5. EXPERIMENTAL
I. Development of Float Method

A. Design:

The float was designed so as to keep it in equilibrium in triple distilled water at 27.5°C to nearly 28.0°C, a working range chosen for the present investigation. This particular range was employed because of its closeness to room temperature, thereby doing away with the need of control of room temperature.

Quartz was preferred to glass as the material of construction of the float, as its thermal expansion is appreciably smaller than that of glass. Other properties of quartz that led to its choice were its great elasticity, permanence, mechanical strength and extreme insolubility. The float has a quartz bulb of nearly 11 mm diameter with a long solid quartz stem at the bottom. The bulb was made by blowing a quartz tube of 10 mm diameter and fixing the bulb to a solid quartz rod of 4.5 mm diameter and 50 mm length. The final adjustment of the density of the float was made by adding to, or removing from the stem of the float, small portions of quartz. The sketch of the float is given in Figure (2). The absolute density for a check up, was determined to a fair degree of accuracy by making use of the displacement principle of Archimedes, which states that the buoyant effect of a liquid upon an immersed body is directly proportional to the weight of the liquid displaced. Ethyl ether was employed as the immersion medium. The ether was purified by distillation and the middle fraction having a constant boiling point was used. Water present as an impurity in the ether, was initially removed.
FIGURE 2: SKETCH OF THE FLOAT, FLOAT CHAMBER AND GAS HOLDER
by keeping it in contact with anhydrous ammonium sulphate for 24 hours. The final traces of water were got rid of by making use of sodium metal thereby decomposing water and evolving it in the form of gaseous hydrogen. The contact between sodium and ether was maintained for 48 hours after which the ether was collected and distilled. For finding the loss of weight of float in ether, arrangement was made for the measurement of "at the spot" temperature of ether inside the balance chamber by means of a calibrated Beckman thermometer. Use was made of the following formula for finding the density of ether at the measured temperature. (International Critical Tables).

\[ d_t = (d_s + 10^{-3} \alpha(t-t_s) + 10^{-6} \beta(t-t_s)^2 + 10^{-9}(t-t_s)^3) \times 10^4 \]

\[ d_s = 0.73629 \text{ g/m}^3 \]
\[ \alpha = 1.1138 \]
\[ \beta = 1.237 \]
\[ 10^4 = 0.1 \]
\[ t_s = 0 \]
\[ \gamma = 0 \]

The above data is applicable from 0°C to 70°C.

Weighings were done in an electrically operated Sartorius Chemical Balance, capable of reading correctly up to fourth decimal place. The wire generally employed for suspending the float was substituted by a human hair to minimise the error caused by the variation in immersion depth. The air was thoroughly washed in ether and dried before using for the measurement. Three typical observations made with necessary precautions are given in Table 6.
### Table 6

**Measurement of Density of Float.**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Wt. of float in ether + hair in air (g)</th>
<th>Temperature of Ether (°C)</th>
<th>Density of Ether (g/cm³)</th>
<th>Loss in weight of float (g)</th>
<th>Volume of Float cm³</th>
<th>Density of Float (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4988</td>
<td>24.60</td>
<td>0.70821</td>
<td>1.2263</td>
<td>1.73154</td>
<td>0.99599</td>
</tr>
<tr>
<td>2</td>
<td>0.4972</td>
<td>25.80</td>
<td>0.70909</td>
<td>1.2279</td>
<td>1.73160</td>
<td>0.99595</td>
</tr>
<tr>
<td>3</td>
<td>0.4968</td>
<td>23.60</td>
<td>0.70933</td>
<td>1.2283</td>
<td>1.73162</td>
<td>0.99594</td>
</tr>
</tbody>
</table>

The above values indicate that the float would remain stationary in conductivity water at a temperature of near about 28.5°C. The final determination of the density of the float was effected by finding out the equilibrium temperature of the same in the triple distilled water by observing the temperature at which the float stands stationary inside the column of water. A value of 27.5°C was thus recorded. The same was amply confirmed in later experiments. The difference, most probably is due to the impurities present in ether, because the value of density of ether has been calculated by the above mentioned formula and not through actual measurement.

