

## Module 6 : Reaction Kinetics and Dynamics

### Lecture 30 : Complex Reactions

#### Objectives

After studying this Lecture you will learn to do the following.

- Analyze the kinetics of chain reactions
- Analyses the kinetics of polymerization reactions.
- Rationalize the behaviour of explosive reactions.
- Outline the molecular details of photochemical reactions.
- Explore the steps involved in chemical oscillations.
- Comment on the features involved in homogeneous and heterogeneous catalysis.

#### 30.1 Introduction

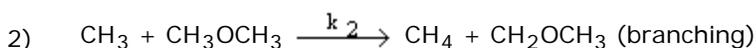
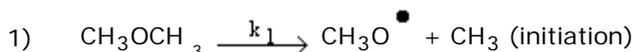
So far, we have considered rather simple reactions, i.e., elementary reactions and reactions involving a few steps in the reaction mechanisms. The variety of real chemical reactions is far wider. In this lecture, we shall consider a few major groups of these complex reactions. A common theme in all these is the involvement of several steps, and often, repeating steps.

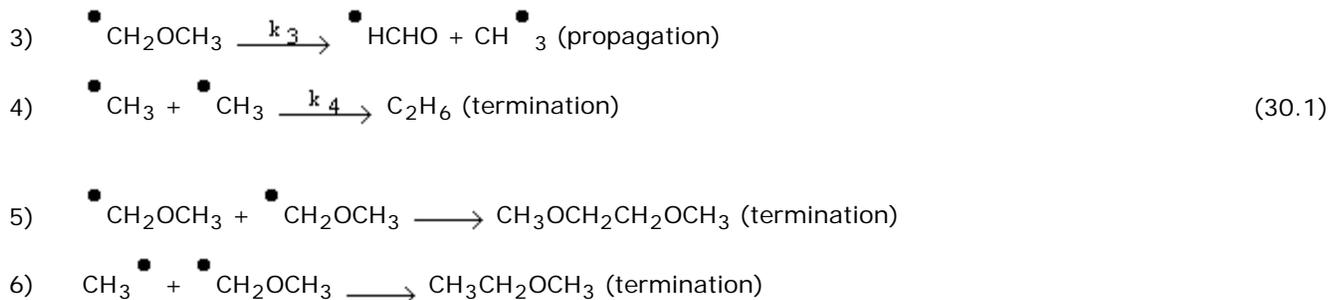
When certain steps repeat very fast, liberating a lot of heat, explosions occur. Several accidents occur all over the world in chemical laboratories, not only while exploring new reactions, but when old reactions are carried out in regimes which are unsafe. When one scales up a reaction from the laboratory scale ( milligrams to grams) to the industrial scale (kilograms to tons) one can not just increase the amounts of reactants 'n' fold. This becomes a problem of chemical engineering wherein mass transfer, heat transfer, diffusion, stirring and so on need to be considered in detail. Another area of wide applicability is catalysis wherein catalysts can be used to enhance the reaction rates and reduce the time and costs for carrying out reactions. Catalysts also alter the reaction mechanisms and thus add a new dimension in chemical kinetics.

#### 30.2 Chain Reactions

In a chain reaction, a reactive intermediate or a "chain carrier" produced in one step of the reaction takes part in a subsequent step. These chain carriers are repeatedly generated during the reaction until they are consumed fully. Typical steps in these reactions are initiation, propagation, branching, inhibition and termination. The chain carriers are usually free radicals which are molecules or fragments with one or more unpaired electrons. We will illustrate the mechanism of chain reactions with two examples.

