Chapter I
INTRODUCTION

1.1 Interaction of radiation with matter

1.1.1 General

Soon after the discoveries of X-rays and radioactivity it was learned that nuclear radiation could cause physical, chemical and bio-chemical changes in matter. The effect of radiation depends on composition of matter, nature of incident radiation and energy deposited by radiation. The term nuclear radiation includes all elementary particles, both charged ($e^-$, $e^+$) and uncharged ($n$) and electromagnetic radiation ($\gamma$) having energies in excess of 100eV. Since the lower energy limit is very high when compared to ionization energies (usually $<15eV$) and chemical bond energies (normally $<1-5eV$), nuclear radiation causes ionization during its passage through matter and hence frequently referred to as ionizing radiation. Absorption of such high energy radiation by matter results in transfer of energy to atoms and molecules in the absorbed material until the impinching particles of radiation attains the same average kinetic energy as the atoms comprising the material, i.e., until thermal equilibrium is reached. This energy transfer results initially in ionization and excitation in the absorbing material leading to changes in physical and chemical properties. Radiation chemistry
deals with the study of these effects brought about by the absorption of ionizing radiations (i.e., irradiation).

### 1.1.2 Interaction of $\gamma$-radiation with matter

The interaction of $\gamma$-radiation with matter occurs principally by means of three mechanisms\textsuperscript{1-4} namely the photoelectric effect, the compton effect and pair production according as the incident $\gamma$-radiation is of low, intermediate or quite high energy. For very high energies the dominant mode is nuclear reaction. Excluding nuclear reaction, in all other process electrons are ejected causing the target to be internally bombarded by energetic electrons. Thus the effect of $\gamma$-radiation are almost exclusively due to electrons liberated by $\gamma$-photons. Gamma photons pass through matter, lose its energy with a single encounter with an atomic electron or nuclear field and get scattered as a photon of lower energy. The primary electron liberated by the $\gamma$-photons act in the bulk of the molecular crystal by ionization and excitation. The four basic solids namely molecular, ionic, metallic and valence crystals behave differently under irradiation.\textsuperscript{5}

#### 1.1.2.1 Chemical consequences of ionization and excitation

In crystalline solids as a result of ionization lattice vacancies are created. Ionization results in simple trapping of electrons and production of electron holes. Thus crystal defects are introduced which increase the energy content of the crystal and subsequent chemical damage. Thus production of damage, displacements and extended lattice defects are the predominant
effects of irradiation in molecular ions.\textsuperscript{6-9} In ionic solids with polyatomic ions eg.\text{NO}_3^-, \text{ClO}_4^- etc the important consequence of electronic excitation and ionization is chemical bond rupture as in molecular crystals. Significant damage has been observed in valence crystals only when radiations, which can knock atoms out of position, are employed. In metallic crystals the conversion of excitation energy to the lattice is very small due to the loose coupling of the conduction electrons to the lattice, no lattice displacements arising exclusively from electronic excitation have been observed. Depending upon the physical state, crystalline nature, molecular structure etc., different consequences are possible. Thus crystalline solids experiences remarkable changes in physical, chemical and biochemical properties upon irradiation which inturn can be exploited in the various areas of science and technology.

1.1.2.2 Survey of methods for production of radiolytic products

The sources for the production of radiolytic products in solids\textsuperscript{10-11} include isotope sources, nuclear reactors and particle accelerators. Natural as well as artificial radioactive isotopes have been used as generator of radiation products, eg., \textsuperscript{210}Po, \textsuperscript{137}Cs, \textsuperscript{60}Co for radiolytic purposes. Of these \textsuperscript{60}Co is the most commonly used \(\gamma\)-ray source. The X-ray machine, cyclotron, Vande Graff accelerator and electron accelerator have been employed most frequently for radiation chemical studies.

Some of the units in use for expressing the dose or the amount of energy absorbed are Rad, Gray and Rontgen.
1.1.2.3 Survey of methods for detection and identification of radiolytic products

The most common type of solid state measurements are those dealing with the optical properties of the radiolytic product. Information on the symmetry of radiolytic products \(^{12-14}\) may be obtained using polarized light for the study of optical absorption. Ultraviolet, visible and infrared measurements have been applied to investigate many radiolyzed systems e.g.: bromates \(^{15,16}\) chlorates \(^{17-19}\) alkali halides \(^{12,20}\) etc. Emission spectra obtained by the excitation of radiolytic centre by photon have proved to be a very useful tool for understanding the interaction of a given radiolytic centre with ions of the crystal and with other centres in the crystal. The alkali halides \(^{12,20}\) and glasses \(^{21}\) represent few examples of the system investigated by this technique. Far more information can be obtained from electron spin resonance spectra. This technique has become important in recent years. ESR has been used to obtain information about radiolytic products in a large series of systems, acetates \(^{22}\) carbonates \(^{23}\) chlorates \(^{24}\) chromates \(^{25}\) cyanides \(^{26}\) nickelates \(^{27}\) nitrates \(^{28,29}\) perchlorates \(^{30-32}\) phosphates, sulphates \(^{33,34}\) and thiosulphates. \(^{35,36}\) EPR is another technique used in the study of \(\gamma\)-irradiated compounds. \(^{37-42}\)

Irradiation of a crystal increase the energy extent of the lattice. Micro calorimetry, \(^{43}\) differential thermal analysis \(^{44}\) and measurement of heat of solution \(^{45}\) have been used to obtain thermochemical information about the number and stability of radiolytic products. Information on radiolytic products can also be obtained by measuring the changes that occur when a coloured
crystal is gradually heated from some low temperature to a high temperature. As the temperature is raised the electrons and holes escape from their traps at an increasing rate. The freed charges may be detected by conductance or thermoluminascence measurements.\textsuperscript{12,46,47} The thermoluminascence technique has proved to be very useful for investigation of crystals irradiated with low dose. Measurements of changes in electrical properties have been used for studying radiation damage effect in ionic solids. Electrical conductivity of $\gamma$-irradiated nickel oxalate was measured during the thermal decomposition and the results were evaluated.\textsuperscript{48} Information concerning the influence of the total number of the radiolytic products rather than the effect of the individual products has been obtained using this technique.\textsuperscript{12,49}

Technique based upon measuring changes in the acoustic energy of the mechanical properties have been used\textsuperscript{50,12} to investigate products in ionic crystal.

