Concentration 1}}\right]^m = \frac{\text{Rate 2}}{\text{Rate 1}}$$

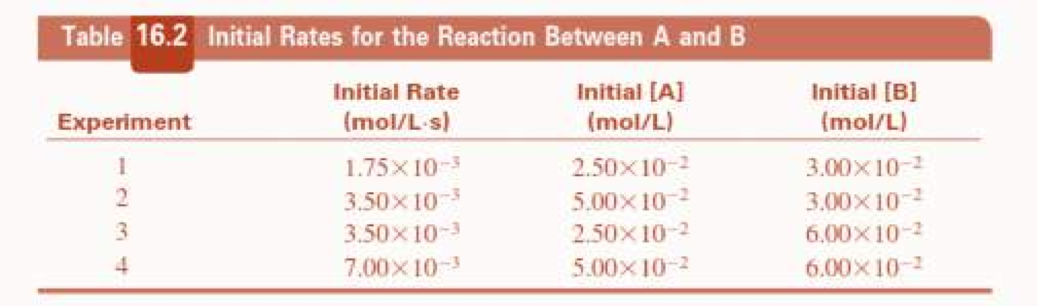


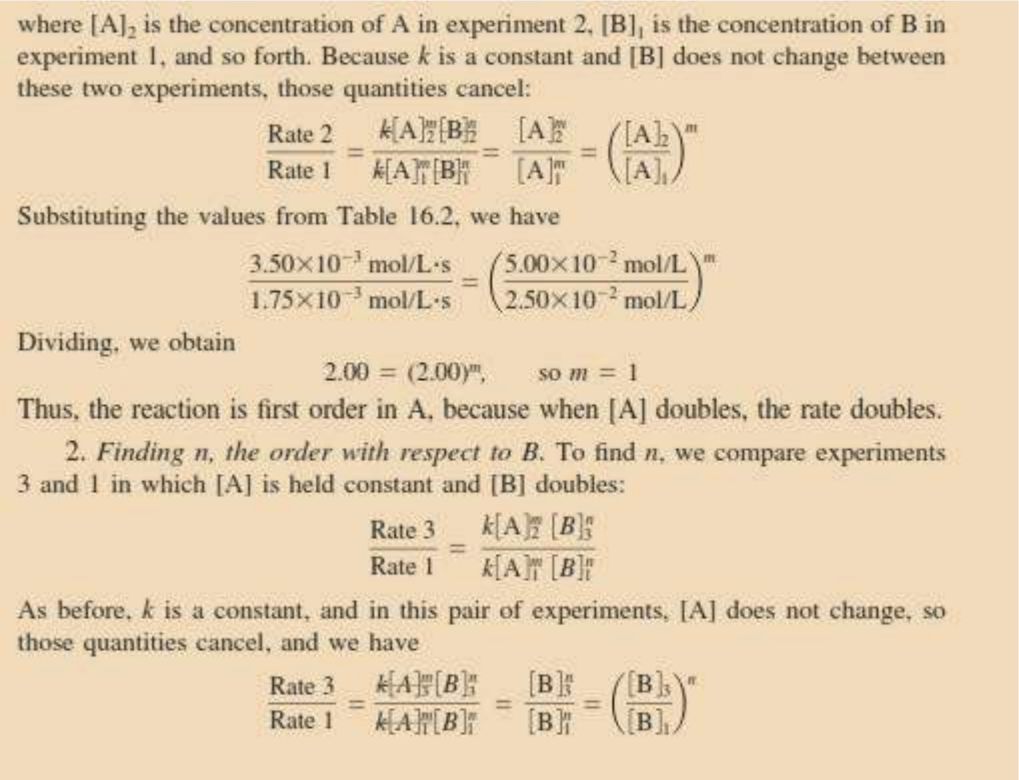
Table 16.2 Initial Rates for the Reaction Between A and B

Experiment	Initial Rate (mol/L·s)	Initial [A] (mol/L)	Initial [B] (mol/L)
1	1.75×10^{-3}	2.50×10^{-2}	3.00×10^{-2}
2	3.50×10^{-3}	5.00×10^{-2}	3.00×10^{-2}
3	3.50×10^{-3}	2.50×10^{-2}	6.00×10^{-2}
4	7.00×10^{-3}	5.00×10^{-2}	6.00×10^{-2}

[A] Finding m, the order with respect to A.

By comparing experiments **1** and **2**, in which **[A]** doubles and **[B]** is constant, we can obtain *m*. First, we take the ratio of the general rate laws for these two experiments:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[A]_2^m[B]_2^n}{k[A]_1^m[B]_1^n}$$



where $[A]_2$ is the concentration of A in experiment 2, $[B]_1$ is the concentration of B in experiment 1, and so forth. Because k is a constant and [B] does not change between these two experiments, those quantities cancel:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[A]_2^m\cancel{[B]_2^n}}{\cancel{k}[A]_1^m\cancel{[B]_1^n}} = \frac{[A]_2^m}{[A]_1^m} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

Substituting the values from Table 16.2, we have

$$\frac{3.50\times10^{-3}\text{ mol/L·s}}{1.75\times10^{-3}\text{ mol/L·s}} = \left(\frac{5.00\times10^{-2}\text{ mol/L}}{2.50\times10^{-2}\text{ mol/L}}\right)^m$$

Dividing, we obtain

$$2.00 = (2.00)^m, \qquad \text{so } m = 1$$

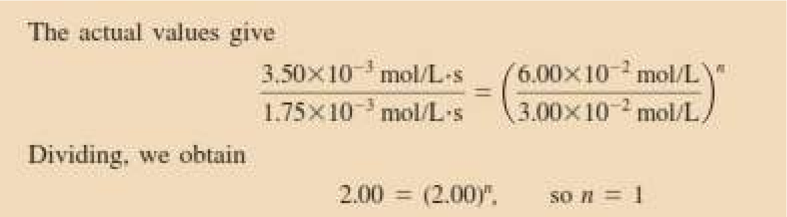
Thus, the reaction is first order in A, because when [A] doubles, the rate doubles.

2. *Finding n, the order with respect to B.* To find n, we compare experiments 3 and 1 in which [A] is held constant and [B] doubles:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[A]_2^m\,[B]_3^n}{k[A]_1^m\,[B]_1^n}$$

As before, k is a constant, and in this pair of experiments, [A] does not change, so those quantities cancel, and we have

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{\cancel{k}\cancel{[A]_3^m}[B]_3^n}{\cancel{k}\cancel{[A]_1^m}[B]_1^n} = \frac{[B]_3^n}{[B]_1^n} = \left(\frac{[B]_3}{[B]_1}\right)^n$$



The actual values give

$$\frac{3.50\times10^{-3}\text{ mol/L·s}}{1.75\times10^{-3}\text{ mol/L·s}} = \left(\frac{6.00\times10^{-2}\text{ mol/L}}{3.00\times10^{-2}\text{ mol/L}}\right)^n$$

Dividing, we obtain

$$2.00 = (2.00)^n, \qquad \text{so } n = 1$$

Thus, the reaction is also first order in B because when [B] doubles, the rate doubles. We can check this conclusion from experiment when *both* [A] and [B] double, the rate should quadruple, and it does. Thus, the rate law, with *m* and *n* equal to 1, is

$$\text{Rate } (v) = k\,[A]\,[B]$$

Note, especially, that while the order with respect to B is 1, the coefficient of B in the balanced equation is 2. Thus, as we said earlier***, reaction orders must be determined from experiment.***

Next, let's go through this process for a real reaction, the one between oxygen and nitrogen monoxide, a key step in the formation of acid rain and in the industrial production of nitric acid:

$$O_2(g) + 2NO(g) \longrightarrow 2NO_2(g)$$

The general rate law is

$$\text{Rate} = k[O_2]^m[NO]^n$$

Table 16.3 shows experiments that change one reactant concentration while keeping the other constant. If we compare experiments 1 and 2, we see the effect of doubling $[O_2]$ on the rate. First, we take the ratio of their rate laws:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[O_2]_2^m[NO]_2^n}{k[O_2]_1^m[NO]_1^n}$$

As before, the constant quantities—k and [NO]—cancel:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[O_2]_2^m\cancel{[NO]_2^n}}{\cancel{k}[O_2]_1^m\cancel{[NO]_1^n}} = \frac{[O_2]_2^m}{[O_2]_1^m} = \left(\frac{[O_2]_2}{[O_2]_1}\right)^m$$

Table 16.3 Initial Rates for the Reaction Between O_2 and NO

Experiment	Initial Rate (mol/L·s)	Initial Reactant Concentrations (mol/L) $[O_2]$	[NO]
1	3.21×10^{-3}	1.10×10^{-2}	1.30×10^{-2}
2	6.40×10^{-3}	2.20×10^{-2}	1.30×10^{-2}
3	12.8×10^{-3}	1.10×10^{-2}	2.60×10^{-2}
4	9.60×10^{-3}	3.30×10^{-2}	1.30×10^{-2}
5	28.8×10^{-3}	1.10×10^{-2}	3.90×10^{-2}

Substituting the values from Table 16.3, we obtain

$$\frac{6.40\times10^{-3}\ \text{mol/L·s}}{3.21\times10^{-3}\ \text{mol/L·s}} = \left(\frac{2.20\times10^{-2}\ \text{mol/L}}{1.10\times10^{-2}\ \text{mol/L}}\right)^m$$