a) Decomposition of dimethyl ether (methoxymethane) in the gas phase

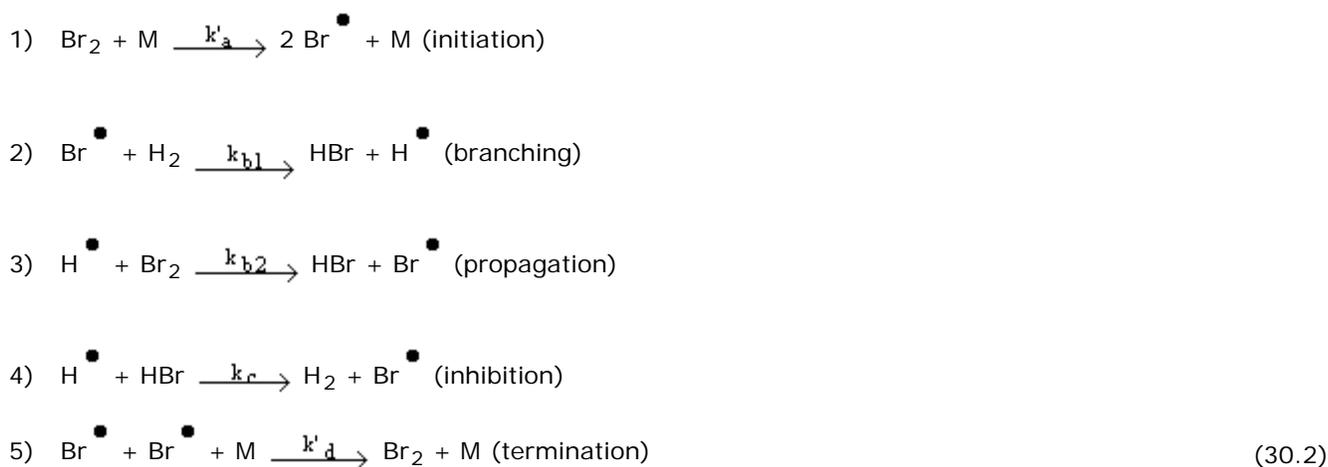




Among these reactions, not all steps are dominant. If the termination step (step 4) is dominant, it can be shown that the order of the reaction with respect to the reactant is 1.5.

b) The gaseous reaction between  $\text{H}_2$  and  $\text{Br}_2$  to give  $\text{HBr}$  is known to have a rate law

$d[\text{HBr}] / dt = k [\text{H}_2] [\text{Br}_2]^{3/2} / \{ [\text{Br}_2] + k' [\text{HBr}] \}$ . The mechanism that rationalizes the above rate law is as follows.



In reaction (1), M is an inert molecule which assists in the process through collisions. Its concentration remains constant during the reaction.

$$\text{In step (1), } d[\text{Br} \bullet] / dt = 2 k'_a [\text{Br}_2] [\text{M}] = 2 k_a [\text{Br}_2] \tag{30.3}$$

where  $[\text{M}]$  has been incorporated into  $k_a$  through  $k_a = k'_a [\text{M}]$

For steps 2) and 3) (30.4)

$$d[\text{HBr}] / dt = k_{b1} [\text{Br} \bullet] [\text{H}_2] \tag{30.5}$$

$$d[\text{HBr}] / dt = k_{b2} [\text{H} \bullet] [\text{Br}_2] \tag{30.6}$$

For reaction (4),  $d[\text{HBr}] / dt = -k_c [\text{H} \bullet] [\text{HBr}]$

For the termination reaction,

$$d[\text{Br} \bullet] / dt = 2 k'_d [\text{M}] [\text{Br} \bullet]^2 = -2 k_d [\text{Br} \bullet]^2 \tag{30.7}$$

If we know the values of the rate constants, we can numerically study the time evolution of all the concentrations on the computer. The steady state approximation gives an approximate and quick solution setting  $d[\text{H} \bullet] / dt = d[\text{Br} \bullet] / dt = 0$  in the steady state approximation,

$$d [ H^\bullet ] / dt = 0 = k_{b1} [ Br ] [ H_2 ] - k_{b2} [ H ] [ Br_2 ] - k_c [ H ] [ HBr ]$$

$$d [ Br^\bullet ] / dt = 0 = 2k_a [ Br_2 ] - k_{b1} [ Br ] [ H_2 ] + k_{b2} [ H ] [ Br_2 ] + k_c [ H ] [ Br ] - 2k [ Br ]^2 \quad (30.8)$$

