EXPERIMENTAL METHODS
FIG. 1. THERMOGRAVIMETRIC ANALYSIS OF LiIO₃
FIG. 2. THERMOGRAVIMETRIC ANALYSIS OF NaIO₃
**EXPERIMENTAL METHODS**

Iodate Samples

Analytical reagent grade sodium iodate, potassium iodate and iodic acid were used without further purification while lithium iodate was prepared by the following method.

Commercially available lithium carbonate was purified following the Caley and Lveing method as they claim that even C.P. or Reagent Grade \( \text{Li}_2\text{CO}_3 \) contains 1% of impurities. This method produces very pure \( \text{Li}_2\text{CO}_3 \) which can rapidly be converted practically into any lithium salt desired, by treatment with the proper pure acid. Lithium carbonate thus prepared was reacted with A. R./iodic acid solution to form lithium iodate according to Rammelsberg's method. Lithium iodate thus obtained was recrystallized twice and carefully dried before use and stored in a desiccator.

Tests for water of crystallization performed thermogravimetrically are presented in Figs. 1 and 2 for lithium and sodium iodates respectively and these are found to be anhydrous. The respective melting point so determined as well as the decomposition temperature of these iodates matched with values reported in literature.

The iodate samples were first ground in an agate mortar and sieved between 100 and 120 mesh. Weighed quantities of these were used for \((n,\gamma)\) irradiation.
FIG. 3(a). THE NEUTRON SOURCE WITH MECHANICAL ARRANGEMENTS FOR IRRADIATION

FIG. 3(b). SOFT GLASS SHELL FOR IRRADIATION OF IODATE SOLUTION BY THERMAL NEUTRONS
Irradiation of Solid Samples

About 1 g of pure and dry iodate sample was taken and vacuum sealed in soft glass tubings. It was then irradiated at room temperature for 100 min in a 13-curie (nominal) $^{124}\text{Sb}^{(+}\text{Be})$ photo-neutron source (flux $\sim 10^6$ n cm$^{-2}$ sec$^{-1}$) the neutrons being thermalized by about 20 cm of paraffin [Fig. 3(a)]. Irradiations at 0°C and lower temperatures were carried out in a small Dewar flask using desired coolants *viz.* ice, dry ice or liquid nitrogen. As for irradiations at higher than room temperature, a specially designed electric furnace maintained at a specific temperature ($\pm 1^\circ\text{C}$) was used. The irradiations were carried out under conditions of constant geometry so that the activity produced in all the samples was almost same. Immediately after neutron bombardment the samples were analysed or else treated thermally or by gammas prior to analysis.

Irradiation of Aqueous Solutions of Iodates

Irradiation of iodate solutions was carried out by taking the solution between two walls of a specially made double walled, soft glass shell and the $^{124}\text{Sb}^{(+}\text{Be}}$ source was allowed to plunge into the cavity of the shell, as shown in Fig. 3(b). This operation was carried out for different concentrations of the iodate solution under study, duration of irradiation being limited to 100 minutes.

Chemical Separation

The solid samples were dissolved in 20 ml of ice cold
water within 1 min after the end of the neutron-irradiation. The iodide and/or iodine produced were separated from the parent iodate ion by a method similar to the one used by Libby \(^{(51)}\). Ice cold 0.3 \(\text{ml} \) solution of 0.1 \(\text{M} \) potassium iodide was added to the iodate solution and acidified. Iodine was liberated according to the stoichiometric relation,

\[
\begin{align*}
\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ & \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}. \\
\end{align*}
\]

The liberated iodine acted as a carrier for all the radioactive iodine formed directly in the \(\text{(n,}\gamma)\) reaction as well as for the \(\text{I}_{28}^-\) oxidised to iodine as per the above relation. The whole of the iodine so obtained was extracted with 20 \(\text{ml}\) of Merck's extra pure carbon tetrachloride, using only \(\sim 5 \text{ ml}\) at a time. The fourth \(\text{CCl}_4\) extract was colourless and was found to give no more measurable activity, thus ensuring complete extraction of the radiiodine. This extraction procedure was carried out at nearly 0\(^\circ\text{C}\) and the time spent was less than two minutes.

To verify that all of the non-iodate fraction has been separated out, again 0.3 \(\text{ml} \) of KI solution was added to the above iodate fraction and the iodine produced was similarly extracted by 20 \(\text{ml}\) of \(\text{CCl}_4\) and this \(\text{CCl}_4\) layer gave no measurable activity while the water layer containing the iodate showed no loss of activity. The experiment clearly shows that (i) the separation between the iodate and iodine is complete and (ii) no detectable exchange between iodine
and iodate takes place during the chemical separation under the conditions of the experiment.