Dividing, we obtain

$$1.99 = (2.00)^m$$

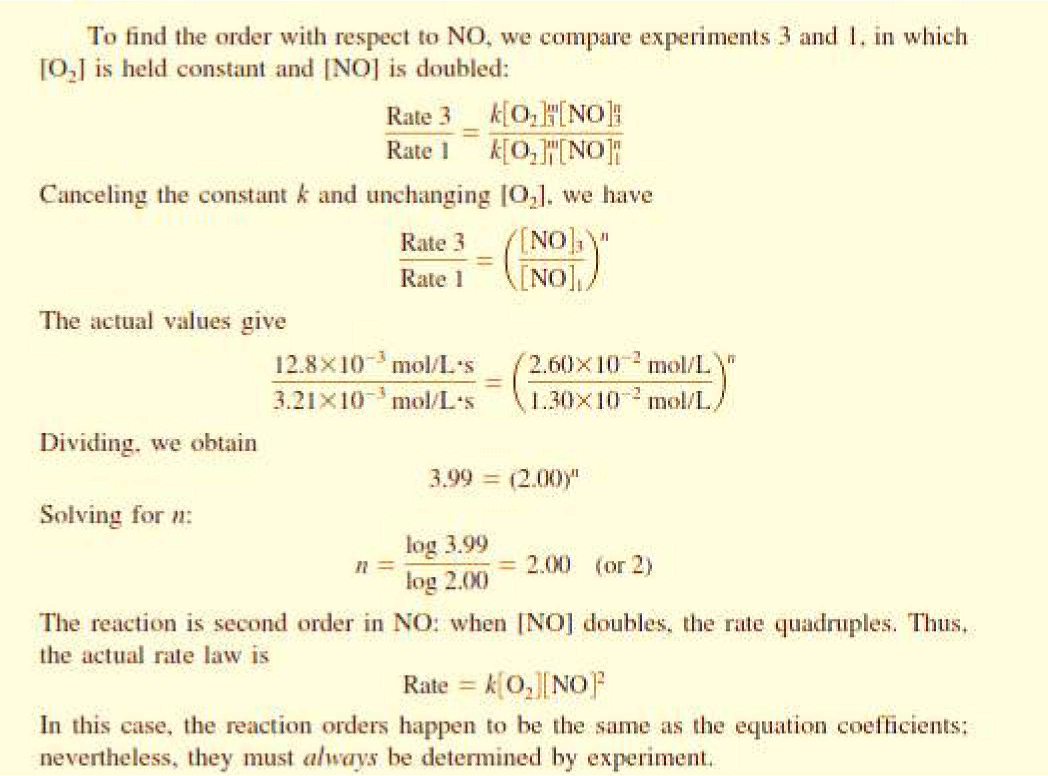
Rounding to one significant figure gives

$$2 = 2^m, \qquad \text{so } m = 1$$

Sometimes, the exponent is not as easy to find by inspection as it is here. In those cases, we solve for m with an equation of the form $a = b^m$:

$$m = \frac{\log a}{\log b} = \frac{\log 1.99}{\log 2.00} = 0.993$$

which rounds to 1. Thus, the reaction is first order in O_2: when $[O_2]$ doubles, the rate doubles.



To find the order with respect to NO, we compare experiments 3 and 1, in which $[O_2]$ is held constant and [NO] is doubled:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[O_2]_3^m[NO]_3^n}{k[O_2]_1^m[NO]_1^n}$$

Canceling the constant k and unchanging $[O_2]$, we have

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \left(\frac{[NO]_3}{[NO]_1}\right)^n$$

The actual values give

$$\frac{12.8\times10^{-3}\ \text{mol/L}\cdot\text{s}}{3.21\times10^{-3}\ \text{mol/L}\cdot\text{s}} = \left(\frac{2.60\times10^{-2}\ \text{mol/L}}{1.30\times10^{-2}\ \text{mol/L}}\right)^n$$

Dividing, we obtain

$$3.99 = (2.00)^n$$

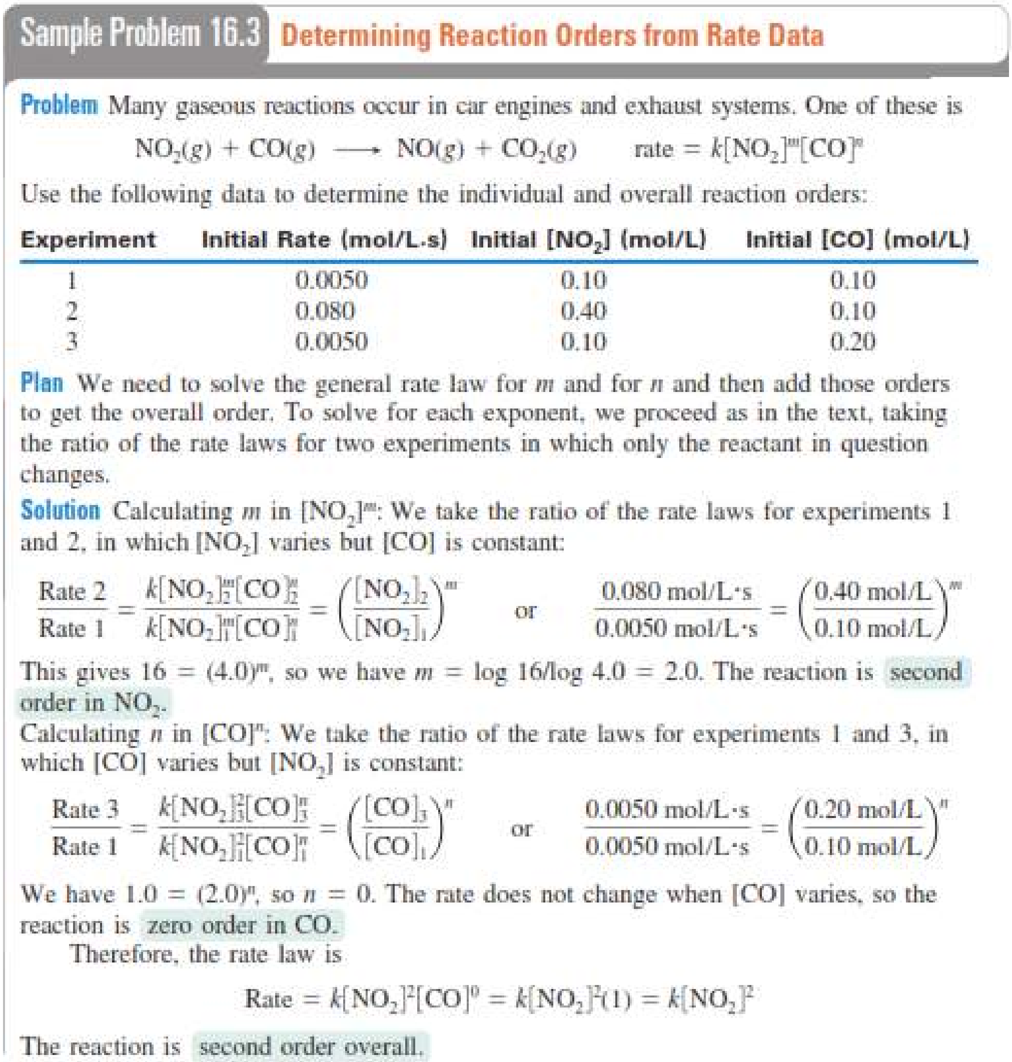
Solving for n:

$$n = \frac{\log 3.99}{\log 2.00} = 2.00 \quad \text{(or 2)}$$

The reaction is second order in NO: when [NO] doubles, the rate quadruples. Thus, the actual rate law is

$$\text{Rate} = k[O_2][NO]^2$$

In this case, the reaction orders happen to be the same as the equation coefficients; nevertheless, they must *always* be determined by experiment.



Sample Problem 16.3 Determining Reaction Orders from Rate Data

Problem Many gaseous reactions occur in car engines and exhaust systems. One of these is

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \qquad \text{rate} = k[NO_2]^m[CO]^n$$

Use the following data to determine the individual and overall reaction orders:

Experiment	Initial Rate (mol/L·s)	Initial $[NO_2]$ (mol/L)	Initial [CO] (mol/L)
1	0.0050	0.10	0.10
2	0.080	0.40	0.10
3	0.0050	0.10	0.20

Plan We need to solve the general rate law for m and for n and then add those orders to get the overall order. To solve for each exponent, we proceed as in the text, taking the ratio of the rate laws for two experiments in which only the reactant in question changes.

Solution Calculating m in $[NO_2]^m$: We take the ratio of the rate laws for experiments 1 and 2, in which $[NO_2]$ varies but [CO] is constant:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[NO_2]_2^m[CO]_2^n}{k[NO_2]_1^m[CO]_1^n} = \left(\frac{[NO_2]_2}{[NO_2]_1}\right)^m \quad \text{or} \quad \frac{0.080 \text{ mol/L·s}}{0.0050 \text{ mol/L·s}} = \left(\frac{0.40 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^m$$

This gives $16 = (4.0)^m$, so we have $m = \log 16/\log 4.0 = 2.0$. The reaction is second order in NO_2.