The application of dissolution techniques for determination of radiolytic products has almost entirely been limited to the use of water or aqueous solution of inorganic or organic substances as solvents for the irradiated crystals, although the use of liquid ammonia as the solvent has been reported.\textsuperscript{51} Identification of gases liberated during the dissolution process has been carried out by gas chromatography\textsuperscript{15} or the usual methods of gas analysis.\textsuperscript{52, 53} The non gaseous compounds have been identified by spectrophotometric method. Studies by Prince\textsuperscript{54-56} have indicated that a
detailed investigation of the non gaseous products may yield valuable information about the radiation decomposition process. Prince showed that the rather complex system of stable products formed upon dissolution of unirradiated perchlorates can be investigated by different types of chemical analysis. By using ceric solution as a solvent for irradiated crystalline nitrates Cunningham\textsuperscript{57} was able to show that NO and O\textsuperscript{2-} are formed on the irradiated crystals and act as a precursors for nitrate, which was previously assumed to be a primary radiation product.

1.1.2.4 Mechanism of radiolytic decomposition of inorganic solids

Radiolytic decomposition of various compounds containing oxyanions have been extensively studied.\textsuperscript{58-63} A considerable amount of work has been done on the chemical damage induced by ionizing radiation in systems containing oxyanions such as nitrate, perchlorate, thiosulphate etc. and the damage fragments of radiolysis have been identified.\textsuperscript{64-75} The subject has been reviewed by Zakharov, Nevostreev\textsuperscript{76} and by Johnson.\textsuperscript{3} The radiolytic products have been identified by chemical methods, X-ray diffraction studies, spectral analysis and chromatographic techniques.\textsuperscript{77-90}

Gamma radiolysis of a few complexes has been reported. Aqueous solutions of nickel(II) diethylene triamine penta acetate complex\textsuperscript{63} were irradiated using \(\gamma\)-rays both in the presence and in the absence of oxygen. A radiolytic mechanism has been proposed and discussed. It has been suggested that the radiolytic degradation of the ligand is due to the formation of OH\textsuperscript{-} during radiolysis.
I\textsuperscript{-}-radiolysis of folic acid and its complexes\textsuperscript{91} were studied in aqueous solution at doses ranging from 2 to 20 krad and also from 2 to 10 Mrad using \textsuperscript{60}Co source. The variations in IR, UV and visible spectra due to their radiolysis were recorded.

As our study is based on irradiation of nitrate complexes, the proposed mechanism for radiation induced decomposition of nitrates is outlined.

**Nitrate**

The radiolytic fragments are NO\textsubscript{2}\textsuperscript{-}, O\textsubscript{2}, NO\textsubscript{2}, (NO\textsubscript{2})\textsuperscript{+}, (NO\textsubscript{3})\textsuperscript{-} NO\textsubscript{3}, NO, O\textsubscript{2}, NO\textsubscript{2}, O\textsubscript{3}, O\textsuperscript{4}, O\textsubscript{2}, N\textsubscript{2}O\textsubscript{3} and N\textsubscript{2}O\textsubscript{4}\textsuperscript{92-131} The possible effect of irradiation on nitrate may be schematically shown as below.

\[
\begin{align*}
\text{NO}_3^- & \rightarrow \text{NO}_3, \text{NO}_3^* \\
\text{NO}_3^- & \rightarrow \text{NO}_2 + \text{O} \\
\text{NO}_3^- & \rightarrow \text{NO}_2^- + \text{O} \\
\text{NO}_3^- & \rightarrow \text{NO}^- + \text{O}_2 \\
\text{NO}_3^- & \rightarrow \text{NO}_2^- + \text{O}^- \\
\text{NO}_3^- & \rightarrow \text{NO}^- + \text{O}_2^- \\
\text{Electron capture} & \rightarrow (\text{NO}_3)^-, (\text{NO}_2)^- 
\end{align*}
\]
A different scheme has also been proposed

\[ \text{NO}_3^- \rightarrow \text{NO}_2^+ + \text{O} \]  \hspace{1cm} 1.8

The oxygen fragment reacting as

\[ \text{NO}_2^+ + \text{O} \rightarrow \text{NO}_3^- \]  \hspace{1cm} 1.9

\[ \text{NO}_3^- + \text{O} \rightarrow \text{NO}_2^+ + \text{O}_2 \]  \hspace{1cm} 1.10

And also

\[ \text{O} + \text{O} \rightarrow \text{O}_2 \]  \hspace{1cm} 1.11

According to Cunniham\textsuperscript{132,133} the primary fragments in low temperature irradiation of crystalline nitrates are NO and \( \text{O}_2^- \)

\[ \text{NO}_3^- \rightarrow \text{NO}^+ + \text{O}_2^- \]  \hspace{1cm} 1.12

when crystals are irradiated at room temperature or above, the primary radical species back react to produce \( \text{NO}_2^- \) and O.

\[ \text{NO} + \text{O}_2^- \Leftrightarrow \text{NO}_3^- \Leftrightarrow \text{NO}_2^+ + \text{O} \]  \hspace{1cm} 1.13

### 1.1.2.5 Applications of \( \gamma \)-irradiation

Various research and development on radiation application have been conducted for the peaceful uses of nuclear energy. Thus radiation is being widely utilized in such fields as industry, agriculture and medicine. Research and development on radiation application also covers radiation processing, development of technologies for the environmental conservation
and effective utilization of agricultural resources, the effect of irradiation on semiconductors and electronic devices and the application of radiation to biotechnology etc. Semiconductor nano materials and micro materials can be prepared by gamma irradiation. Gamma radiation has been applied to synthesise the nano composite semiconductor constituted of zinc and cadmium sulphide. Gamma rays have the ability to effect molecular changes and so it is used to alter the property of semi precious stones. It changes white topaz to blue topaz.

A large number of chemical synthesis employing γ-radiation has been shown to be technically feasible and economically viable. Ionizing radiation generates ionized and excited atoms in all materials. These excited species decompose to yield highly reactive free radicals, which are precursors for further reaction like oxidation, reduction, polymerization etc.

Gamma radiation is used to sterilize medical equipments, removing decay causing bacteria from many food stuff or preventing fruit and vegetables from sprouting to maintain freshness and flavour. Due to their tissue penetrating power gamma rays have a wide variety of medical uses such as in CT scans and radiation therapy.

Despite their cancer causing properties they are also used to prevent some type of cancer. In the procedure called gamma-knife surgery, multiple concentrated beam of gamma rays are directed on the growth in order to kill the cancer cells. Gamma rays are also used for diagnostic
purposes in nuclear medicines. Several gamma emitting radio isotopes are used to diagnose spread of cancer to the bones. Low doses of gamma irradiation could have beneficial effects on health. Thus application of gamma radiation technology to health care, industry, food and agriculture are of direct benefit to society.