For the rate of production of HBr, we have, using equations for steps 2,3 and 4,

$$d [ HBr ] / dt = k_{b1} [ Br ] [ H_2 ] + k_{b2} [ H ] [ Br_2 ] - k_c [ H ] [ HBr ] \quad (30.9)$$

Substituting the steady state concentrations of  $H^\bullet$  and  $Br^\bullet$ , we get

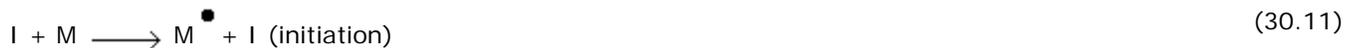
$$d [ HBr ] / dt = 2 k_{b1} (k_a / k_d)^{1/2} [ H_2 ] [ Br_2 ]^{3/2} / \{ [ Br_2 ] + (k_c / k_{b2}) [ HBr ] \} \quad (30.10)$$

As mentioned in the beginning, the initiation step of chain reactions could be either thermal or photochemical. Electric sparks are very good initiators. Propagation steps are usually rapid. The concentration of M can be used to control the process.

### 30.3 Polymerization Reactions.

Polymers are molecules that are built from a large number of one or more monomer units. We will consider elementary examples of polymerization, with relatively straightforward mechanisms. Our body too contains a large number of "polymeric systems" such as DNA and proteins but the mechanisms for making these molecules is complex.

In chain polymerization, an initiator molecule I interacts with a monomer M to give a reactive monomer unit.



The reactive  $M^\bullet$  can repeatedly react with other units and propagate the chain through the following propagation steps



Two large units  $M_k^\bullet$  and  $M_l^\bullet$  can combine to terminate the sequence of reactions



In a polymerization reaction, chains of varying lengths are formed. The art of polymer synthesis is to restrict the growth to a narrow range of desired chain lengths.

To get an approximate rate law let us make a few assumptions. 1) The total radical concentration R is constant during a major part of the reaction wherein we can apply the steady state approximation, 2) The rate of propagation  $k_p$  is the same for all n,  $M_n^\bullet + M \longrightarrow M_{n+1}^\bullet$ .

3) The rate of termination  $k_T$  does not depend on chain length  $M_k^\bullet$  and  $M_l^\bullet$  and 4) there are no side reactions leading to chain truncation, transfer or branching.

If  $k_i$  is the initiation rate, the rate of formation of R is given by

$$d [ R ] / dt = k_i [ M ] [ I ] - 2 k_T [ R ]^2 \quad (30.14)$$

$$\text{In the steady state approximation, } d [ R ] / dt = 0 \text{ which leads to } [ R ] = \{ k_i [ M ] [ I ] / 2 k_T \}^{1/2} \quad (30.15)$$

The rate of propagation of chains is the rate at which the monomer is consumed, and is given by

$$d [ M ] / dt = - k_p [ R ] [ M ] \quad (30.16)$$

Substituting the value of R, we have

$$d [ M ] / dt = - k_p ( k_i / 2 k_T )^{1/2} [ I ]^{1/2} [ M ]^{3/2} \quad (30.17)$$

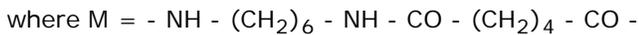
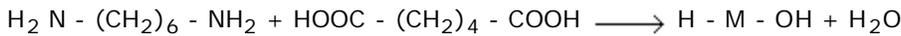
The polymer chains are long if the termination rate  $k_T$  is much slower than the propagation rate. If  $k_p$  and  $k_T$  are equal, the chain lengths will be very short. A measure of the polymer chain length is the kinetic chain length  $l$ , defined by

$l = \text{rate of propagation} / \text{rate of initiation}$ .

$$l = \{ k_p / (2 k_T k_i)^{1/2} \} [ M ]^{1/2} / [ I ]^{1/2} \quad (30.18)$$

This implies that lower the initiation rate and  $[ I ]$ , higher the chain length.