Calculating n in $[CO]^n$: We take the ratio of the rate laws for experiments 1 and 3, in which [CO] varies but $[NO_2]$ is constant:

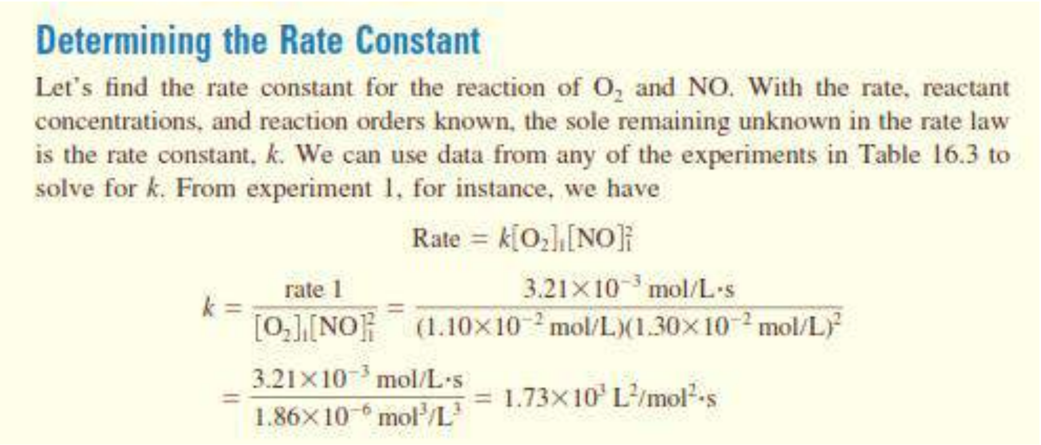
$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[NO_2]_3^2[CO]_3^n}{k[NO_2]_1^2[CO]_1^n} = \left(\frac{[CO]_3}{[CO]_1}\right)^n \quad \text{or} \quad \frac{0.0050 \text{ mol/L·s}}{0.0050 \text{ mol/L·s}} = \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^n$$

We have $1.0 = (2.0)^n$, so $n = 0$. The rate does not change when [CO] varies, so the reaction is zero order in CO.

Therefore, the rate law is

$$\text{Rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2(1) = k[NO_2]^2$$

The reaction is second order overall.



Determining the Rate Constant

Let's find the rate constant for the reaction of O_2 and NO. With the rate, reactant concentrations, and reaction orders known, the sole remaining unknown in the rate law is the rate constant, k. We can use data from any of the experiments in Table 16.3 to solve for k. From experiment 1, for instance, we have

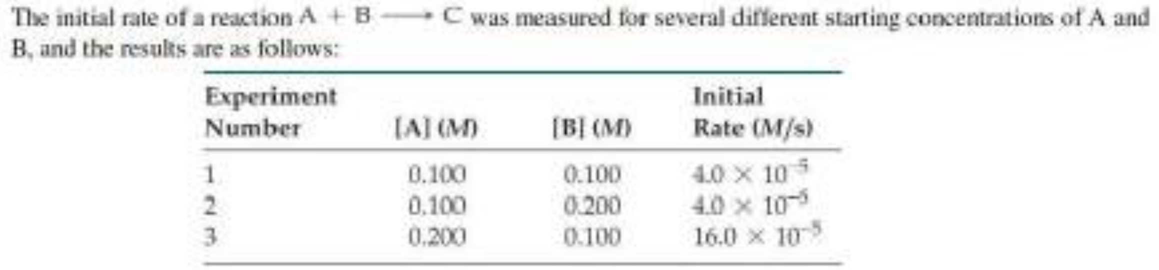
$$\text{Rate} = k[O_2]_1[NO]_1^2$$

$$k = \frac{\text{rate 1}}{[O_2]_1[NO]_1^2} = \frac{3.21\times10^{-3}\ \text{mol/L·s}}{(1.10\times10^{-2}\ \text{mol/L})(1.30\times10^{-2}\ \text{mol/L})^2}$$

$$= \frac{3.21\times10^{-3}\ \text{mol/L·s}}{1.86\times10^{-6}\ \text{mol}^3/\text{L}^3} = 1.73\times10^3\ \text{L}^2/\text{mol}^2\text{·s}$$

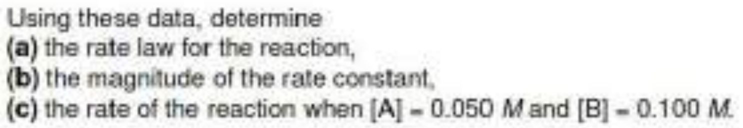
QUESTION FOR REVIEW

Q#1



The initial rate of a reaction $A + B \longrightarrow C$ was measured for several different starting concentrations of A and B, and the results are as follows:

Experiment Number	[A] (*M*)	[B] (*M*)	Initial Rate (*M*/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}



Using these data, determine
(a) the rate law for the reaction,
(b) the magnitude of the rate constant,
(c) the rate of the reaction when [A] = 0.050 *M* and [B] = 0.100 *M*.

Solution:

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Q#2

Consider the generic reaction:

$$A + B + C \rightarrow D$$

Assuming the above reaction was analyzed using the initial rate method at 25°C, use the data below to determine:

1. The order of reaction with respect to each reactant and the overall order of the reaction. **Summarize your findings in the form of a complete rate equation**.
2. The value of *k* at this temperature.
3. What is the rate of reaction when the concentrations of *each* reactant is 0.50 M,

Experiment	Initial concentrations ($molL^{-1}$)			Initial rate
	A	B	C	($molL^{-1}s^{-1}$)
1	0.10	0.10	0.50	1.5×10^{-6}
2	0.20	0.10	0.50	3.0×10^{-6}
3	0.10	0.20	0.50	6.0×10^{-6}
4	0.10	0.10	1.00	1.5×10^{-6}

Solution:

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THEORIES OF CHEMICAL KINETICS

As we know that the concentration and temperature has major effects on **REACTION rate.** Chemists employ two model to explain this effects:

1. **Collision Theory**
2. **Activated Complex Theory**

COLLISION THEORY

The basic tenet of collision theory is that particles—atoms, molecules, or ions—must collide to react. This theory also relies on the concepts of collision energy and molecular structure to Explain the effects of concentration and temperature on rate. The following point must be noted for the collision theory about reaction rate:

- ☞ In order for molecules to react they must collide.
- ☞ As temperature increases, the molecules move faster and the collision frequency increases.
- ☞ The greater the number of collisions the faster the rate.
- ☞ Reaction rate should increase with an increase in temperature.
- ☞ Reaction rate should increase with an increase in the concentration of reactant molecules.

ARRHENIOUS EQUATION

[Effect of Temperature on Reaction rate]

Most reactions speed up as temperature increases. (**Example: food spoils when not refrigerated.**)

$$K = f\,(T)$$

Where "f" is function.

Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:

- ☞ The number of collisions per unit time.
- ☞ The fraction of collisions that occur with the correct orientation.
- ☞ The fraction of the colliding molecules that have an energy greater than or equal to $\mathbf{E_a}$.

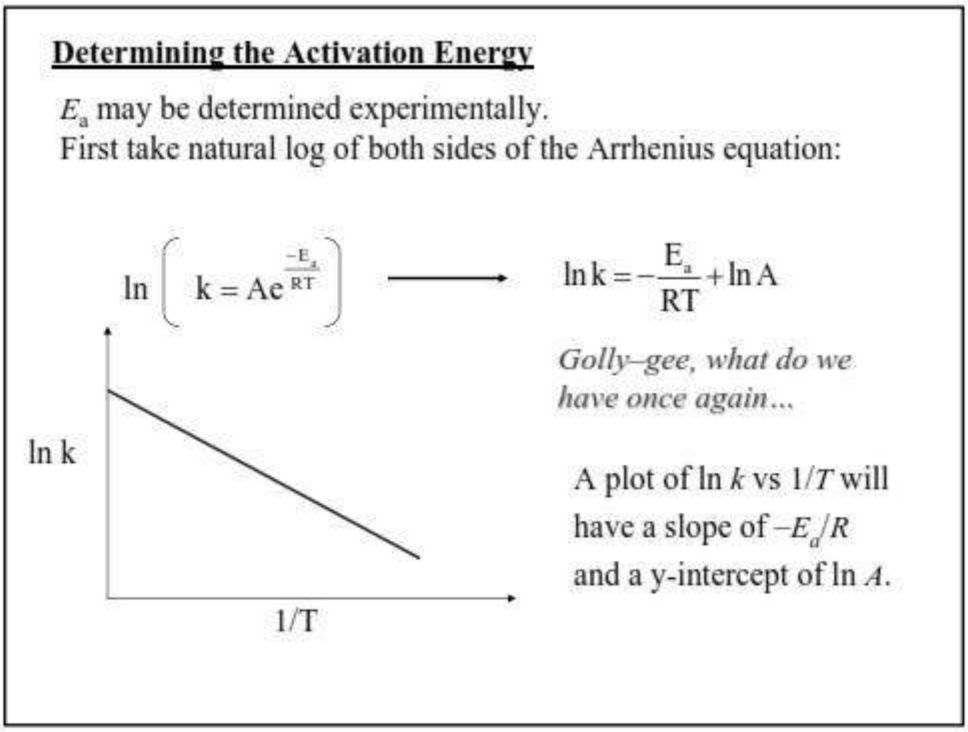
From these observations Arrhenius developed the aptly named ***Arrhenius equation***.

$$k = Ae^{-\frac{\mathrm{Ea}}{\mathrm{RT}}}$$

Where:

K is the rate constant
T is the temperature in K
E_a. is the activation energy
R is the ideal-gas constant (8.314 J/K mol)

Where A is known as *frequency or pre–exponential factor*. Both *A* and *E*a are *specific to a given reaction*.