1.2 Thermal Studies
1.2.1 Role of crystal defects on thermal decomposition of solids

The understanding of crystalline solids has generally grown from the increasing knowledge of the regular lattice structure as well as different lattice defects. In general a step of predominant importance to reactivity in decomposition reaction is nucleation i.e., the formation of nuclei and their subsequent growth. The process of nucleation occurs when fluctuation in the local energy of the crystal are sufficient to provide the necessary activation energy for the formation of a nucleus. Nucleation is favoured at definite localized spots where the activation energy is least. Potential nucleus forming sites are generally associated with lattice imperfections like vacancies, interstitials, dislocations, grain boundaries etc. These regions of lattice imperfections possess higher reactivity. The reactant molecules at such points are less well coordinated on the crystal than the molecules in the perfect regions and hence will decompose more readily. As irradiation leads to an increase in defect concentration, number as well as growth of potential nucleus forming sites is increased. Consequently the decomposition reactivity is enhanced. Literature survey revealed that thermal process is enhanced upon irradiation in most cases with a few exceptions where the reverse is
true. It is established that the pre-treatment with energetic radiation can accelerate the thermal decomposition of solids.

1.2.2 The effect of irradiation on thermal decomposition of inorganic salts

The effect of irradiation on thermal decomposition of crystalline inorganic salts has been extensively studied. Most of the thermal studies of inorganic compounds containing oxyanions were made by the gas evolution method. In recent years thermogravimetric (both isothermal and non-isothermal) methods are employed for the thermal studies. It is observed that the general effects of irradiation on thermal decomposition of solids include abbreviation of the induction period and enhancement of rate constant for both the acceleratory and decay stages of the reaction with or without affecting the energy of activation. In systems containing molecular ions irradiation produces chemical damages, displacements and extended lattice defects which provide and facilitate formation and growth of nucleation centres.\textsuperscript{3, 6, 7} The effect of irradiation is attributed to lattice defects as well as radiation damage. Studies concerning the influence of $\gamma$-radiation on thermal decomposition of inorganic salts containing oxyanions and the kinetics thereon are well documented. Reported investigations are reviewed. They are classified according to the respective thermoanalytical method employed.

1.2.2.1 Evolved gas analysis

In gas evolution method decomposition is followed at each temperature by measuring the pressure of gas evolved at different times $t$ of heating.
The effect of preirradiation by γ-rays at varying doses on subsequent thermal decomposition of differently treated sample of zinc hydroxy azide\(^{134}\) has been reported. The influence of γ-irradiation on thermal decomposition of calcium azide\(^{135}\) has also been studied. The thermal decomposition of γ-irradiated sodium bromate\(^{136}\) potassium bromate,\(^{137}\) barium bromate,\(^{138}\) calcium bromate,\(^{139}\) lead bromate\(^{140}\) and cadmium bromate\(^{141}\) by gas evolution method have been reported. Irradiation enhanced thermal decomposition lowering activation energy.

Thermal decomposition studies of gamma irradiated lead nitrate and strontium nitrate\(^{142,143}\) have been carried out by gas evolution method. The decomposition occurs in four stages in both cases. The linear stage is absent in both. The acceleratory and decay stages follow the Prout –Tompkin relationship. The effect of γ-irradiation on thermal decomposition of a mixture of barium oxalate and copper oxide,\(^{144}\) yttrium oxalate and coperoxide\(^{145}\) studied by gas evolution method have been reported. The mechanism of the decomposition was also studied. It was found that irradiation enhanced decomposition rate reducing activation energy. Thermal decomposition of oxalates of uranium, thorium, barium, samarium silver, lead, nickel, hydrated barium oxalates and barium titanyl oxalate by gas evolution method have been reported.\(^{146-154}\)

In all cases irradiation enhanced thermal decomposition lowering activation energy. The mechanism for the thermal decomposition was also studied.
Thermal decomposition kinetics and mechanism of γ-irradiated magnesium oxalate and magnesium oxalate-Titanium oxide\textsuperscript{155} have been studied by gas evolution method. Kinetics of the thermal decomposition of γ-irradiated barium perchlorate\textsuperscript{156, 157} and ammonium perchlorate\textsuperscript{158} have been studied. In barium perchlorate irradiation enhanced decomposition rate due to the formation of additional nuclei and the kinetics of decomposition is considered in relation to the change in state of the material during the decomposition.

1.2.2.2 Isothermal technique

In isothermal method the degree of transformation at constant temperature is recorded as a function of time.

Thermal decomposition of γ-irradiated paladium acetate was studied by isothermal method.\textsuperscript{159} The results showed that kinetics of isothermal decomposition of palladium acetate was governed by random nucleation reaction. Isothermal decomposition of unirradiated and irradiated erbium acetate has been investigated at different temperatures.\textsuperscript{160} It was observed that irradiation enhanced the rate of decomposition without modifying the mechanism of thermal decomposition. The effect of gamma irradiation on thermal decomposition of acetates of hydrated gadolinium, uranium, samarium, thallium, zinc, silver and cobalt\textsuperscript{161-167} has been studied by isothermal method. It is observed that irradiation retards the thermal process in the case of cobalt acetate and gadolinium acetate and enhances the same in uranyl acetate, samarium acetate and thallous acetate.
Influence of $\gamma$-irradiation on isothermal decomposition of zinc-uranylacetate has been investigated.\textsuperscript{22}

Isothermal decomposition of gamma irradiated calcium azide\textsuperscript{168} and barium azide\textsuperscript{169} have also been reported. The effect of gamma irradiation on isothermal decomposition of caesium bromate\textsuperscript{170} has been studied. Gamma irradiation effect on isothermal decomposition characteristics of ammonium permanganate\textsuperscript{86} has been extensively studied. Effect of doping in irradiated permanganate has also been studied and observed that doping increase the rate of thermal decomposition.\textsuperscript{171} It is also found that effect of grinding of some permanganate\textsuperscript{172-173} eliminates the linear stage. In rubidium permanganate the reduction of particle size was found to increase the reaction rate.\textsuperscript{174} The comparative study of the magnitude of the irradiation effect on the permanganate of lithium, sodium and caesium precludes the creation of incipient nuclei by the Compton recoil effect.\textsuperscript{175} The formation of essential sites occurs as a result of cationic displacements following multiple ionization by gamma rays.

1.2.2.3 Non-isothermal technique

In non-isothermal thermogravimetric methods the degree of transformation is recorded as a function of time or temperature.

Thermal decomposition of irradiated manganese acetate tetrahydrate\textsuperscript{176} was studied by dynamic thermogravimetry. Thermal decomposition of unirradiated and $\gamma$-irradiated hydrated gadolinium acetate\textsuperscript{161}
was studied using isothermal and dynamic gravimetric techniques. Integral methods using Coats-Redfern equation was applied in dynamic data analysis. The results showed that kinetics of isothermal and non-isothermal decomposition for accelerating stage was governed by phase boundary process. The effect of $\gamma$-irradiation on the thermal decomposition of uranyl acetate, samarium acetate, thallous acetate, zinc acetate, zinc uranyl acetate and cobaltous acetate have been studied by non-isothermal methods. Thermal decomposition of $\gamma$-irradiated silver acetate was studied. Kinetic and thermodynamic parameters were evaluated and calculated.