The above polymerization scheme was based on addition reactions. In another scheme, during each step when a monomer is added, a small molecule such as water is eliminated, as exemplified in the example of nylon given below.



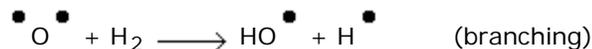
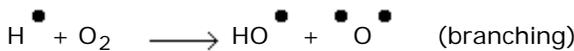
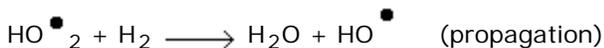
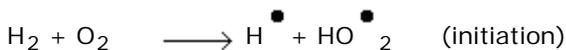
(30.19)

In each step an amide linkage (- CO - NH -) is formed by eliminating a water molecule. The chain lengths generally increase until a significant monomer fraction remains in solution. The polymerization process can be controlled either by sudden cooling, addition of scavengers (which reduce the radical/ion concentrations) or by removing the polymeric material from the reaction mixture.

### 30.4 Explosion reactions.

Explosions occur when the rate of one or more steps in a reaction suddenly increases in a very short period of time. The sudden increase in the rate could be due to autocatalysis (i.e., a radical once produced, goes on producing more radicals of the same type). Often, the heat produced in reactions is so large that the container can not accommodate the heat, leading to an explosion. We will illustrate a mechanism for explosion through the  $H_2 + O_2$  reaction, which involves the participation of radicals such as  $H^\bullet$ ,  $O^\bullet$ ,  $OH^\bullet$ ,  $HO_2^\bullet$

The major steps in this explosion reaction are :



(30.20)

The dots on H, OH etc represent radicals (containing unpaired electrons). For explosions to occur, the reaction mixture needs to attain specific temperatures and pressures. These ranges are shown in the figure below.

**Figure 30.1 Pressure vs temperature for an explosion reaction showing several explosion limits.**

We notice from the figure that at pressures between  $10^2$  and  $10^5$  Pa, explosions occur over 700 K. At a given temperature, say 800, K there is a pressure dependence too. Along the line ab at 600 K, explosion occurs only above  $P = 10^6$  Pa. At 800K, along the line cdef explosion first starts around  $10^3$  Pa. Between  $10^4$  Pa to  $5 \times 10^5$  Pa, there is a no explosion region and above  $5 \times 10^5$  Pa, we have an explosion region once again. These variations are due to the dominance of different reactions in different temperature and pressure regimes. At the pressure at d (i.e., when the first explosion limit is reached), diffusion of the radicals to the end of the container is prohibited and the surface termination of radicals through reactions such as



is reduced and branching reactions dominate in the bulk of the container. As the pressure reaches e, in the region ef, gas phase terminations get an opportunity to reduce the radical populations through reactions with neutral gas species M present in the reaction mixture.



The  $\text{HO}_2$  radical is relatively quite stable.

Above the limit f, branching reactions and autocatalytic steps dominate (as the diffusion is considerably reduced) and one enters the explosive region once again.

In several other explosive processes, similar underlying schemes are involved. Obtaining the complete rate expressions for these schemes is a challenging task as the approximations such as steady state or preequilibrium hardly apply and the number of reactions involved is also quite large.