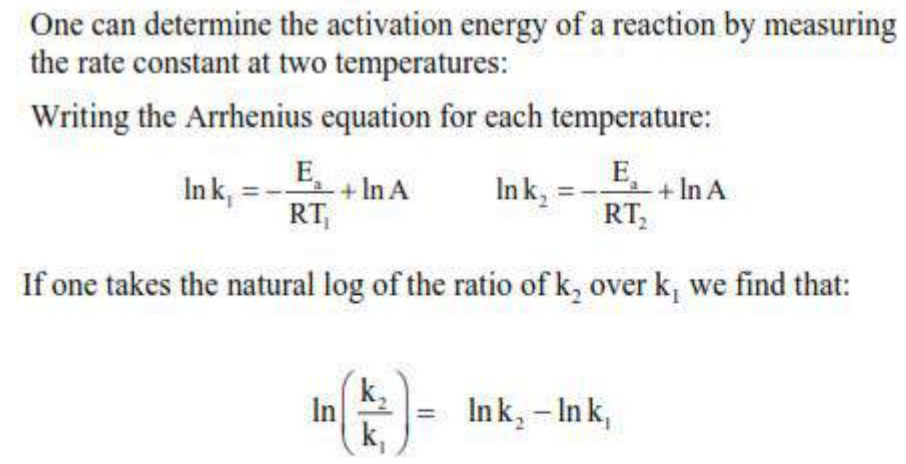
Determining the Activation Energy

E_a may be determined experimentally.
First take natural log of both sides of the Arrhenius equation:

$$\ln\left(k = Ae^{\frac{-E_a}{RT}} \right) \longrightarrow \ln k = -\frac{E_a}{RT} + \ln A$$

Golly–gee, what do we have once again…

A plot of ln *k* vs 1/*T* will have a slope of $-E_a/R$ and a y-intercept of ln *A*.



One can determine the activation energy of a reaction by measuring the rate constant at two temperatures:

Writing the Arrhenius equation for each temperature:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \qquad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

If one takes the natural log of the ratio of k_2 over k_1 we find that:

$$\ln\left(\frac{k_2}{k_1}\right) = \ln k_2 - \ln k_1$$

Substituting in the values for E_a into the equation:

$$\ln k_2 - \ln k_1 = \left(-\frac{E_a}{RT_2} + \cancel{\ln A}\right) - \left(-\frac{E_a}{RT_1} + \cancel{\ln A}\right)$$

Lookie what happens…

Knowing the rate at two temps yields the rate constant.

or

Knowing the E_a and the rate constant at one temp allows one to find $k(T_2)$

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Example: The activation energy of a first order reaction is 50.2 kJ/mol at 25°C. At what temperature will the rate constant double?

---

(1) $k_2 = 2k_1$

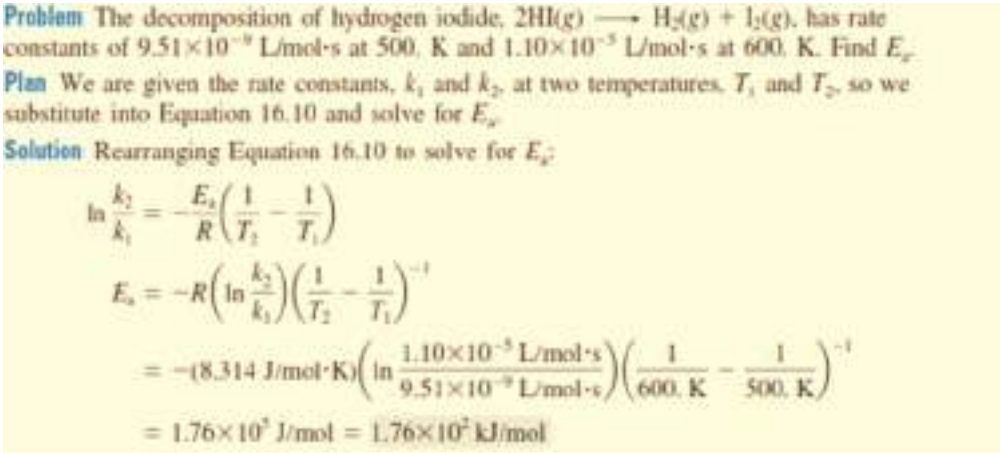
(2) $\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{2k_1}{k_1}\right) = \ln(2) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

(3) $\frac{E_a}{R} = \frac{50.2\ \text{kJ/mol} \times \frac{10^3\,\text{J}}{1\,\text{kJ}}}{8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}} = 6.04 \times 10^3\,\text{K}$

(4) $\ln(2) = 0.693 = 6.04 \times 10^3\,\text{K} \times \left(\frac{1}{298\text{K}} - \frac{1}{T_2}\right)$

A 10°C change of temperature doubles the rate!!

(5) $\frac{1}{T_2} = 3.24 \times 10^{-3}\,\text{K}^{-1} \longrightarrow \boxed{\mathbf{T_2 = 308\ K}}$



Problem The decomposition of hydrogen iodide, $2HI(g) \longrightarrow H_2(g) + I_2(g)$, has rate constants of 9.51×10^{-9} L/mol·s at 500. K and 1.10×10^{-5} L/mol·s at 600. K. Find E_a.

Plan We are given the rate constants, k_1 and k_2, at two temperatures, T_1 and T_2, so we substitute into Equation 16.10 and solve for E_a.

Solution Rearranging Equation 16.10 to solve for E_a:

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$E_a = -R\left(\ln\frac{k_2}{k_1}\right)\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^{-1}$$

$$= -(8.314\ \text{J/mol·K})\left(\ln\frac{1.10\times10^{-5}\ \text{L/mol·s}}{9.51\times10^{-9}\ \text{L/mol·s}}\right)\left(\frac{1}{600.\ \text{K}}-\frac{1}{500.\ \text{K}}\right)^{-1}$$

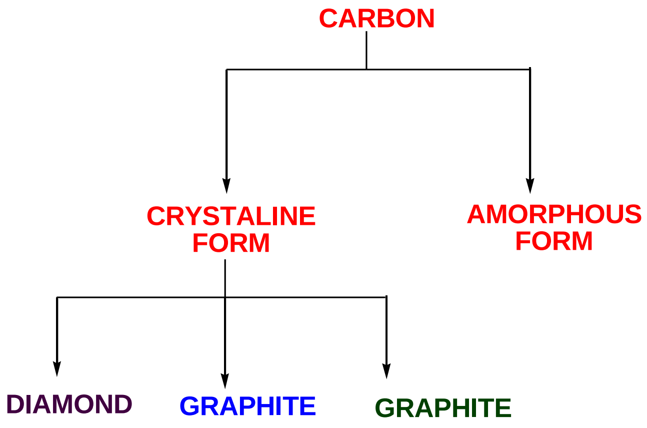
$$= 1.76\times10^{5}\ \text{J/mol} = 1.76\times10^{2}\ \text{kJ/mol}$$

ALLOTROPY

The phenomenon of existence of a chemical in two or more form differing in physical properties but having almost same chemical nature is known as ALLOTROPY. This different form is known as **ALLOTOPPES**.

Carbon Exist in two different allotropic form.

A. Crystalline form
B. Amorphous form



GRAPHITE

Graphite is one of the SOFEST materials known. It is a **black or bluish-grey** colour with metallic lustre and a greasy feel. The word Graphite is comes from Greek word which meanings "to **write**"

STRUCTURE OF GRAPHITE

The following characteristic of the structure of graphite as thus:

- Each carbon atom in graphite is linked to three other carbon atoms forming a hexagonal rings stacked one on another.
- The graphite has two dimensional layered structure.
- Within the layer each carbon atom is bonded to three others by normal Covalent bond.
- The remaining fourth valence electron(s) of each carbon atoms are free and not involved in covalent bond formation.
- **This free electron(s) accounts for the electrical conductivity of graphite.**
- Between the layers, there are week forces of attraction called "**Vander Waals Forces". These layers are able to slide over each other easily making graphite graphite soft, slippery and useful as lubricant.**

Properties of Graphite:

- **LUSTRE:** It has a metallic lustre and it is opaque to light. It marks the paper black.
- **STABILITY:** It is a very stable allotrope of carbon but at very high temperature and pressure it can be transformed into **artificial diamond**.
- **Chemical Reactivity:** Chemically graphite is more reactive than diamond.
- **Density:** It has a density of 2.25g/cc. The lower density of graphite is due to large distance between the layers of carbon atom in graphite. The layer of graphite is separated by large distance due to **week vander waals'** force between them.
- **Conductivity:** Graphite is good conductor of Electricity due to the presence of free or mobile electrons.
- **Solubility:** It is soluble in Organic solvent(s) but insoluble in water.
- **Melting Point:** It has a high melting point (373^0C)

NB: It is soft and is used as LUBRICANT because of its layer structure which can easily SLIP over each other.

Application of Graphite:

- **Making lead pencils:** It used for making lead pencils by mixing with clay or finely powdered sand, as it leaves a marks on paper.
- **Making Electrode:** It is used for making **ELECTRODES** because it is chemically inactive and a good conductor of electricity.
- **In a nuclear reactors:** It used as a moderator (to slow down the speed of neutrons) in nuclear reactor.
- It is used for making **REFRACTORY CRUCIBLES** because it has high melting point and is good conductor of heat.

Q#1: Why is Graphite used as lubricant?

Q#2. Why is graphite used for making lead pencils?

Q#3: Graphite conduct electricity whereas diamond does not?

FULLERENES

Fullerenes is naturally occurring allotrope of carbon atom in which 60 carbon atom are linked to form a stable structure. I is discovered in 1985 by Robert Curl, Harold Kroto and Richard Smally at Rice University, Texas, United State of America.

