The work presented in this thesis is divided into three major parts as follows:

The first part (Introduction) deals with a review of literature on the chemical effects following \((n, \gamma)\) reaction in gases, liquids and solids. A brief introduction is given regarding the chemical damage following \((n, \gamma)\) reaction in organic compounds. Some of the theories proposed by different investigators to account for the recoil reactions are also considered. This part further deals with the retention studies in some inorganic crystals and effects due to subsequent thermal and radiation annealing. The kinetics involved in these annealing processes are also presented in brief.

Methods

The second part (Experimental) describes details of experiments carried out for the irradiation and annealing processes, as also the details and precautions for activity measurements in carbon tetrachloride and in water layers. Experiments are also described for gamma radiolysis and thermogravimetric analysis of iodates.

The third part (Results and Discussion) is devoted to the chemical effects following thermal neutron capture in crystals of iodates (lithium, sodium and potassium iodate, as well as iodic acid) and the variation in initial retention due to irradiation with neutrons obtained from different sources. The findings regarding the effects of temperature
of irradiation and dissolution as well as effects due to cation, crystal structure, etc. are also presented.

Further, the results of pre- and post-thermal and gamma treatments of neutron irradiated iodates are presented. The important observations are as follows:

1. The retention of $^{128}$I at room temperature in the iodate systems studied is found to lie between 67 and 80 per cent for irradiation with an (Sb-Be) photoneutron source and between 65 and 76 per cent with a (Pu-Be) neutron source which is free from gammas. These results suggest that major part of the initial retention cannot be attributed wholly to radiation annealing by the gammas present in the (Sb-Be) source. The initial retention, however, is considered to be due to (i) failure of the bond rupture subsequent to the neutron capture, (ii) reformation of the target molecule by rapid geminate recombination of the fragments, (iii) recombination of the recoil fragments due to cage effect, (iv) reformation by epithermal reactions, and (v) annealing reactions induced by heat and/or ionizing radiation during irradiation.

2. Retention increases with the atomic number of the alkali metal, e.g. KI$O_3$ has a higher initial retention than NaI$O_3$ and HIO$_3$ while the anomalously high retention of LiI$O_3$ could be due to its different crystal structure. LiI$O_3$ has a hexagonal lattice while iodates of other alkali metals are believed to have a structure close to that of perovskite family.
(3) Change of irradiation temperature (from -195 to 90°C) is found to vary the retention widely. The difference between the lowest and highest values is 35, 20, 22 and 21 per cent for HIO₃, LiIO₃, NaIO₃ and KIO₃ respectively. In the case of HIO₃ and LiIO₃ no further change in retention was observed unlike in NaIO₃ and KIO₃, when the irradiation temperature was lowered from -80 to -195°C.

(4) Lithium iodate showed a 4 per cent increase in retention when irradiated at 0°C and dissolved at 30°C. However, irradiation at 30°C and dissolution at 0°C showed no change in retention in the iodate systems.

(5) Pre-thermal treatment up to 24 hours at temperatures in the range 90 to 350°C showed a decrease in retention by 8 per cent in LiIO₃, but no significant change in NaIO₃ and KIO₃ was observed when identically treated. On the contrary, HIO₃ showed a small increase of 3 per cent following pre-thermal treatment at 90°C.

(6) Gamma treatment for doses from 3 to 120 Mγ-rad prior to neutron irradiation showed no significant change in initial retention in LiIO₃; but in KIO₃ the retention decreased from 79 to 71 per cent and remained constant from 84 Mγ-rad onwards. A similar observation was also made in NaIO₃ for a dose of 72 Mγ-rad i.e. after a slight initial decrease of 3 per cent, its retention remained constant at 70 per cent. In the case of HIO₃, however, an increase in retention by about 9 per cent was observed for a gamma dose of 48 Mγ-rad.
and thereafter a constant or saturation value was obtained for higher doses.

(7) Gamma radiolysis of iodates subjected to a maximum dose of 120 Mrad, produced $0.23 \times 10^{-4}$ M of extractable iodine per gram of HIO$_3$; similarly the yield of iodine was much less in other iodates for the same gamma dose.

(8) Gamma annealing of all the neutron irradiated iodates led to an increase in retention by 3-4 per cent for a dose of about 0.1 M$^{-1}$rad.

(9) The rate of isothermal annealing, in general, was found to be fast in the beginning but slowed down later leading to a constant value of retention at each temperature.

(10) Almost 100 per cent retention was obtained at highest annealing temperature employed for all the iodates under study.

(11) The pseudo-plateau value at any annealing temperature was higher for iodate samples irradiated at 0°C compared to those irradiated at 30°C, though the initial retention value was lower for irradiation at 0°C compared to irradiation at 30°C.