The thermal decomposition of $\gamma$-irradiated potassium bromate, zinc bromate, calcium bromate and sodium bromate were studied by dynamic thermogravimetry. Kinetic analysis of thermoanalytical data revealed that irradiation enhances the decomposition and the effect increase with the irradiation dose. The activation energy is decreased on irradiation. The mechanism for the thermal decomposition was also investigated. It is seen that the rate controlling process is a phase boundary reaction assuming spherical symmetry and follows the equation.

$$[1-(1-\alpha)^{1/3}] = kt$$

Thermal decomposition of $\gamma$-irradiated manganese carbonate has been reported. The DTA investigation showed that $\gamma$-irradiation greatly enhanced the thermal decomposition of manganese carbonate yielding $\text{MnO}_2$ which was more readily decomposed at about 430°C yielding $\text{Mn}_2\text{O}_3$.
Thermal decomposition of basic cobalt and copper carbonates have been studied.\textsuperscript{184} It is seen that thermal stability of Co$_3$O$_4$ is enhanced up to 850°C upon irradiation. Thermal decomposition studies of $\gamma$-irradiated silver carbonate\textsuperscript{185} has also been made. The thermal decomposition studies of silver cyanamide irradiated with $\gamma$-rays, has also been reported.\textsuperscript{186} The thermal decomposition of irradiated silver oxide\textsuperscript{187} has been studied and it is seen that irradiation has no effect on thermal decomposition. Effect of $\gamma$-radiation on thermal decomposition of Co$_3$O$_4$, Cu$_2$O and CuO has been reported. Studies showed that irradiation decreases the thermal stability of Co$_3$O$_4$ and increased that of Cu$_2$O and CuO.\textsuperscript{188}

The thermal decomposition of $\gamma$-irradiated potassium chlorate has also been studied by dynamic thermogravimetry.\textsuperscript{189} The rate of decomposition increased with irradiation dose while the activation energy decreased. The mechanism for decomposition followed Avrami model equation.

The thermal decomposition of $\gamma$-irradiated anhydrous cadmium nitrate was studied by dynamic thermo gravimetry.\textsuperscript{190} The reaction order, activation energy, frequency factor and entropy of activation was calculated by Coats-Redfern method. Irradiation enhances the thermal decomposition and the effect increase with irradiation dose. Non- isothermal thermogravimetric studies of $\gamma$-irradiated strontium nitrate\textsuperscript{191} and lead nitrate\textsuperscript{192} have been reported. The mechanism for the thermal decomposition of
aluminium nitrate\textsuperscript{193} and lanthanum nitrate\textsuperscript{194} has also been carried out. In lanthanum nitrate the decomposition proceeds via three consecutive stages characterized by different activation energies. Irradiation enhanced decomposition and the effect increased with irradiation dose. The mechanism of the reaction was studied.

Non-isothermal thermogravimetric studies of irradiated zinc oxalate, hydrated ferric oxalate and manganese oxalate have been reported\textsuperscript{195-197}. In hydrated ferric oxalate crystals, the fractional decomposition as well as rate of reaction increases with increase in irradiation dose up to 10Mrads after which both of these decrease. Analysis of thermoanalytical data revealed that irradiation lowers $E$, $Z$ and $\Delta S$ values for zinc oxalate while in manganese oxalate these values reached a minimum and then increased. In manganese oxalate a change in mechanism for thermal decomposition of irradiated sample is observed. The effect of $\gamma$-irradiation on thermal decomposition of ammonium oxalate monohydrate\textsuperscript{198} and calcium-gadolinium oxalate\textsuperscript{199} by dynamic thermo gravimetry has been reported. Kinetic analysis revealed that activation energy for the dehydration step is much higher than that in the non-irradiated sample.

The thermal decomposition kinetics and mechanism of $\gamma$-irradiated lanthanum-barium oxalate\textsuperscript{200} and barium oxalate\textsuperscript{201} in presence of dysprosium oxide have been studied by rising temperature technique. It is seen that irradiation as well as mixing enhances the rate of reaction and decrease the activation energy, the effect being prominent in the latter case.
Studies on non-isothermal decomposition of $\gamma$-irradiated potassium permanganate has been reported by Protashchik.\textsuperscript{202} Studies showed that rate of decomposition of the substance is increased upon irradiation. According to Erofeev and Protashchik\textsuperscript{203} radiation affects the rate of thermal decomposition of potassium permanganate by increasing the number of potential centers on which the appearance of growth centers of nuclei of the solid product would be possible.

\subsection*{1.2.3 Complexes}

While the effect of $\gamma$-radiation on thermal decomposition of inorganic salts is well documented, literature concerning the same in inorganic complexes is scanty. However thermal decomposition studies of only a few $\gamma$-irradiated complexes have been reported.

\subsubsection*{1.2.3.1 Isothermal method}

Isothermal decomposition kinetics of $\gamma$-irradiated cobalt (II) succinate and cobalt (II) malonate have been investigated.\textsuperscript{204,205} In succinate complex irradiation enhanced both the decomposition and dehydration reaction without modifying their mechanisms. The activation energy decreased with increasing irradiation dose. In malanato complex the activation energy for the dehydration stage decreased upon irradiation while the same for the decomposition stage remained unaltered. The kinetics of dehydration is controlled by a phase boundary mechanism while the decomposition reaction is controlled by a first order mechanism.
The thermal decomposition of \( \gamma \)-irradiated complexes of mandel hydroxamic acid with Co, Mn, Ba and Cd were studied thermogravimetrically under isothermal condition. The effect of \( \gamma \)-irradiation on the kinetic parameters of thermal decomposition is discussed. Radiation did not modify the mechanism of the reaction but accelerated the dehydration steps in the case of Co and Mn complexes. Kinetic studies on the thermal decomposition of \( \gamma \)-irradiated cobalt crotonato complex were studied using isothermal thermogravimetric method. The isothermal study indicated that the decomposition reaction proceeds in accordance with the three dimensional phase boundary mechanism. Irradiation enhances the decomposition reaction but does not modify its mechanism. The activation energy decreases as the radiation dose increases. Thus irradiation enhanced the decomposition reaction and activation energy was decreased as the radiation dose increased. Isothermal decomposition studies of \( \gamma \)-irradiated \([\text{Co(NH}_3\text{)}_6]\text{Cl}_3\) has also been reported. It was seen that pre-treatment reduced the length of the induction period and increased the rate of decomposition without modifying the mechanism of thermal decomposition which was proceeded by a nucleation and growth. The activation energy reduced from 46.82 to 20.22 kJ/mol upon irradiation.

### 1.2.3.2 Non-Isothermal method

Thermal decomposition of \( \gamma \)-irradiated cobalt crotonato complex has also been studied under non-isothermal conditions. The study indicated that the decomposition reaction proceeds in accordance with the
three dimensional phase boundary mechanism. Irradiation enhances the decomposition reaction but does not modify its mechanism. The activation energy decreases as the radiation dose increases.