**Verification of Chemical Separation**

About 1 g of inactive sodium iodate crystals was dissolved in 20 ml of pure water and to this 0.3 ml of 0.1M Na$_{131}$I was added and the above chemical separation effected. No appreciable atom transfer or exchange between iodine and iodate was observed at about 0°C or even at room temperature (25°C) for the duration of about two minutes, since no measurable activity was found in the iodate layer. Similarly, when sodium iodate labelled with $^{131}$I was used for verification of the separation technique, it was found that no $^{131}$I activity appeared in the iodine, extracted by CC$_4$Cl$_4$. This is in agreement with the findings of Myers and Kennedy (100) under identical conditions of iodine and iodate concentrations as well as the acidity and temperature, that the half-time of exchange is over hundred hours at room temperature. It is reasonable to assume $^{128}$I behaves in the same way i.e. there is no exchange between I$^-$ and $^{128}$IO$_3^-$ under the conditions of our experiment.

Some experiments were also performed by using a saturated solution of iodine in carbon tetrachloride as a carrier for the extraction of radioactive iodine and its lower oxidation states from the ice cold solution of irradiated iodate. The results obtained by this and the above procedures agreed fairly for all the (n,$\gamma$) irradiated samples
(solid or solution) and also for the annealing experiments. This method as well as other chemical separation methods\(^{(45,100,101)}\) are lengthy and slow. Since the total activity produced in the sample is limited because of low neutron flux available in the \(^{124}\text{Sb}[\alpha\text{Be}]\) source, as compared to reactor-irradiation, only the first method was adopted as the most feasible one.

**Radioactivity Measurements**

The activities of water and carbon tetrachloride layers were measured by a liquid G.M. counter. The effects due to the difference in the densities of these two solutions was determined as follows:

A stock solution of dilute potassium iodide was \((n,\gamma)\) irradiated for 100 minutes and exactly 20 ml of this was taken for counting in a liquid G.M. counter. Another aliquot of the same volume was acidified and sufficient quantity of \(\text{KIO}_3\) was added to liberate all the iodine. Then 20 ml each of different organic solvents *viz.* n-hexane (density 0.659), toluene (0.866), benzene (0.879), chloroform (1.489), carbon tetrachloride (1.594) and iodobenzene (1.824) were used to extract the liberated radiiodine, using only a few ml of the solvent at a time, so that after the final extraction no activity was left in the water layer. The activity in the organic layer was again measured by the liquid G.M. counter. The values of density of water and the organic solvents were corrected for the iodide and the iodine present, respectively. A curve of the ratio of activities in the water
FIG. 4. VARIATION OF THE RATIO OF ACTIVITIES OF $^{128}$I IN WATER AND IN ORGANIC SOLVENTS WITH DENSITY OF THE SOLVENTS
layer and in the organic solvent was plotted against the density of the latter, as shown in Fig. 4.

It has been noted that for a constant activity of the liquid filling the counter up to the reference mark, the counting rate decreases with increasing density and average atomic number of the solution used. In addition, the counting efficiency further depends on the type and energy of radiation and the geometrical arrangement of the solution relative to the counting tube. The values reported by Levev in the case of $^{128}$I almost lie on the curve, shown in Fig. 4. Willard et al. have mentioned the large influence due to average atomic number of density of the solvent in the case of measurement of activity of $^{82}$Br and $^{36}$Cl.

The density correction factor for the activity measured in carbon tetrachloride layer so determined is found to be 1.26 and this correction has been applied throughout the present work.

**Thermal Treatment**

For experiments involving thermal treatment prior to neutron irradiation, about 1 g of pure, dry, and sieved (100-120 mesh) powder of the iodate sample was taken in a soft glass tubing and heated for a specific time in an electric furnace maintained at a desired temperature. No thermal decomposition was observed even at the highest temperature studied. The samples then were cooled to the
room temperature and then \((n,\gamma)\) irradiated as described earlier.

On the other hand, for post-thermal annealing of the neutron irradiated samples, these were heated in a paraffin oil thermostat, the desired temperature (below \(125^\circ C\)) being maintained and controlled electronically with an accuracy of \(\pm 0.2^\circ C\). For annealing at higher temperatures (upto \(400^\circ C\)), an electric furnace was used in which the temperature was maintained to within \(\pm 1^\circ C\). No thermal decomposition of any of the samples was observed over the temperature range studied.