(12) As the temperature was raised, the pseudo-plateau value increased for HIO$_3$ samples irradiated and annealed at 30, 60, 75 and 90°C. A gradual increase in the difference was observed between these plateau values and the corresponding plateau values obtained for HIO$_3$ samples irradiated at 0 or 30°C but annealed at 30, 60, 75 and 90°C.
(13) For all the iodates studied, a linear relationship was obtained between the change in retention $\Delta R$ and the reciprocal of absolute temperature, $(T)^{-1}$ of annealing.

(Here, $\Delta R = [R_p - R_o]$, $R_p$ being the maximum retention or the pseudo-plateau value observed at a particular temperature and $R_o$ is the initial retention for samples irradiated at 0 or 30°C). By extrapolation of the linear plot to the temperature axis, the threshold temperature of annealing for the iodate systems is calculated and is found to be dependent upon the irradiation temperature. The findings are as follows:

<table>
<thead>
<tr>
<th>Iodate</th>
<th>Threshold temperature of thermal annealing for irradiation at</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$0^\circ C$</td>
</tr>
<tr>
<td>HIO$_3$</td>
<td>14.3</td>
</tr>
<tr>
<td>LiIO$_3$</td>
<td>-14.0</td>
</tr>
<tr>
<td>NaIO$_3$</td>
<td>-11.3</td>
</tr>
<tr>
<td>KIO$_3$</td>
<td>-24.3</td>
</tr>
</tbody>
</table>

(14) The kinetics of the isothermal annealing in the iodate systems is studied by applying a classical treatment considering the decrease in the concentration of the radiofragments which are yet destined to anneal at each time $t$, and the difference in retention $\Delta R_t = (R_p - R_t)$, where $R_t$ represents the retention at time $t$ for a particular temperature.
of annealing. The plot of log $\frac{R_t}{R_0}$ against time gave straight lines, (here, $R_0 = (R_p - R_o)$, $R_o$ being the initial retention at $t = 0$) and from the slopes of these, the respective first order rate constants $k$ (min$^{-1}$) were calculated at each annealing temperature, for all the iodates under study. Thus the overall kinetics of annealing reactions is found to be of the first order.

(15) From the Arrhenius plot, the activation energy calculated for lithium, sodium and potassium iodates is found to be about 1.9, 1.6 and 1.3 kcal/mole, respectively. This plot, not being a straight line in the case of HIO$_3$, suggests that more than one activation energy is involved in this case.

(16) Studies of $(n,\gamma)$ reaction in aqueous solutions of iodates showed a dependence of retention with concentration of the solution. At the highest concentration, the maximum retention obtained was less by about 40 per cent compared to the retention in crystalline iodates. By extrapolation of the % retention versus concentration plot, the minimum retention at zero concentration is found to be between 25-29% in the different iodate solutions studied.

(17) The recoil energy following $(n,\gamma)$ event generally exceeds the lattice energy of the crystal resulting in a finite separation of the recoil species. However, most of the separated fragments do not possess enough energy at room temperature to overcome the barrier for recombination. During
thermal annealing the necessary energy is provided to
increasing proportions of fragments to overcome the energy
barrier thereby resulting in an increasing proportion of
the combination of these fragments to form the parent mole-
cule. Considering all the possible species produced during
the radiolysis of the iodates, the following mechanism is
suggested.

\[ \text{IO}_3^- \rightarrow \text{IO}_3^- \text{[initial event]} \]

The species then dissociates, resulting in

\[ \text{IO}_3^- \rightarrow \begin{cases} 
*\text{IO}_2^- + 0 \\
*\text{IO}^- + \text{O}_2 \\
*\text{I}^- + 3\text{O} \text{ (or } \text{O}_2 + \text{O}) 
\end{cases} \]

Further, on heating back reactions involving oxygen atoms
may occur as follows.

\[ *\text{IO}_2^- + 0 \rightarrow *\text{IO}_3^- \]
\[ *\text{IO}^- + 0 \rightarrow *\text{IO}_2^- \]

The \( *\text{IO}_2^- \) may dissociate to give

\[ *\text{IO}_2^- \rightarrow *\text{IO}^- + 0, \]

while the oxygen atoms recombine over a third body,

\[ \text{O}_2 + \text{O} + \text{M} \text{ (third body)} \rightarrow \text{O}_2 + \text{(M)}. \]
However, if the reformation of $^{129}_{\text{I}}$ is not wholly accounted by the recombination of non-iodate species and oxygen atoms, then an isotope exchange mechanism in the solid state between the radio-fragments (iodide and iodine) and inactive iodate ions would be a reasonable explanation for the thermal annealing reactions.