The molecular structure looks like a FOOTBALL or domed roof of the stadium developed by American Engineer Buckminster Fuller. Thus it was named as **BUCKMINISTER FULLERENE. I is often called BUCKY BALL (tiny soccer ball) for short.**

STRUCTURE OF FULLERENE:

1. Fullerene having the Principle axis, Icosahedral (20 face) group (I) Symmetry.
2. The structure composed of SPHEROID hexagonal and pentagonal ring patter in their structure.
3. The double bond confine in hexagonal ring rather it in pentagonal ring(s) to avoid the ring strain in the structure.
4. This double bond(s) are poor delocalization of electrons leading to the high reactivity of the FULLERENE molecule.
5. Fullerene may undergoes variety of chemical reaction:
    - ☞ Addition reaction (including cycloaddition reaction)
    - ☞ Substitution reaction (doping reaction of BORON)
    - ☞ Polymerization reaction.

Q#1: What is FULLERENE? Describe its structural feature.

Properties of FULLERENE:

1. **Nature:** It is yellow powder.
2. It is soluble in organic solvent (i.e. toluene/benzene)
3. It is non-conductor and preferably an electric insulator.
4. It is more reactive than diamond and graphite.

Application of FULLERENE: Fullerene are used as:

- ❖ Super Conductor
- ❖ Semiconductor
- ❖ Lubricant
- ❖ Catalysts.

BIOMEDICAL APPLICATION OF FULLERENE

The hydrophobic spheroid and the radical sponge character of fullerene are responsible for the activity in different fields. There are few application of fullerene in biology:

- Fullerene in drug and gene delivery.
- Anti-oxidant activity.
- Antiviral activity [the water soluble form of Bucky balls has veridical(killing) effects against AIDS(acquired immune deficiency syndrome) virus]
- Fullerenes has photosensitize activity.

Q#1: Discuss the biomedical application of fullerene.

SOLID STATE

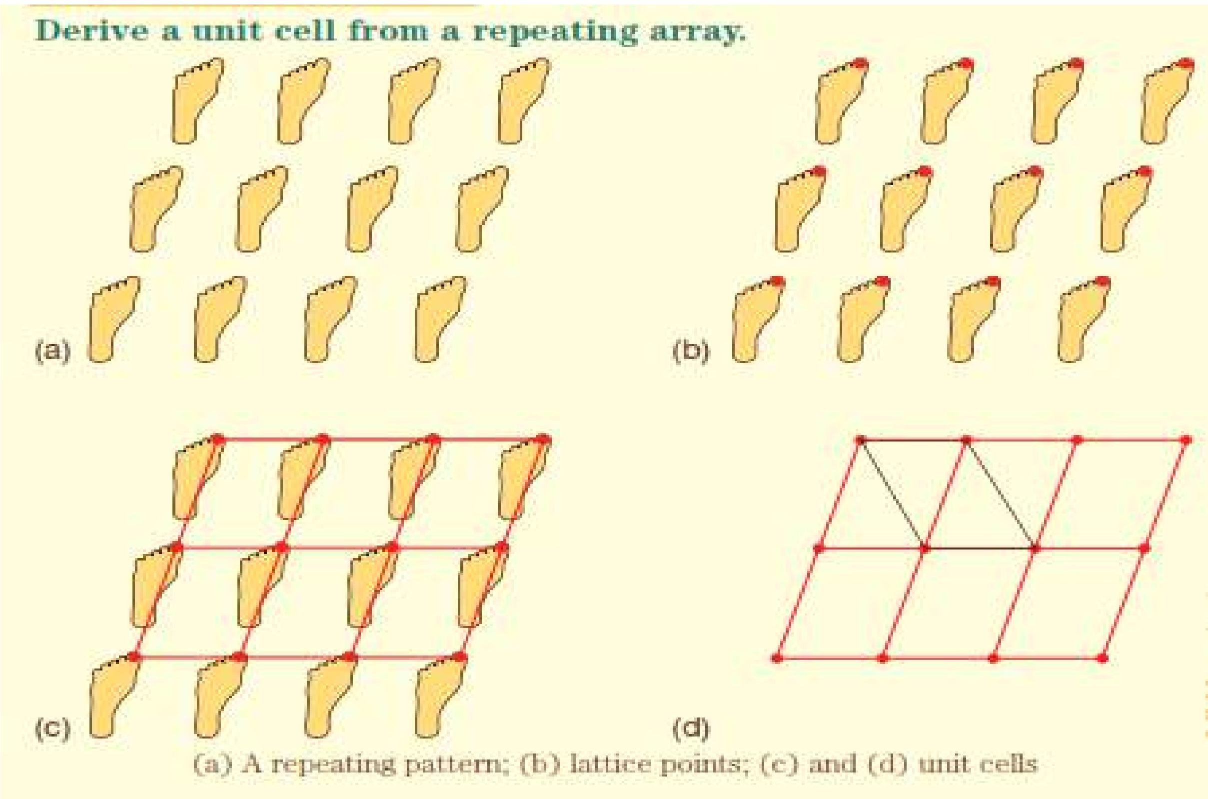
Course Content:

1. **Type of Unit Cell**
2. **Space Lattice(Cubic System)**
3. **Density of the Unit Cell**
4. **X-diffraction**

UNIT CELL [Building block of Crystal]

Crystalline solids consist of a repeating three-dimensional array of particles (atoms, ions, or molecules). This repeating pattern has:

- **TRANSLATIONAL SYMMETRY**(moved without rotated) in certain direction
- An identical pattern can be seen.
- **Lattice Point:** location of identical points in the repeating pattern called **LATTICE POINT.**
- **CRYSTAL LATTICE:** Collection of lattice points is called **CRYSTAL LATTICE.**
- **UNIT CELL:** The smallest repeated unit of crystal lattice is called **UNIT CELL**.



(a) A repeating pattern; (b) lattice points; (c) and (d) unit cells

TYPE OF UNIT CELL

There are four basic type of unit cells:

1. **Simple Unit Cell**
2. **Body-centred Unit Cell**
3. **Face –centred Unit Cell**
4. **Base-Centred Unit Cell**

In the cubic system there are there are three type of unit cell:

1. **Simple Cubic system**
2. **Body-centred cubic system**
3. **Face-centred cubic system**

(Please refer the table for the type of unit cell)

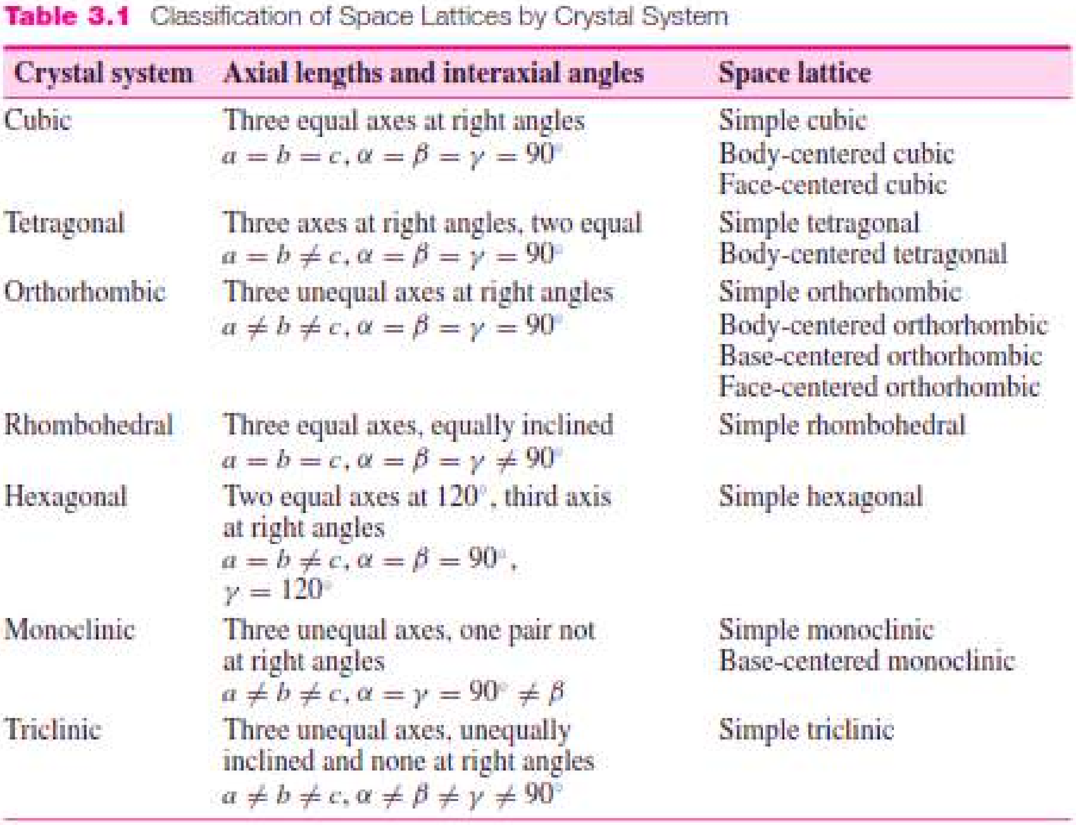


Table 3.1 Classification of Space Lattices by Crystal System

Crystal system	Axial lengths and interaxial angles	Space lattice
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90^\circ$	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple tetragonal Body-centered tetragonal
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic
Rhombohedral	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	Simple rhombohedral
Hexagonal	Two equal axes at 120°, third axis at right angles $a = b \neq c, \alpha = \beta = 90^\circ,$ $\gamma = 120^\circ$	Simple hexagonal
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$	Simple monoclinic Base-centered monoclinic
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple triclinic