Effect of gamma irradiation on non-isothermal decomposition kinetics of bis(diethylenetriamine)cobalt(II)nitrate and bis(diethylenetriamine)zinc(II)nitrate have been studied in nitrogen atmosphere at a heating rate of 10°C/minute. The data were analysed by Coats-Redfern, Freeman-Carroll and Horowitz-Metzger methods. The results showed that irradiation enhanced thermal decomposition in both the complexes. Activation energy and associated kinetic parameters are lowered upon irradiation and the extent of lowering is higher in cobalt complex compared to zinc complex. Order of the reaction for each step was found to be unity. The mechanism for deamination and decomposition is controlled by R_2 function except for the deamination of unirradiated cobalt complex where the process is governed by R_3 function.

Effect of variation of irradiation dose on non-isothermal decomposition of bis(diethylenetriamine)cobalt(II)nitrate has also been investigated. The data were analysed by the integral method of Coats-Redfern, differential method of Freeman Carroll and approximation method of Horowitz – Metzger. Kinetic parameters for deamination were found to decrease upon irradiation, the effect being increasing with irradiation dose. Kinetic parameters for decomposition of the deaminated complex also decrease upon irradiation up to 50 Mrad and thereafter the process was found to be retarded. Order of the reaction for each step was found to be unity. The
mechanism of deamination of unirradiated bis(diethylene triamine) cobalt(II) nitrate is governed by $R_3$ function, ie phase boundary reaction with spherical symmetry while the same in pre-treated samples is $R_2$ ie. Phase boundary reaction with cylindrical symmetry. Decomposition of the deaminated complex is governed by $R_2$ function in both irradiated and unirradiated samples.

Effect of $\gamma$-radiation on non-isothermal decomposition of nickel(II) complexes of diethylene triamine, pyridine and 2-amino pyridine has been carried out. Irradiation enhanced thermal decomposition of the complexes, lowering activation energy, frequency factor and entropy of activation.

**1.2.4 Summary of Effect of Irradiation on Thermal Decomposition**

Solid state reactivity can be altered by pre exposure to energetic radiation. The observed general effects of irradiation on thermal decomposition of solids include abbreviation of the induction period and enhancement of rate constants for both acceleratory and decay stages of reaction. Exceptions are also reported in which irradiation retard the thermal process and inhibit the decomposition due to formation of long lived trapped radicals and holes in the host lattice.

**1.3 X-ray diffraction studies of irradiated solids**

Lattice imperfection caused by irradiation influence the x-ray diffraction pattern of a substance and indeed this was one of the early ways in
which radiation damage was observed. Any imperfections give rise to local changes in diffracted or transmitted x-ray intensities. The presence of defects in a crystalline lattice may change both the unit cell size and the physical size of the crystal. The quantity and structure of a new phase which accumulates during radiolysis and also the accompanying changes in the degree of imperfection of the crystal, can be studied by x-ray\textsuperscript{15,212} and electron diffraction\textsuperscript{213,214} method.

1.3.1 Review on the reported investigation

X-ray diffraction study revealed the use of gamma radiation for the synthesis of nano particles. The effect of $\gamma$-radiation on the surface and catalytic properties of manganese oxide revealed that gamma irradiation decreased the particle size of manganese oxide.\textsuperscript{215} Cadmium sulphide nano particles with mean size 2.3nm have been successfully prepared by irradiating an ethanolic solution of cadmium chloride and carbon disulphide with $^{60}$Co $\gamma$-ray.\textsuperscript{216} Highly water soluble and bio compatible L-cystene capped cadmium sulphide nano particles having narrow size distribution were synthesized for the first time by $\gamma$-irradiation technique without using any additional stabilizer.\textsuperscript{217} Gamma radiation has been applied to synthesise the nano composite semiconductor constituted of zinc and cadmium sulphide ultra fine particles at room temperatures by utilizing homogeneous release of S$^2$- ions from the decomposition of sodiumthiosulphate.\textsuperscript{218} Effect of $\gamma$-irradiation on surface and catalytic purpose of Co$_3$O$_4$ doped with NiO have been studied.\textsuperscript{219} The results revealed that $\gamma$-irradiation brought a significant decrease in the
particle size of $\text{Co}_3\text{O}_4$. Colloidal silver nano particle were synthesized by $\gamma$-radiation method and stabilized by poly(4-vinyl pyridine) to form highly stable suspension in ethylene glycol.\textsuperscript{220}

A change in texture and crystal structure of zinc acetate\textsuperscript{165} cobaltous acetate,\textsuperscript{157} palladium acetate,\textsuperscript{159} zinc uranyl acetate\textsuperscript{22} and hydrated aluminium nitrate\textsuperscript{193} by $\gamma$-irradiation was studied using scanning electron microscopy and x-ray diffraction techniques.

X-ray diffractogram were recorded for unirradiated and irradiated manganese carbonate.\textsuperscript{183} The relative intensity of the main diffraction line of $\text{MnCO}_3$ was found to suffer a two-fold increase after $\gamma$-irradiation. Indeed no broadening in the diffraction lines of $\text{MnCO}_3$ was observed in the case of irradiated solid indicating the absence of any change in the lattice parameter of $\gamma$-irradiated manganese carbonate XRD and SEM of $\gamma$-irradiated calcium carbonate\textsuperscript{23} in egg shell was carried out.

The effect of ionizing radiation on chloramphenicol\textsuperscript{221} was studied by XRD. No significant change relative to the unirradiated sample was observed as a result of irradiation with the dose of 25kGy, besides free radical generation. But higher doses were found to produce changes in colour and change in the XRD spectrum.

In order to verify the change of crystallinity upon irradiation x-ray diffraction of ciprofloxacin\textsuperscript{222} was examined for non irradiated and irradiated drug powder samples. The irradiated samples showed less degree of crystallinity as evidenced by fewer peaks of lower intensity. The characteristic
of diffraction peaks relevant to crystalline ciprofloxacin nearly disappeared with increasing the dose of radiation from 15 to 100kGy. The difference in x-ray pattern suggests the formation of amorphous ciprofloxacin upon irradiation and as the irradiation dose increases the amorphous form was predominant.

Study of γ-irradiation effects on chitosan microparticles were carried out. Size and crystallinity of the chitosan microparticles did not change much after γ-irradiation.

X-ray diffraction studies of nickel(II) complexes of diethylene triamine, pyridine and 2-aminopyridine were carried out before and after γ-irradiation. From x-ray diffraction studies unirradiated and irradiated complexes are found to be orthorhombic. Irradiation changed lattice parameters.