The float was always kept clean and grease free. Care was taken not to handle the float with bare hands. The float was cleaned in a hot mixture of concentrated sulphuric acid and nitric acid and always kept in triple distilled water while not in use. While transferring the float to the float chamber or taking it out of the same, a clean long glass rod with a ring in the end
was employed. The rod is shown in Figure (2). Before use, the float is rinsed a few times with the sample itself.

B. **Experimental Set Up**

Figure (3) gives the flow sheet of the equipment employed for the analysis of the sample.

1) **Float Chamber**: A straight glass (Pyrex) tube of 30 mm o.d. and 550 mm length was employed as the float chamber. The diameter of the float chamber was so selected as to accommodate both Beckmann thermometer bulb, and the quarts float. The additive diameters of the float and thermometer bulb, is about 70 mm; 4 mm of clearance was allowed between the thermometer bulb and the float for the free movement of the latter. The same clearance was allowed between the float and the wall. However, while the float had crossed the thermometer bulb, the clearance became nearly 10 mm on each side of the float. This amount of clearance was found essential to make the wall effect negligible. Higher diameter of float chambers could not be used, because of the very large quantity of the samples required for analysis and also because of the horizontal temperature gradient in the float chamber predominant to much higher degree in wider tubes, thereby tending to give erroneous readings, if the vertex plane of fall of the float is altered even to a slight extent.

Another design tried for the float chamber with a view to reduce the amount of sample required for analysis comprised of a 40 mm o.d. glass tube fused to a 20 mm o.d. tube of the same material at the bottom. This arrangement provided a pocket for
FIG. 3. FLOAT METHOD FOR HEAVY WATER ANALYSIS.
the thermometer bulb in the wider tube, whereas more height of fall of the float could be achieved in the narrower range tube. However, the arrangement did not yield concordant results and had to be abandoned.

The tube used was sufficiently long as to ensure that the sample in the float chamber is well immersed in the bath and still half of the length is left above the bath, thereby making it possible to clamp it rigidly so that the vigorous stirring of the thermostatic bath would not cause any disturbance by way of vibration of the sample in the float chamber. The float chamber was kept completely clean and grease free. The chamber was rinsed with the sample before transferring the sample in it.

ii) Thermostatic Bath: A rectangular tank of 30 liter capacity was employed as the bath in which the float chamber containing nearly 100 cc of sample was fixed. The tank was filled with distilled water upto a capacity of 27 litres. The temperature of the bath was slowly and regularly raised by means of a Colora Ultra-thermostat. The water in the bath was always in circulation, the amount pumped from the thermostat and fed to the bottom of the tank being the same as that siphoned back from the tank to the thermostat. As no necessity was felt for the finer control of the bath temperature, the bath was not lagged. To overcome the vertical temperature gradient existing in the bath, the water was kept in vigorous agitation by means of a two bladed, vertical shaft stirrer, with speed of nearly 1000 r.p.m. To avoid heat transfer from the motor of the stirrer to the thermostatic bath,
use was made of a perspex sleeve to connect the shaft of the motor with the stirrer. The depth of the stirrer was kept the same as that of the float chamber in the thermostat bath.

iii) Thermometers: Two Beckmann thermometers, set almost to the same range were fixed - one inside the float chamber such that the bulb of the thermometer just dipped into the sample, leaving enough space for the free movement of the float, - and the other thermometer inside the bath at the same height as that of the sample thermometer. Temperature in both the thermometers was recorded upto third decimal place. Use was made of magnifying lens with a cross wire for taking readings of the temperatures, thereby considerably reducing the error introduced due to parallax. Both thermometers were first calibrated against a standard certified thermometer of range 24 to 50°C, which could be read upto third decimal place.

iv) Nitrogen: A very slow stream of nitrogen gas was maintained in the float chamber above the water sample, so that no carbon dioxide or oxygen from the atmosphere would dissolve in the samples. The rate of nitrogen stream was so adjusted that there was more or less a stagnant atmosphere of this gas above the sample, thereby not affecting the isotopic composition of the sample to a significant degree by evaporation.