CUBIC SYSTEM

The most symmetrical crystal system is defined by a cubic unit cell, where all cell edges are identical and all angles between unit cell edges are equal to 90°.In this unit we study solids that have cubic unit cells, and it is useful to visualize what happens when identical cubic unit cells pack together. Consider a perfect cubic unit cell, which has **12 edges, 6 faces, and 8 corners**. When identical cubes are packed together in three dimensions,

- each cube face is shared by two adjacent unit cells;
- each cube edge is shared by four adjacent unit cells; and

- each cube corner is shared by eight adjacent unit cell

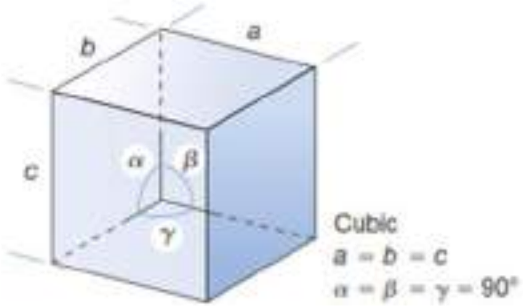
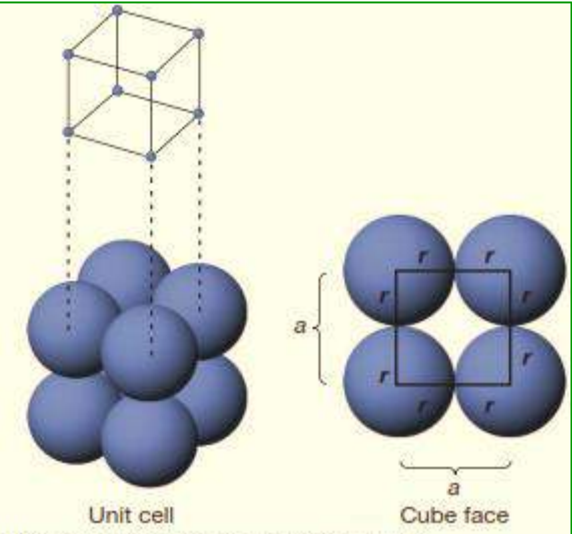


Fig1: Cubic Unit Cell

[A] SIMPLE CUBIC UNIT CELL

The **simple cubic** (SC) **unit cell**, also called a **primitive cubic** (PC) **unit cell**, consists Of one lattice point on each corner of a cube. In simple cubic lattice:



Representations of a simple cubic unit cell

1. One lattice point/one metal atom, per unit cell.

   8(corner atoms) x 1/8 = 1 atoms/unit cell
2. SC unit cell has six coordination number (CN) i.e. each atom in the unit cell has six nearest neighbour atom.
3. The edge length of an SC unit cell is twice the atomic radius of the metal.

   Edge Length **(a) = 2r**
4. Volume of the cube is calculated by cubing the edge length.

   $$v = (a)^3$$
5. The volume of atom is calculated, using the equation for the volume of sphere.

   $$V = \frac{4}{3}\pi r^3$$
6. Percent occupied space in unit cell:

   $$\% \text{ occupied space} = \frac{\text{Volume of 1 atom}}{\text{Total volume of unit cell}}\ x\ 100 \qquad [a = 2r]$$

   $$= \frac{(4/3)\pi r^3}{(2r)3} x100$$

   $$= 54.2\%$$
7. The %Void space = 100 - 54.2 = 48.8 = 49%

[The low packing efficiency of the SC lattice means that this structure type is rarely found in any metals (polonium is one reported example)].

[B] BODY-CENTERD CUBIC UNIT CELL

In BCC unit cell we see that:

- The central atom (fig 3.4 a) is surrounded by 8 nearest neighbours atom and said to have coordination number EIGHT (8).
- There is total of 1(at the centre) + $8x\frac{1}{8} = 2\frac{atom}{unit}cell$

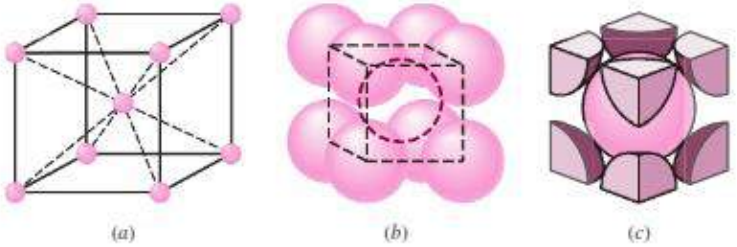


Figure 3.4
BCC unit cells: (a) atomic-site unit cell, (b) hard-sphere unit cell, and (c) isolated unit cell.

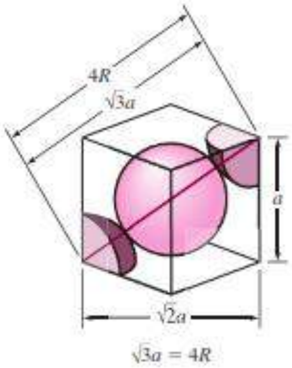
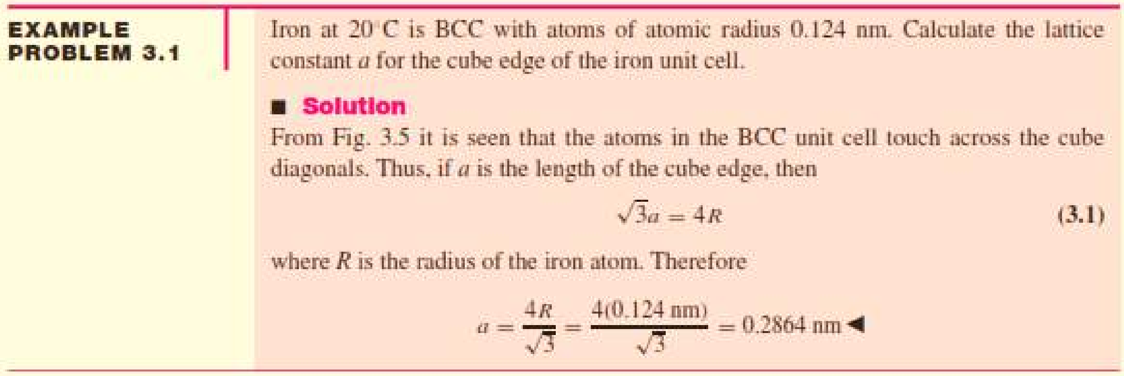


Figure 3.5
BCC unit cell showing relationship between the lattice constant *a* and the atomic radius *R*.

- BCC unit cell are not in contact along the unit cell edge; instead, the atoms make contact along the diagonal that connects opposite corners of the cube, called the body diagonal as indicated in fig3.5.
- The relationship between the length of the cube side **a** and the atomic radius **R** is calculated.

$$\sqrt{3a} = 4r \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ldots \qquad (1)$$

$$a = \frac{4r}{\sqrt{3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (2)$$



EXAMPLE PROBLEM 3.1

Iron at 20°C is BCC with atoms of atomic radius 0.124 nm. Calculate the lattice constant *a* for the cube edge of the iron unit cell.

■ **Solution**

From Fig. 3.5 it is seen that the atoms in the BCC unit cell touch across the cube diagonals. Thus, if *a* is the length of the cube edge, then

$$\sqrt{3}a = 4R \qquad (3.1)$$

where *R* is the radius of the iron atom. Therefore

$$a = \frac{4R}{\sqrt{3}} = \frac{4(0.124\ \text{nm})}{\sqrt{3}} = 0.2864\ \text{nm} ◀$$

- If the atoms in the BCC unit cell are considered to be spherical, an atomic packing factor (APF) can be calculated by using the equation.

$$\text{Atomic Packing Fraction (APF)} = \frac{\textbf{Volume of atom in BCC unit cell}}{\textbf{Volume of BCC unite cell}}$$

Since there are two atom per BCC unit cell, so the volume of atom in BCC unit cell:

$$v(atom\ per\ unit\ cell) = 2\left(\frac{4}{3}\ \pi r3\right) = 8.373r^3$$

The volume of BCC unit cell:

$$v(unit\ cell) = (a)^3$$

We know that the edge length of BCC unit cell (a) is:

$$a = \frac{4r}{\sqrt{3}}$$

$$v(unit\ cell) = (a)^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \quad 12.32\ r^3$$

Therefore the Atomic Packing Fraction (APF) for the BCC unit cell:

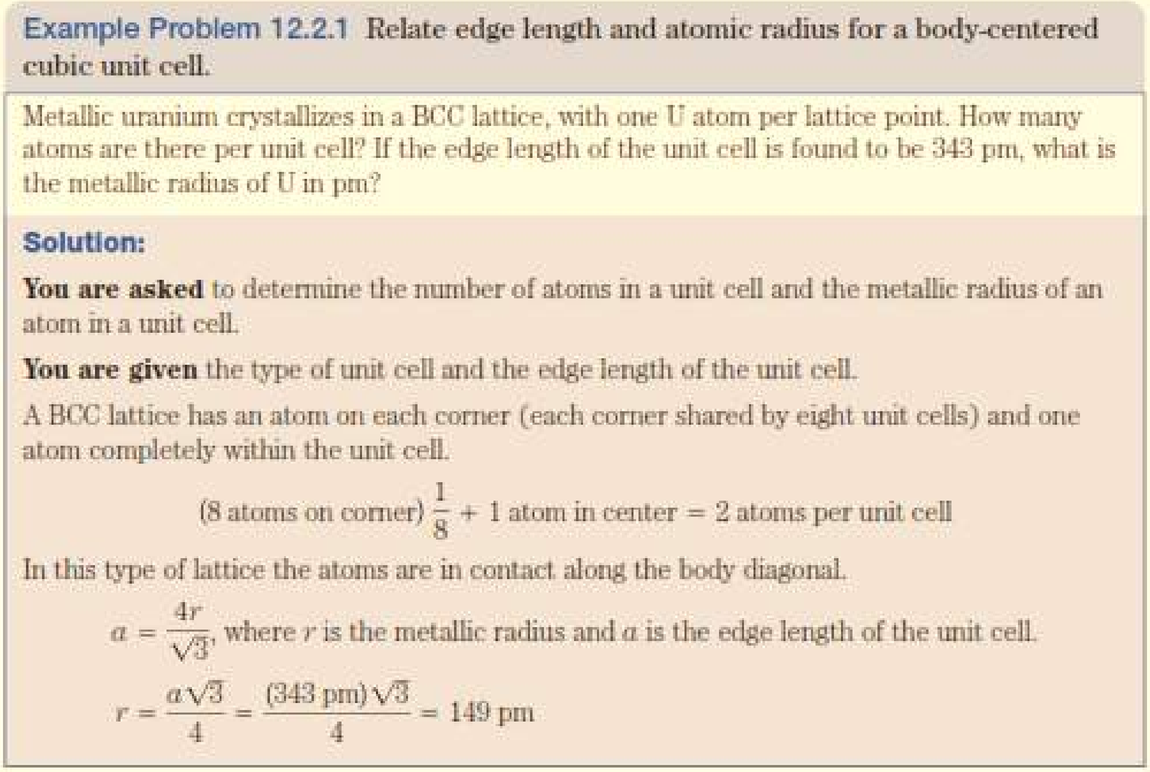
$$\text{APF} = \frac{\text{v(atoms per unit cell)}}{\text{v(unit cell)}} = \frac{2\left(\frac{4}{3}\pi r3\right)}{\left(\frac{4r}{\sqrt{3}}\right)3} = \frac{8.373\text{r}3}{12.32\ \text{r}3} = 0.68$$

$$= 68\%$$

That is, **68 percent of the volume of the BCC unit cell is occupied** by atoms and the remaining **32 percent is empty space**. Many metals such as **iron, chromium, tungsten molybdenum, and vanadium have the BCC crystal** structure at room temperature

EXAMPLE PROBLEM 3.2

Calculate the atomic packing factor (APF) for the BCC unit cell, assuming the atoms to be hard spheres.



Example Problem 12.2.1 **Relate edge length and atomic radius for a body-centered cubic unit cell.**

Metallic uranium crystallizes in a BCC lattice, with one U atom per lattice point. How many atoms are there per unit cell? If the edge length of the unit cell is found to be 343 pm, what is the metallic radius of U in pm?

Solution:

You are asked to determine the number of atoms in a unit cell and the metallic radius of an atom in a unit cell.

You are given the type of unit cell and the edge length of the unit cell.

A BCC lattice has an atom on each corner (each corner shared by eight unit cells) and one atom completely within the unit cell.

$$(8 \text{ atoms on corner}) \frac{1}{8} + 1 \text{ atom in center} = 2 \text{ atoms per unit cell}$$

In this type of lattice the atoms are in contact along the body diagonal.

$$a = \frac{4r}{\sqrt{3}}, \text{ where } r \text{ is the metallic radius and } a \text{ is the edge length of the unit cell.}$$

$$r = \frac{a\sqrt{3}}{4} = \frac{(343 \text{ pm})\sqrt{3}}{4} = 149 \text{ pm}$$

[C] FACE-CENTERED CUBIC UNIT CELL

For FCC unit cell:

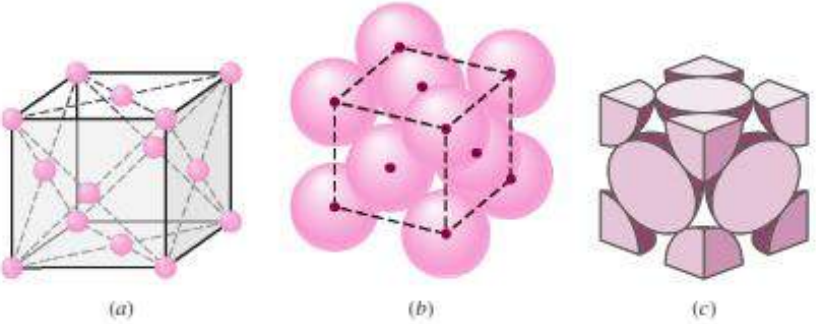


Figure 3.6
FCC unit cells: (*a*) atomic-site unit cell, (*b*) hard-sphere unit cell, and (c) isolated unit cell.

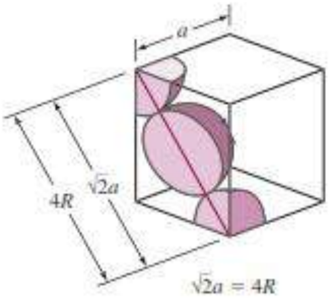


Figure 3.7
FCC unit cell showing relationship between the lattice constant *a* and atomic radius *R*. Since the atoms touch across the face diagonals, $\sqrt{2}a = 4R$.

- Four atom per unit cell
- Relationship between the length of cube side a and the atomic radius r

$$\sqrt{2a} = 4r$$

$$a = \frac{4r}{\sqrt{2}}$$

$$v(atom\ per\ unit\ cell) = 4\left(\frac{4}{3}\,\pi r3\right)$$

The volume of FCC unit cell:

$$v(unit\ cell) = (a)^3$$

We know that the edge length of BCC unit cell (a) is:

$$a = \frac{4r}{\sqrt{2}} = \left(\frac{4r}{\sqrt{2}}\right)3$$

Therefore the Atomic Packing Fraction (APF) for the FCC unit cell:

$$\text{APF} = \frac{\text{v(atoms per unit cell)}}{\text{v(unit cell)}} = \frac{2\left(\frac{4}{3}\pi r3\right)}{\left(\frac{4r}{\sqrt{2}}\right)3} = 0.74$$

74%

The APF for the FCC crystal structure is **0.74**, which is greater than the **0.68** factor for the BCC structure. The APF of 0.74 is for the closest packing possible of "spherical atoms." Many metals such as aluminium, copper, lead, nickel and iron crystalized in FCC unit cell.

Summary of Cubic Unit Cells

Lattice	Atoms per Unit cell	Edge Length-Atomic Radius Relationship	Coordination Number	APF
Simple cubic	**1**	**a = 2r**	**6**	**52.4**
Body-centered	**2**	$a = \frac{4r}{\sqrt{3}}$	**8**	**68.0**
Face-centered cubic	**4**	$a = \frac{4r}{\sqrt{2}}$	**12**	**74.0]**

DENSITY OF UNIT CELL

Density of Unit Cell :

$$= \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{\text{zxM}}{\text{a3xNo}}$$

a = Edge length of unit cell in cm
z = number of atoms per unit cell
M = Molar mass
N_0 = Avogadro's number (6.023×10^{23})

Relationship between nearest neighbour distance (d) and radius of atom (r) and edge of unit cell (a) for unit cell of a cubic crystals.

SC	BCC	FCC
$d = a$	$d = \frac{\sqrt{3}}{2}.a$	$d = \frac{a}{\sqrt{2}}$
$r = \frac{a}{2}$	$r = \frac{\sqrt{3}}{4}.a$	$r = \frac{a}{2\sqrt{2}}$ or
z =1	z = 2	z = 4

1. Calculation of Density of FCC unit cell

A. **Copper crystallizes into a fcc lattice with** edge **length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm.**

Solution:

z = 4
M = 63.5 g mol^{-1}
a = 3.61×10^{-8} cm

$$\mathbf{d} = \frac{\text{z.M}}{\text{a3.NA}} = \frac{4\ x\ 63.5}{(3.61\ x\ 10-8)3x\ 6.23\ x\ 10\ 23} = 8.96\ \text{gcm} - 3$$

.

X-Ray Diffraction

BRAGG'S EQUATION:

In 1913 the father-and-son, W.L. Bragg and W.H. Bragg worked out a mathematical relation to determine interatomic distances from X-ray diffraction patterns. This relation is called the **Bragg equation.** They showed that:

- **A.** **The X-ray diffracted from atoms in crystal planes obey the laws of reflection.**
- **B.** **The two rays reflected by successive planes will be in phase if the extra distance travelled by the second ray is an integral number of wavelengths.**

DERIVATION OF BRAGG EQUATION

X-rays falling on the crystal surface. Two successive atomic planes of the crystal are shown separated by a distance *d*. Let the X-rays of wavelength λ strike the first Plane at an angle **Θ**. Some of the rays will be reflected at the same angle. Some of the rays will penetrate and get reflected from the second plane.

These rays will reinforce those reflected from the first plane if the extra distance travelled by them (CB + BD) is equal to integral number, *n*, of wavelengths.