### 30.5 Photochemical Reactions.

The absorption of light by a molecule leads to its excited state. If the excited state is unstable, the absorbed light is emitted back through fluorescence. If the excited state is long lived (nano-seconds, microseconds), the molecule may decay into other excited states and finally decay to the ground state by transferring energy to the medium during collisions. The excitation energy could be either a laser light (which can be tuned to specific excitation wavelengths) or could be sunlight, which is the main source of energy for all natural photochemical reactions such as photosynthesis. The range of frequencies in the sunlight is from UV to the far infrared. The photochemical efficiency of a reaction induced by light is called the quantum efficiency and it is defined by

quantum efficiency or quantum yield =  $\phi$  = number of molecules reacted / number of photons (30.23) absorbed

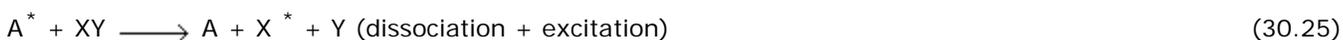
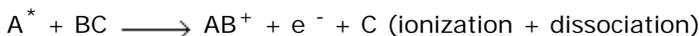
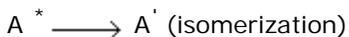
Figure 30.2 Common physical features associated with absorption of light. The molecule, on excitation goes from the ground state S to the excited state S\*. During this process, the spin of the excited electron is unchanged and it is a singlet. This excitation can be given out as fluorescence. This excitation can cross over to an excited triplet state, T\*. Usually T\* is long lived and decays slowly to the ground state through phosphorescence.

If we know the wattage (W) and the wavelength ( $\lambda$ ) of a source, we can calculate the number of photons generated per second,  $n_s$ , by

$$n_s = W / (h c / \lambda) \quad (30.24)$$

If we know the duration of time (t) over which the light was incident, the number of photons incident is given by  $n_s t$ . One mole of photons is one einstein.

The excited state resulting from light absorption may be denoted by A\*. A\* may be a singlet (all spins paired) or a triplet (two unpaired spins). This excited state may be involved in several chemical changes such as ionizations, dissociations, isomerizations, induced dissociations and so on.



### 30.6 Chemical Oscillations

Chemical oscillations are necessary to drive the beating of the heart, the glycolytic cycle in our body, to maintain the concentrations of metabolites and other hormones in the body and for several other processes in

nature. In oscillatory chemical reactions, the concentrations of reactants and products vary periodically in time and/or space. The iodine clock reaction is a famous example. A few well known mechanisms for chemical oscillations are :

**a) The Lotka - Volterra mechanism :**



**b) The Brusselator mechanism :**



Here the concentrations of only X and Y vary and A and B are held at fixed concentrations.

**c) The Oregonator mechanism :**



Here,  $X = \text{HBrO}_2$ ,  $Y = \text{Br}^-$  and  $Z = 2\text{Ce}^{4+}$ . The concentrations of A, B, C and D are held fixed.

These reactions have generated a lot of interest. These reactions are far removed from equilibrium; they involve autocatalytic steps ( such as  $A + X \longrightarrow 2X$ , with the reactants regenerating themselves) and the reacting system must be able to exist in two steady states (otherwise, the system will end up in the minimum free energy state of thermal equilibrium).

In the iodine clock reaction, the decomposition of  $\text{H}_2\text{O}_2$  is catalysed by  $\text{IO}_3^- / \text{I}_2$ . The production of  $\text{O}_2$  is discontinuous and proceeds in bursts leading to the oscillations in the concentrations of  $\text{I}_2$ .



In another well known "beating mercury heart" reaction, a 1 ml drop of mercury is covered by a dilute solution of a strong acid ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ) and crystals of an oxidizing agent ( $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ ) are added to it. If an iron wire just touches the mercury globule, the "heart" (mercury globule) pulsates 2 to 3 times per second. The electrochemical cell formed is shown below.