v) Ultra-Thermostat: Ultra-thermostat of the K type, obtained from 'Colora' company of Germany was employed for attaining the regular and steady increase in the temperature of the bath. The thermostat is capable of controlling the temperature of its
contents inside upto ± 0.01°C, which when pumped into the thermostatic bath is capable of maintaining the temperature with much higher constancy. For maintaining a constant temperature, use is made of the mercury thermoregulator. The thermostat finds application in closed as well as open systems. Two heaters of 500 and 1000 watts are provided for supplying the adequate amount of heat required. The set up is provided with a thermometer to note the temperature of the thermostat. However, this thermometer offers a rough check up only. Arrangement is also provided in the thermostat for cooling system, thereby making it possible to control the temperature at a value below the prevailing temperature of the room.

vi) Cooling System: A separate cooling system was made use for bringing about a regular fall of temperature of the float chamber. The cold water was circulated through the cooling coil of the ultra thermostat. The water obtained from the tap, after the measurement of its flow and the temperature, was cooled by passing it through a copper coil which was kept immersed in an ice-water bath. The temperature of the cooling water was recorded at the inlet as well as the outlet sides of the cooling coil. To avoid heat transfer from the atmosphere to the cooling bath, the bath was kept in a wooden box and the intervening space was filled with cotton lagging to strike its proper insulation.

vii) Cathetometer and Stop-watches: To note the absolute value of the distance travelled by the float in the liquid, use was made of the cathetometer, which was capable of reading up to third decimal place of a centimeter. The stop-watches used could read up to one tenth of a second accurately.
C. Preparation of Standard Samples:

The samples were prepared by dilution of 10.17 mol% of heavy water, by means of triple distilled water. Calculations were made for the weight required of both to make 100 gm of standard sample each. The weighings of small amounts of heavy water required for the dilution were made by difference in weight method. A well cleaned, perfectly dry fractional pipette was employed for transferring the heavy water. Care was taken not to allow heavy water of high concentrations to come in contact with atmosphere for a long period because of its hygroscopic nature thereby ensuring little or no dilution while weighing. It is essential to produce a set of five standard samples in the range of concentration from normal to 0.06 mol% D₂O. Triple distilled water used for the purpose of dilution, was prepared from ordinary distilled water by subjecting it to further distillations with alkaline potassium permanganate to oxidise organic matter and then over silver turnings. Utmost care was taken to ensure complete evaporation and condensation to avoid isotopic fractionation during the purifying procedure. A typical calculation for the preparation of 0.05% (mole) D₂O is given as under:

1) Preparation of 0.05 mol% D₂O: Samples available
   a) Triple distilled water having 0.0145 mol% D₂O
   b) 10.17 mol% D₂O

For 100 moles of standard sample to be prepared,

let the amount of triple distilled water to be used = x moles
the amount of 10.17 mol% D₂O sample = (100 - x) moles.

D₂O moles present in x moles of triple distilled water

\[ \frac{0.0145}{100} \times x \]

D₂O moles present in (100-x) moles of 10.17 mol% D₂O sample

\[ \frac{(100-x) \times 10.17}{100} \]
Moles of D₂O required for 100 moles of the final sample = 0.05. Striking a material balance for D₂O,

\[
\frac{0.0145 \times 100}{100} + \frac{(100-x) \times 10.17}{100} = 0.05 \text{ or } 10.1555 \times x = 1012 \\

x = 99.6504.
\]

Hence for 100 moles of the standard sample of 0.05 mole% D₂O, the moles of triple distilled water required = 99.6504

The moles of 10.17 mole % D₂O required = \((100-99.6504)\) = 0.3496

Molecular weight of triple distilled water = 18.016 g/mole.

Molecular weight of pure H₂O = 18.01571

Molecular weight of pure D₂O = 20.02836

To calculate the molecular weight of 10.17 mole % D₂O sample, the following relationship was applied:

Molecular weight of P% D₂O = \(M_2 + \frac{(100-P)M_1}{100}\) \((161)\)

Where \(P\) is the mole percent heavy water of the sample, \(M_1\) the molecular weight of the pure water and \(M_2\) the molecular weight of the pure heavy water.