**Determination of the exact temperature of the Sample During Thermal Treatment**

A chromel-alumel thermocouple was connected to a suspended mirror galvanometer with a lamp and scale arrangement and the deflection was calibrated to read the change of temperature of the sample in contact with the thermocouple tip. It was observed that 1 g of any iodate sample in contact with the thermocouple took about 5 minutes to drop down to \(0^\circ C\) from a certain temperature \((40^\circ C)\), when the sample was plunged into an ice bath. On the other hand, to reach temperatures of the order of 30-90\(^\circ C\) of the heated oil bath, starting from \(0^\circ C\), it requires less than 3 minutes, as shown in Fig. 5. Hence, the assumption of the 'furnace' temperature as the temperature of the sample under study is justified for periods longer than 5 min.

The conditions for this experiment were exactly the
FIG. 6. TWIN $^{60}$Co SOURCE USED FOR $\gamma$-IRRADIATION.
same as mentioned in the thermal annealing experiments described earlier. A calibration curve (figure not given) was also drawn for the galvanometer deflection versus the rise of temperature in 1 g of the iodate sample.

**Gamma Treatment**

About 50 g each of various iodates were crushed, ground, and sieved to between 100 and 120 mesh. These were taken into glass stoppered bottles and irradiated with a kilocurie 60Co source. The samples were placed in position near this gamma source (Fig. 6) where the dose rate had been previously determined by Fricke's dosimeter. After subjecting the iodate samples to the desired gamma dose these were taken out and thoroughly mixed up to homogenize. Then 1.0 g of these gamma treated samples was next subjected to (n,γ) radiolysis to study the effect of additional chemical damage induced by the gammas prior to neutron irradiation.

In another set of experiments, the iodate samples were first (n,γ) irradiated at 0°C and then taken in a Dewar flask containing ice and subjected to known gamma doses. These gamma-annealed samples were then chemically analysed by the usual method.

**Gamma Radiolysis of Iodates**

(i) *Spectrophotometric estimation of iodine and iodide*

A calibration curve was first drawn for the optical density versus molarity of iodine solution in carbon tetra-
chloride (Fig. 7). The sodium thiosulphate solution used to standardize the solution of iodine in carbon tetrachloride was itself standardized by oxalic acid solution.

Samples irradiated to known gamma dose were dissolved in water so that the liberated iodine trapped in the crystal lattice was freed and made to dissolve in water. Carbon tetrachloride was used to extract the whole of the iodine evolved. Optical density of this iodine in carbon tetrachloride was measured and hence the amount of iodine produced was calculated. Further, since the resulting water layer of the iodate solution (free from extractable iodine) might still contain traces of iodide, it was acidified and any further iodine liberated (according to the stoichiometric relation given on page 41) was extracted in 10 ml of CCl₄ and its optical density was measured. Thus by the use of the calibrated curve, the amount of iodine and iodide produced due to gamma irradiation was determined for all the iodates under study.

(ii) Potentiometric estimation of iodide

Potentiometric titration using silver-silver iodide electrodes was tried to estimate the iodide produced in the gamma irradiated iodates. This method did not seem to be convenient as the results were not reproducible. This may be due to the coloured solid deposition (perhaps iodine evolves during the titration) taking place on the silver electrode dipping in the gamma irradiated iodate solution.
However, Boyd and Larson\(^{(104)}\) have reported micropotentiometric estimation of I\(^{-}\) in gamma irradiated KIO\(_3\), presumably using the same type of cell.

**Iodate Solutions**

(i) **Preparation of iodate solutions**

The maximum solubility of the iodates was first determined at room temperature. Then 100 ml saturated solution of each was prepared and its exact molarity determined. These were used as stock solutions for further dilution. Thus iodate solutions of various concentrations starting from saturated solution to about 0.01M, were prepared for the \((n,\gamma)\) radiolysis. Below about 10 mM concentration, the activity produced is immeasurably low.

(ii) **pH measurement of iodate solutions**

A Beckman's pH meter with glass electrodes was standardised by standard buffer solutions, viz. potassium hydrogen phthalate solution (Conc. 0.05M, pH = 4.01 at 25°C) and borax solution (Conc. 0.01M, pH = 9.18 at 25°C). The pH of the iodate solutions were measured observing the usual precautions.

**Irradiation of Solid Samples by Neutrons from a Pu-Be Source**

A few samples of each iodate were irradiated at room temperature for 100 min with a 5 curie, Pu-Be neutron source in which the neutrons are produced by \(^9\text{Be}(\alpha, n)^{12}\text{C}\) reaction and are thermalised by 30 cm of paraffin surrounding the source. The thermal neutron flux in this case is about one-tenth of that of the Sb-Be source. The total iodine activity in 1 g of the irradiated iodate being less than 2,000 c.p.m., the thermal and gamma annealing experiments were not feasible.