### Figure 30.4 The beating mercury heart



(30.30)

In the cell, Fe is the negative electrode. When there is Fe...Hg contact, Fe is oxidized to  $\text{Fe}^{2+} + 2\text{e}^-$ ; the solvated  $\text{Fe}^{2+}$  diffuses into solution and the electrons are adsorbed on the Hg surface giving it a negative charge (due to adsorption of  $\text{Hg}^{2-}$  on the surface). This negative charge on the drop repels the negative electrode and the electrical contact breaks. When the adsorbed negative ions desorb into the solution, the liquid drop assumes a spherical shape. The electrical contact to Fe is reestablished and the cycle repeats, exhibiting a beating mercury heart. Of course, watching this heart beat is far more dramatic than reading about it!

a)

b)

### Figure 30.5

Chemical Oscillations. a) if  $X = \text{predator}$  and  $Y = \text{prey}$ , the densities of predators and preys keep on oscillating with time.  $X = \text{IO}_3^-$  and  $Y = \text{I}_2$  in the iodine clock reaction. b) When  $X$  is plotted versus  $Y$ , it shows a periodic behaviour. c) In special situations, all initial compositions lead to the same final cycle called the limit cycle. Three different initial paths leading to the limit cycle are shown.

### 30.7 Catalysis

This is another very active area in chemical kinetics. We need to be in the look out for better catalysts in petrochemical, polymer and pharmaceutical industry because more efficient and less degradable catalysts save crores of rupees. A catalyst enhances the reaction rate without taking part in the reaction stoichiometry. This enhancement is usually done by reducing the activation energy. Enzymes or biocatalysts play a critical role in metabolism. For example, the activation energy for the hydrolysis of sucrose is 107 kJ/mol. The enzyme saccharase reduces this to 36 kJ/mol, enhancing the hydrolysis rate by a factor of  $10^{12}$  at the body temperature! Without this, we may be unable to digest sugar all our life!

A heterogeneous catalyst is in a phase different from the reacting medium. (e.g., a solid or a powder catalyzing a gas phase reaction). A homogeneous catalyst is in the same medium as the phase of the reaction mixture.

Hydrogenation of ethylene can be catalysed by several powdered metals. The mechanism of the reaction has been shown to be different in the presence of different metal catalysts and three such experimental findings are shown below



$$d[\text{C}_2\text{H}_6] / dt = k_1 [\text{H}_2] [\text{C}_2\text{H}_4] / (1 + K_1 [\text{C}_2\text{H}_4])^2 \quad (30.32)$$

(copper powder catalyst)

$$d[\text{C}_2\text{H}_6] / dt = k_2 [\text{H}_2] [\text{C}_2\text{H}_4] / (1 + k_2 [\text{C}_2\text{H}_4]) \quad (30.33)$$

(nickel surface catalyst)

$$d[\text{C}_2\text{H}_6] / dt = k_3 [\text{H}_2]^{1/2} [\text{C}_2\text{H}_4] \quad (30.34)$$

(iridium powder / film catalyst)

Not only is the reaction rate enhanced, the reaction path is also altered. In the intermediate steps, adsorption on the catalyst surface plays an important role.

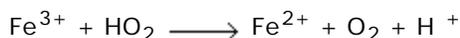
### Figure 30.6 Adsorbed $\text{H}_2$ and ethylene on a catalyst surface.

A  $\text{C}_2\text{H}_4$  molecule colliding with an adsorbed  $\text{H}_2$  can combine with it with much smaller activation energy and then the product is desorbed.

### Figure 30.7 Potential energy diagram in heterogeneous catalysis

Fig 30.7 shows the reduced activation energy in heterogeneous catalysis. The activation energy for the decomposition of ammonia is 350 kJ / mol. The value of this activation energy is reduced when the reaction is catalyzed by tungsten (160 kJ/mol), molybdenum (140 kJ /mol) and osmium (200 kJ/mol). The need for cheaper and easily renewable catalysts can not be overemphasized.

Common examples of homogeneous (one phase) catalysis are acid- base catalysis, enzyme catalysis, gas phase catalysis (e.g., conversion of SO<sub>2</sub> to SO<sub>3</sub> catalysed by NO) and catalysis by metal ions. The mechanism in the catalysis of 2 H<sub>2</sub>O<sub>2</sub> → 2 H<sub>2</sub>O + O<sub>2</sub> by Fe<sup>2+</sup> ions which reduce the activation energy from 70 kJ / mol to 42 kJ / mol is shown below.