That is,

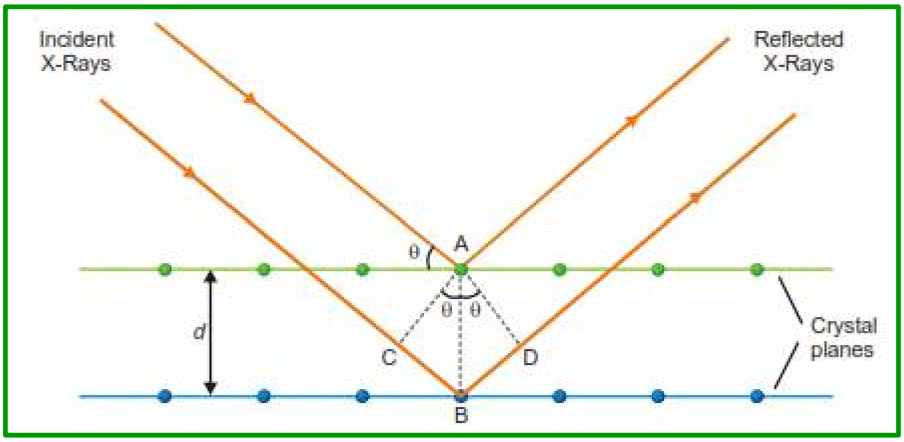


Fig: 1 Reflection of X-Rays from two different planes of a crystal.

$$n\lambda = CB + BD \quad \ldots\ldots\ldots \quad 1$$

Geometry showed that:

$$CB = BD = AB \sin\Theta \quad \ldots\ldots\ldots\ldots \quad 2$$

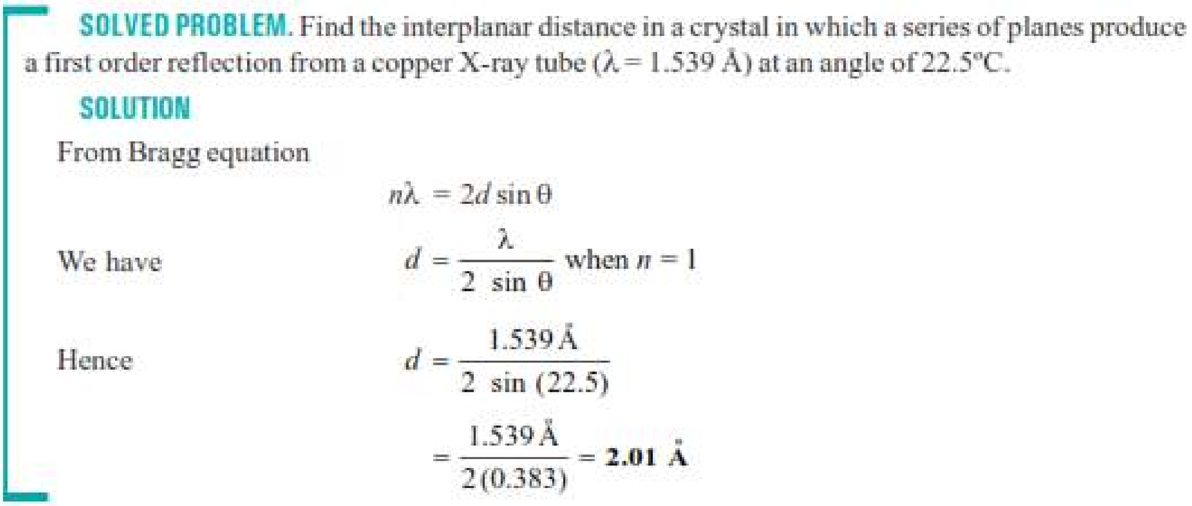
From (1) and (2) it follow that

$$n\lambda = 2\,AB \sin\Theta$$

Or

$$\boxed{n\lambda = 2\,d \sin\Theta}$$

This is known as the **Bragg equation.** The reflection corresponding to *n* = 1 (for a given series of planes) is called the first order reflection. The reflection corresponding to *n* = 2 is the second order reflection and so on.



SOLVED PROBLEM. Find the interplanar distance in a crystal in which a series of planes produce a first order reflection from a copper X-ray tube (λ = 1.539 Å) at an angle of 22.5°C.

SOLUTION

From Bragg equation

$$n\lambda = 2d\sin\theta$$

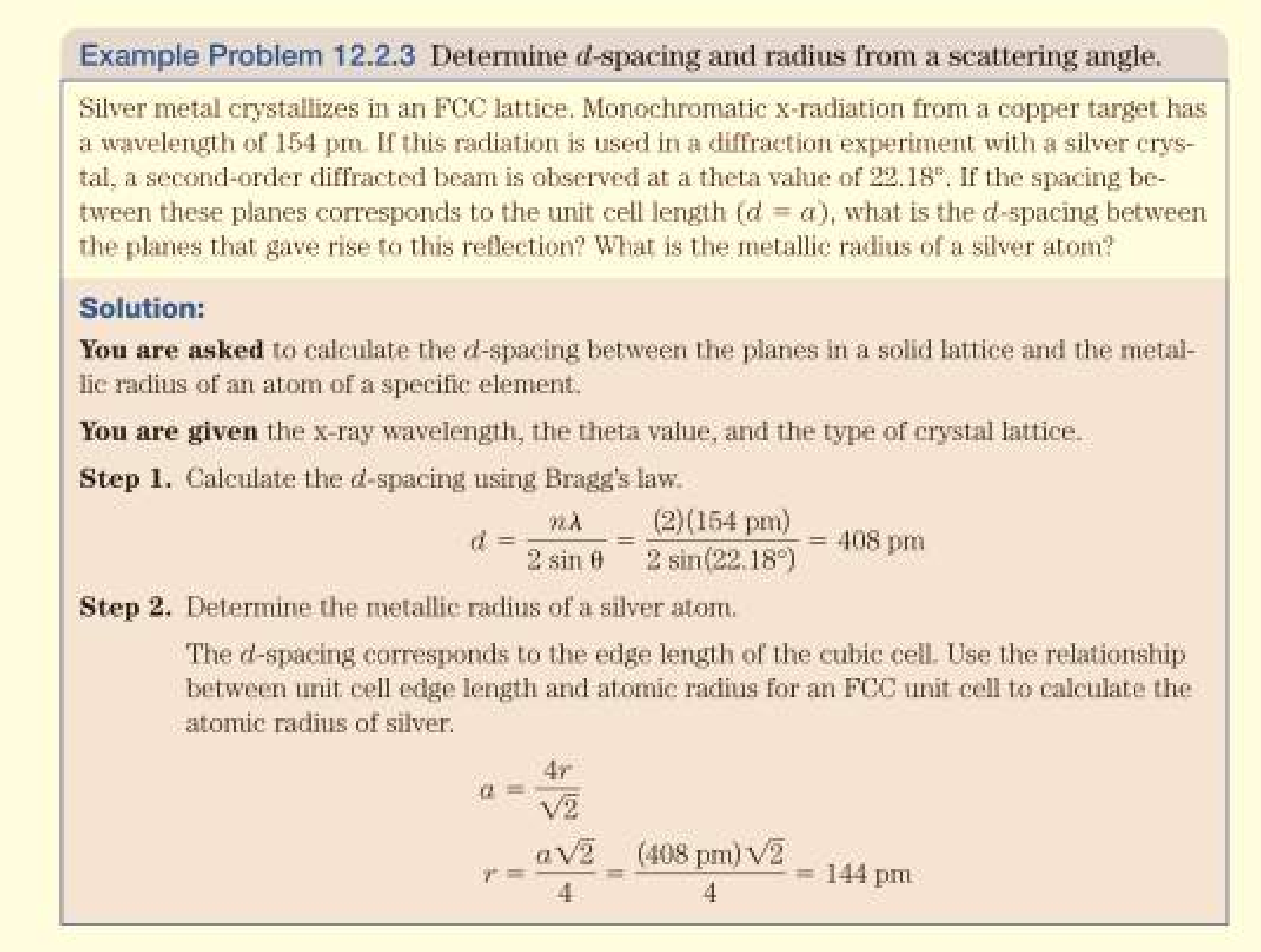
We have

$$d = \frac{\lambda}{2\ \sin\ \theta} \text{ when } n = 1$$

Hence

$$d = \frac{1.539\,\text{Å}}{2\ \sin\ (22.5)}$$

$$= \frac{1.539\,\text{Å}}{2(0.383)} = \mathbf{2.01\ \text{Å}}$$



Example Problem 12.2.3 **Determine *d*-spacing and radius from a scattering angle.**

Silver metal crystallizes in an FCC lattice. Monochromatic x-radiation from a copper target has a wavelength of 154 pm. If this radiation is used in a diffraction experiment with a silver crystal, a second-order diffracted beam is observed at a theta value of 22.18°. If the spacing between these planes corresponds to the unit cell length ($d = a$), what is the d-spacing between the planes that gave rise to this reflection? What is the metallic radius of a silver atom?

Solution:

You are asked to calculate the d-spacing between the planes in a solid lattice and the metallic radius of an atom of a specific element.

You are given the x-ray wavelength, the theta value, and the type of crystal lattice.

Step 1. Calculate the d-spacing using Bragg's law.

$$d = \frac{n\lambda}{2\sin\theta} = \frac{(2)(154\text{ pm})}{2\sin(22.18°)} = 408\text{ pm}$$

Step 2. Determine the metallic radius of a silver atom.

The d-spacing corresponds to the edge length of the cubic cell. Use the relationship between unit cell edge length and atomic radius for an FCC unit cell to calculate the atomic radius of silver.

$$a = \frac{4r}{\sqrt{2}}$$

$$r = \frac{a\sqrt{2}}{4} = \frac{(408\text{ pm})\sqrt{2}}{4} = 144\text{ pm}$$

Reference:

1. A Text Book of Physical chemistry, Atkins P, Paula, de Julio
2. A Text Book of Physical chemistry, Bahal, B.S , Bahal, Arun
3. A Text Book of Physical chemistry, Silby, Robert J. Alberty , Robert A., Bawendi, Moungi G.