Effects induced by γ-irradiation on intraband transitions in Sr\(^{2+}\) doped ammonium zinc chloride crystal were studied. Considerable changes were observed in the x-ray diffraction pattern of ammonium zinc chloride after doping with Sr\(^{2+}\) in different concentrations and after irradiating with γ-rays of different doses. The effect of γ-radiation and Sr\(^{2+}\) content on optical parameters of (NH\(_4\))\(_2\) ZnCl\(_4\) xSr\(^{2+}\) single crystals (x = 0.00, 0.020, 0.039, 0.087 or 0.144) has been investigated.

The effect of chemical non-stoichiometry and γ-irradiation on the unit cell parameters of ammonium tetrachlorozincate has been studied. The unit cell parameters of crystal grown from solution with NH\(_4\)Cl/ZnCl\(_2\) molar ratio 1:1, apparently non-stoichiometric, are nearly the same as those given
for ammonium tetrachlorozincate in the literature. The 2:1 ratio is actually pseudo-stoichiometric due to the hygroscopic nature of ZnCl₂.

The changes in texture and crystal structure of silver acetate induced by γ-irradiation were studied by x-ray diffraction technique. The results evaluated, regards to utilization of silver acetate as industrial catalyst.

The effect of γ-irradiation on the polymer electrolyte PEO-NH₄ClO₄ has been done. X-ray study showed that irradiation affects the structure of materials at different scales, thus changing physical and chemical properties.

Structural changes of the IR-transmitting tellurite, gallate and aluminate glasses caused by γ-irradiation was studied by x-ray diffraction.

X-ray diffraction studies of γ-irradiated lithium nitrate and lanthanum nickelate have been reported. Studies of γ-irradiated lithium nitrate evidenced the distortion of lattice planes. X-ray photoelectron spectroscopy showed that γ-irradiation of lanthanum nickelate in the presence of moisture leads to reduction of the transition metal (Ni³⁺ to Ni²⁺) which in turn facilitates the formation of O²⁻ and surface carbonate species.

The effect of γ-radiation on the surface and catalytic properties of Co₃O₄ doped with nickel oxide, manganese oxide doped with MoO₃ and V₂O₅ have been studied. The x-ray diffraction study revealed that gamma irradiation decreased the particle size of cobalt oxide and manganese oxide.
Comparison of x-ray diffraction patterns of non-irradiated and irradiated double metal phosphates of zirconium, titanium and hafnium\textsuperscript{229} have been reported.

Poly(lactide-co-glycolide)nanoparticle incorporating ciprofloxacin were prepared and subjected to $\gamma$-radiation.\textsuperscript{230} The effect of $\gamma$-radiation on the particle size and drug release was evaluated by x-ray analysis.

1.3.2 Summary

X-ray diffraction pattern of crystalline solids are considerably affected by irradiation. The observed general effects include lattice distortion, changes in crystalline identity, crystallinity and relative intensity. X-ray studies have also revealed that particle size can be decreased by irradiation. Systems in which no significant changes are observed have also been reported.

1.4 Electronic spectral studies of irradiated solids

Gamma irradiation causes remarkable changes in the intensities of most of the absorption bands of metal complex. The rate of change depends on the nature of metal ions. The absorption bands in the electronic spectra of metal complexes can be broadened by many vibrational transitions. The magnitude of ligand field parameter $Dq$ is sensitive to metal-ligand bond length. Since the M-L bond vibrates continuously $Dq$ also fluctuates so that electronic transition will occur over wide range of energies, resulting in broadening of bands.
1.4.1 Review

Studies concerning the effect of gamma radiation on the electronic spectra of complexes are rare. Electronic spectra of diethylenetriamine complexes of cobalt(II) and nickel(II)\textsuperscript{231} before and after gamma irradiation have been reported. Results showed that CFSE is affected by irradiation in these complexes. The bands in the uv spectra of the irradiated complexes are broad and this is possible only if the field strength fluctuate over a significant range of energy.

Effect of γ-irradiation on the electronic spectra of nickel(II) complexes of diethylenetriamine, pyridine and 2-amino pyridine has been investigated.\textsuperscript{211} The parameters LFSE, $B^1$ and $\beta$ were calculated from the uv-visible spectra of the complexes. Irradiation decreases LFSE and increased Racah parameter $B^1$ and the covalency factor $\beta$ of the complexes except in nickel(II) complex of diethylenetriamine where the effect of irradiation is insignificant.

Gamma radiolysis of ampicillin cobalt complex in aqueous solutions was studied at doses from 20 to 100 Gy, using a Cs source.\textsuperscript{232} The variations in UV spectra due to their radiolysis were shown. The results showed an increase in absorbance values with increasing dose and this dependence is linear in the dose range studied.

Effect of γ-radiation on folic acid and its complexes were studied in aqueous solution at doses ranging from 2 to 10 k rad and from 2 to 10 M
rad using $^{60}$Co source.\textsuperscript{91} The variations in their uv-visible spectra due to radiolysis were studied.

Mixed ligand complexes of 5-arylazo-8-hydroxy quinoline and $\alpha$-amino acids with Co(II), Ni(II) and Cu(II) were studied before and after $\gamma$-irradiation.\textsuperscript{233} Electronic spectra of the complexes were studied.

The electronic absorption spectra of dithizone and its metal complexes of Hg, Cd and Zn doped in poly(methyl methacrylate) has been investigated before and after gamma irradiation\textsuperscript{234} It is found that the complex formation resulted in significant changes in both the position and the intensity of electronic bands of dithiozone. Gamma radiation causes remarkable decrease in the intensities of most of the bands of complex. Rate of decrease depends on nature of metal ions.

Gamma irradiation induced changes in the structure of poly(acrylamide) treated with metal chloride were investigated by following the corresponding variations in the uv spectra.\textsuperscript{235} Careful examination of uv spectra revealed that irradiation of the specimens results in appearance of an absorption peak at 275nm whose intensity depends on the applied dose and nature of metal ions.

Gamma irradiation for various spin cross over iron(III) complexes were performed in order to examine the spin transition mechanism.\textsuperscript{236} The difference of the spin transition mechanism was reflected
in the difference of the fractions that the electronic state of the ion atoms changed to low spin at low temperature and the results were explained by using a phenomenological model.

The uv-visible absorption spectrums of transition metal doped cabal glasses\textsuperscript{237} were measured before and after gamma irradiation. The absorption spectrum of the undoped glass exhibit charge transfer bands due to iron trace impurities which eventually affect the induced absorption due to some transition metals and that due to the host base glass in the uv region.

Potassium nitrate in pellet form has been used in dosimetric materials for high \(\gamma\)-dose measurements in the industrial application of radiation.\textsuperscript{238} The evaluation technique is based on the changes observed in the optical properties of solution prepared with irradiated and non-irradiated pellets by means of spectrophotometric analysis. The parameters studied were absorption spectra before and after \(\gamma\)-irradiation, sensitization concentration, signal stability etc.