### 30.8 Problems

30.1) Derive a rate law for the reaction scheme in equation (30.1) using the following steps. Obtain  $d[\text{CH}_3^\bullet] / dt$  from reactions involving  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  and  $d[\text{CH}_2\text{OCH}_3^\bullet] / dt$  in terms of  $k_2$  and  $k_3$ . Set both to zero in the steady state approximation. Adding the two, get  $[\text{CH}_3^\bullet] = \{ k_1 [\text{CH}_3\text{OCH}_3] / 2 k_4 \}^{1/2}$ . The rate of the reaction can be expressed in three ways as  $d[\text{CH}_4] / dt$  or as  $d[\text{HCHO}] / dt$  or as  $-d[\text{CH}_3\text{OCH}_3] / dt$ . Show that all three lead to  $k_2 (k_1 / 2 k_4)^{1/2} [\text{CH}_3\text{OCH}_3]^{3/2}$ . Assume that the rate of initiation is much greater than the rate of propagation.

30.2) Obtain the steady state concentration of H<sup>•</sup> and Br<sup>•</sup> in eq (30.8).

30.3) A branched chain reaction sequence may be written as  $\text{A} \longrightarrow \text{B}$ ;  $\text{A} + \text{R} \xrightarrow{k} \text{B} + n \text{R}$ ,  $n > 1$ . The second reaction is the branching reaction. If the rate law for R is  $d[\text{R}] / dt = k (n-1) [\text{R}]$ , how does the concentration

of [R] increase with time?

- 30.4) In the three models for oscillatory reactions proposed in equations (30.26), (30.27) and (30.28), identify the autocatalytic steps
- 30.5) If one radical produces 3 radicals per second and these three radicals each produce three more radicals in the next second and the process continues for 1 minute, how many radicals will be present after 1 minute? Assume that there are no termination reactions.
- 30.6) What is the mechanistic difference between the iodine clock reaction and the "mercury heart " reaction?
- 30.7) What brings about the decrease and the eventual termination of oscillations in concentrations in oscillatory reactions?
- 30.8) Distinguish between free radical polymerization and condensation polymerization.
- 30.9) Dacron (polyethylene terephthalate) is formed by the condensation of ethylene glycol with terephthalic acid. Let  $C_0$  be the initial concentrations of both the acid and the glycol. If the reaction order is one with respect to both the acid and the glycol, using second order kinetics show that the degree of polymerization at time  $t$  is given by  $C_0 / C(t) = 1 / (1-p)$  where  $p$  is the fraction of the functional group consumed at time  $t$ .
- 30.10) List examples of reactions catalyzed by acids bases and metal ions. Distinguish between homogeneous and heterogeneous catalysis.

### Recap

In this Lecture you have learnt the following

### Summary

In this lecture, we have described the kinetics and mechanisms of reactions which are often classified as complex. Chain reactions and polymerization reactions involve a large number of repeated steps. Steady state approximations can also be used here whenever the intermediates (such as radicals) are short lived. Explosions occur when the rates of one or more steps of a reaction increase suddenly and when the heat produced in the reaction is so large that the container can not accommodate it.

Photochemical reactions are induced by light. The excited states are quite reactive and can induce a number of reactions like associations, dissociations, ionizations, and so on. Quantum yield or quantum efficiency is the number of reactant molecules reacted per each photon absorbed. In photosynthesis, the quantum efficiency is about 10%. Chemical oscillations are a fascinating class of reactions which involve autocatalysis, more than one steady state and wherein, the reaction conditions are far away from equilibrium.

The last section dealt with homogeneous (one phase) and heterogeneous (more than one phase) catalysis. Catalysts reduce the activation energy and enhance the reaction rate without taking part in the reaction stoichiometry. They generally alter the reaction mechanism by providing a facile path for the reaction to occur.