The surface change of ciprofloxacin\textsuperscript{222} due to irradiation was verified by spectrophotometric scanning of dissolved powder from both unirradiated and irradiated samples. All the samples showed identical and super imposed peaks at wave length 329, 316, 277, 214 in the uv range which is matched with the reported monograph of the drug. In addition no trace of any peaks was noticed in the visible range indicating that no radiolytical intermediates were formed during irradiation. Thus, surface changes can be
explained by the displacement of the atoms and trapping of electrons in the negative ion vacancies leading to imperfections and these induce colour change without changing the chemical build up of the molecule.\textsuperscript{239}

The effect of ionizing radiation on chloramphenicol\textsuperscript{221} was studied by uv. No significant change relative to the unirradiated sample was observed as a result of irradiation with the dose of 25KGY, besides free radical generation. But higher doses were found to produce increase in absorbance.

UV-vis spectrometry was used to monitor antibiotic release experiments performed over amoxicillin\textsuperscript{240} loaded chitosan/PHEMA before and after gamma irradiation.

1.4.2 Summary

Defects caused by irradiation have a profound influence on the electronic spectra of materials. The observed significant changes include decrease in the intensity of bands, shift in $\lambda_{\text{max}}$ and broadening of spectral bands.

1.5 Antimicrobial studies

1.5.1 General

Radiation offers several advantages as a sterilization method that makes it attractive in a growing number of situations over the conventional methods. Radiation sterilization has the advantage of avoiding high temperature as well as toxic chemicals like ethylene oxide. High
penetrability of nuclear radiation enables to cover all parts of the object to be sterilized. Thus the material can be sterilized after final packing in a continuous process. Further no residual radiation is left in the product. Moreover as the single operating variable is the exposure time, the process can be easily monitored and posses the advantage of being considerably economic. Articles sterilized by radiation include a large variety of disposable medicinal products, sutures and implants, pharmaceuticals and cosmetics, biological tissues and so on.\textsuperscript{241-246} Gamma irradiation was proposed in the British Pharmacopoeia\textsuperscript{247} as a suitable sterilization method for sterilizing certain surgical materials and equipments with a dose requirement of 25kGy.

1.5.1.1 Process of activating and inducing antimicrobial properties by irradiation

Irradiation of antimicrobial materials which contain atomic disorder will activate or enhance the antimicrobial effect.\textsuperscript{248} Thus, even materials having a low level of atomic disorder may be activated to an antimicrobial level. Irradiation is performed with any low linear energy transfer form of radiation including beta, gamma and x-rays. Gamma radiation at a dose of 10kGy or greater is preferred.

It is believed that irradiation step is causing one or more of the following changes in the antimicrobial material.

1. Creating further atomic disorder, such as point defects.
2. Enhancing oxygen adsorption/chemisorption to the surface of the antimicrobial material.
3. Activating trapped dopant atoms or molecules such as oxygen O\(^+\) or O\(^-\) and

4. Creating broken or dangling bonds at the surface.

With respect to the second and third proposed mechanisms it is possible that oxygen adsorption/chemisorption and/or activation creates a super saturated concentration of O\(_2\), O\(^+\) or O\(^-\) species in or on the antimicrobial metal surface which results in the more rapid dissolution of the anti microbial metal or species thereof into an aqueous environment through the generation of various chemical species of the antimicrobial metal including oxides and hydroxides.

Process of enhancing antimicrobial activity of materials by irradiation with gamma rays is a topic of recent interest. Literature survey revealed that irradiation is capable of changing the antimicrobial properties of materials. Reported investigations relevant in this area are reviewed.

1.5.2 Review

The influence of gamma irradiation and dry heat sterilization on the properties of a bioadhesive powder mixture containing ciprofloxacin and its corresponding ocular mini tablets\(^{249}\) have been carried out. The influence of the different sterilization methods on the characteristics of the ocular minitablets was investigated by measuring the crushing strength, the friability and the in vitro release of ciprofloxacin from the minitablets. Results proved that \(\gamma\)-irradiation was a better sterilization method for the bioadhesive ocular
minitablets than dry heat sterilization, because it affected the physical properties of the minitablets only to a very small extent. The result showed that gamma irradiated mini tablets containing ciprofloxacin can be considered as a promising formulation to treat bacterial keratitis and conjunctivitis.

Antimicrobial activities of irradiated chitosan\textsuperscript{250} were studied against Escherichia coli. Irradiation of chitosan at 100kGy under dry condition was effective in increasing the activity and inhibited the growth of E.coli completely. Antimicrobial activity assay of chitosan fractionated according to molecular weight showed that $1 \times 10^5 - 3 \times 10^5$ fraction was most effective in suppressing the growth of E.coli. The results showed that low dose irradiation, specifically 100kGy, of chitosan give enough degradation to increase its antimicrobial activity.

Study of gamma-irradiation effects on chitosan microparticles were carried out.\textsuperscript{223} $\gamma$-irradiated microparticles exhibited a slightly higher drug release rate than non-irradiated microparticles.

Poly phenols\textsuperscript{251} of green tea leaf were separated and irradiated at 40kGy to investigate the effect of irradiation on biological and antimicrobial activities. The antimicrobial activities against staphylococcus aureus and streptococcus mutans were higher in the irradiated sample, which showed inhibition of microorganism tested at a lower concentration than those of the non-irradiated sample. Ranges of inhibition zone for growth of E.Coli, S.aureus, S.epidermidis and S.mutans, at 1mg/disc., were 9.3 mm, 10.1, 22.5
and 9.3 mm in non-irradiated control, but 10.8, 11.0, 25.0 and 11.7 mm respectively in irradiated samples. Results indicated that irradiation of polyphenols, the major bioactive compound in green tea, may maintain the biological activities and even increase the antimicrobial activity. The results also demonstrated that irradiation of green tea polyphenols, for removal of dark colour, may find application in the food or cosmetic industries.

The investigation about the radiolytic materials and antimicrobial activities of gamma irradiated acrinol$^{252}$ on liquid dosage form has been carried out to study the application of radiosterilization. Increase of antimicrobial activity was observed with gamma irradiated acrinol solution, but this phenomenon was not long-lasting. The microorganism such as Pseudeomonas aeruginosa or staphylococcus aureus that infect at the lips of wound are highly sensitive to gamma irradiation. They are almost sterilized by the irradiation of 10 kGy. At a low acrinol concentration, the decomposition rate of acrinol by irradiation was relatively high. When 1.0% of acrinol solution was irradiated at a dose of 10kGy, the decomposition of the drug was less than 2% and the variation of antimicrobial activity was negligible.

Physicochemical characterization and bio-activity of ciprofloxacin-PLGA$^{230}$ nano particles have been carried out. Effect of gamma irradiation on the particle size and drug release was evaluated. DSC and XRD analysis of the compounds and the nano particles were performed. The activity of two series of microorganisms, pseudomonas aeruginosa and staphylococcus were examined.
Acrylic acid was grafted onto polypropylene fabric by pre-irradiation method using $^{60}$Co $\gamma$-ray. Antibacterial activities on metallic complexes of acrylic acid-grafted polypropylene fabric were evaluated by a viable cell counting method. Antimicrobial activities of this irradiated fabrics and its metallic salts were studied. The results showed that silver complexed fabric had strong biocidal effect for all bacteria. Iron, copper and zinc complexed fabrics had different antibacterial activities depending on each bacteria.

Characterization of $\gamma$-irradiated chitosan / poly (hydroxy ethyl methacrylate) for biomedical purposes was studied. The obtained results showed that the hydration capacity decrease in the irradiated membrane. It was also found that chitosan/PHEMA membranes present good barrier properties against microbes.

The effect of $\gamma$-irradiation on antimicrobial activity of ciprofloxacin has been tested by agar diffusion technique using Mueller Hinton agar. The study showed that there was no significant change in inhibition zones for all the tested samples. This reveals that antimicrobial activity of ciprofloxacin was not affected by irradiation and still retains its maximum antimicrobial activity at all the tested irradiation doses. This is in accordance with the tests that showed no change in the chemical structure by the drug upon irradiation at doses ranging from 0-100 kGy.

An investigation was carried out to assess the effect on the antibacterial activity of honey, when honey was subjected to a commercial
sterilization procedure using $\gamma$-irradiation. Investigation showed that 25kGy was sufficient to achieve sterility.\textsuperscript{255}

Effect of $\gamma$-irradiation on two heat resistant moulds, Aspergillus fumigatus and Paccilomyces variotii were done. The results showed that the sensitivity of Paccilomyces variotii against $\gamma$-irradiation was more than Aspergillus fumigatus.\textsuperscript{256}

A new antimicrobial agent is produced by irradiation of pyridoxamine under aerobic and anaerobic conditions.\textsuperscript{257} The potency of the agent found is critically related to the wave length and duration of irradiation, $H^+$ ion concentration, temperature and concentration. Irradiated pyridoxamine is active against Escherichia coli and to a lesser degree against Staphylococcus and Streptococcus hemolyticus. Non-irradiated solutions of pyridoxal and sulphapyridine gave complete inhibition growth of E.coli. But irradiation failed to alter this activity. Non-irradiated pyridoxine had no antibacterial potency but upon irradiation, it gave inhibition of growth.

Biological evaluation of pyrazinamide liposomes for treatment of mycobacterium on tuberculosis was studied.\textsuperscript{258} Induced activity of rifamycin\textsuperscript{259} and amoxicillin-tri-hydrate\textsuperscript{260} powder was investigated. Antimicrobial activities of antibiotics sulfafurazole, sulfamethoxazole and sulfacetamide\textsuperscript{261} were studied, before and after gamma irradiation. The results obtained under normal and accelerated stability conditions were observed to be consistent with the unirradiated values.
The radiosterilized pharmaceuticals like ceftriaxone, cefoperazone and cefotetan were studied by ESR technique.

1.5.3 Summary

Radiation sterilization of medical devices, drugs and pharmaceuticals are effective, easier and relatively cheaper. Antimicrobial property is sensitive to radiation treatment. Influence of irradiation on bioactivity seems to be different in different systems. In some cases existing activity is enhanced while in some other cases it remained as such. Cases in which the impact of irradiation resulted in inducement of bioactivity have also been reported.

1.6 Scope of the present investigation

Effect of gamma radiation on thermal decomposition and the kinetics thereon for crystalline salts containing oxyanions are well documented, while the same in metal complexes are scarce. However irradiation effects on thermal decomposition of a few transition metal complexes have been reported. In the present investigation effect of gamma radiation on non-isothermal decomposition kinetics of the following transition metal complexes are studied.

1. tris (ethylenediamine) cobalt(II) nitrate,
2. tris (ethylenediamine) nickel(II) nitrate,
3. tris(ethylenediamine)zinc(II)nitrate,
4. tris(ethylenediamine)cadmium(II)nitrate,
5. dinitratotriethylenetetraminecobalt(II),
6. dinitratotriethylenetetraminenickel(II),
7. dinitratotriethylenetetraminezinc(II),
8. dinitratotriethylenetetraminecadmium(II),
9. dinitratobis(o-toluidine)cobalt(II),
10. dinitratobis(o-toluidine)nickel(II),
11. dinitratobis(o-toluidine)zinc(II) and
dinitratobis(o-toluidine)cadmium(II)

Non-isothermal data were analyzed by integral method using Coats-Redfern equation. The study proposes to find out and compare the thermal and kinetic parameters of unirradiated and irradiated samples of these complexes.

Literature survey revealed that influence of γ-radiation on x-ray diffraction pattern has been investigated in many technologically important materials as well as in simple inorganic salts. However such studies are lacking in transition metal complexes. Therefore a study has been made to ascertain the changes in crystalline features brought about by gamma irradiation in the following complexes.

1. tris(ethylenediamine)nickel(II)nitrate,
2. tris(ethylenediamine)zinc(II)nitrate,
3. tris(ethylenediamine)cadmium(II)nitrate,
4. dinitratotriethylenetetramineneNickel(II) and
dinitratotriethylenetetramine zinc(II).

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Electronic absorption spectral studies of $\gamma$-irradiated metal complexes are rare. The present study also aims at electronic absorption spectral studies of $\gamma$-irradiated complexes. Complexes of cobalt(II) and nickel(II) ie.,

1. tris(ethylenediamine)cobalt(II)nitrate,
2. tris(ethylenediamine)nickel(II)nitrate,
3. dinitratotriethylenetetraminecobalt(II),
4. dinitratotriethylenetetraminenickel(II),
5. dinitratobis(o-toluidine)cobalt(II) and
6. dinitratobis(o-toluidine)nickel(II) were selected for this purpose.

The study proposes to compare LFSE and co-valency factor $\beta$ before and after irradiation.

Ionising radiation is gaining interest as a sterilization process for medicinal products. Literature survey revealed that irradiation is capable of changing the antimicrobial properties of materials. The study on the antimicrobial activities of $\gamma$-irradiated metal complexes is still rare. So an attempt is made to study the effect of gamma radiation on antimicrobial activities of the following complexes

1. tris(ethylenediamine)zinc(II)nitrate,
2. tris(ethylenediamine)cadmium(II)nitrate,
3. dinitratotriethylenetetraminezinc(II),
4. dinitratotriethylenetetraminecadmium(II),
5. dinitratobis(o-toluidine)zinc(II) and
6. dinitratobis(o-toluidine)cadmium(II).