Hence, the molecular weight of the 10.17 mole % D₂O sample = \(10.17 \times 20.02836 + 89.83 \times 18.01571 = 18.2204\) g.

Weight of the 99.6504 moles of triple distilled water = 99.6504 x 18.026 = 1795.3018 g.

Weight of the 0.3496 moles of 10.17 mole % of D₂O = 0.3496 x 18.2204 = 6.3698 g.

Total weight = \((1795.3016 + 6.3698)\) g = 1801.6714 g

Weight of the triple distilled water required to make 100 g of the sample = \(\frac{1795.3016 \times 100}{1801.6714} = 99.6464\) g.

Weight of the 10.17 mole % D₂O sample required = \((100-99.6464)\) = 0.3536 g.
As, with the difference in weight method, it is virtually impossible to take the desired amount of water accurately to the fourth decimal place, the method of approximate adjustment was resorted to, and the weight of it accurately taken. After adding triple distilled water in the same manner, the mole percent of the solution was calculated, which was taken as the value for our calibration curve. Table 7 gives the data of the amounts of the samples calculated and weighed and the exact percentages of the samples used for the calibration curve.

**TABLE 7**

*Data on the preparation of the standard samples of Heavy Water*

<table>
<thead>
<tr>
<th>Cl. No.</th>
<th>Percentage of sample desired</th>
<th>Calculated amount of D₂O sample</th>
<th>Actual amount of D₂O sample</th>
<th>Percentage of the Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.025</td>
<td>0.1046</td>
<td>99.8954</td>
<td>0.1051</td>
</tr>
<tr>
<td>2</td>
<td>0.040</td>
<td>0.2591</td>
<td>99.7409</td>
<td>0.2609</td>
</tr>
<tr>
<td>3</td>
<td>0.050</td>
<td>0.3536</td>
<td>99.6464</td>
<td>0.3540</td>
</tr>
<tr>
<td>4</td>
<td>0.060</td>
<td>0.4481</td>
<td>99.5519</td>
<td>0.4478</td>
</tr>
</tbody>
</table>

**D. Treatment of the Sample:**

Due to the influence of the dissolved impurities on the density of the sample, a standard method of treating the sample was resorted to. Each of the samples was distilled thrice, the second and the third distillation being carried out by using potassium permanganate and the silver turnings respectively. Care was taken to ensure complete evaporation and condensation to avoid fractionation of the sample. Electrical heating mantles were
employed and very regular heating was used during distillation, so that there was no sprouting and no bubbles formed. Such a device nearly did away with any possibility of entrainment of the sample as such. The distillation was then just the slow evaporation of the liquid and its subsequent condensation. No air was used in this case to achieve evaporation, because the air that leaves the condenser is bound to have certain amount of water in it, which would bring about isotopic discrimination of the sample. The removal of the vapour inside the flask and condenser becomes a problem in this case. In some of the cases, the same was achieved by applying suction on the condenser side.

In order to deaerate the sample, it was heated to nearly 60°C for a period of three to four minutes and was then cooled under nitrogen atmosphere. Nitrogen was used because of its low solubility in water. A nitrogen atmosphere was also maintained over the sample throughout. With such pretreatment of the samples no air bubbles were formed over the surface of the float during the experiments and the results were sufficiently concordant.

E. Procedure of analysis:

Nearly 100 cm³ of the sample, treated in the manner as indicated above, was put into the grease free float chamber. The float chamber was first of all rinsed with very small amounts of the sample to be analysed, twice, to avoid dilution of the sample. While transferring the sample to the float chamber, the temperature of the sample was kept a bit higher than that of the room. A Beckmann thermometer was then fixed in the float chamber, so that its bulb was just submerged into the sample.
The slow stream of nitrogen was then passed over the liquid in the float chamber to maintain an atmosphere of this gas. The stream is so slow that it does not lower the surface temperature of the sample in the float chamber by evaporation. The inlet of the gas is kept nearly 150 mm above the surface of the sample.

The well cleaned and rinsed float (quarts) is then lowered into the chamber by means of the glass holder. The holder is used to avoid touching the float, and is shown in Figure (?)..

To achieve a slow and regular rise in the temperature of the bath, the ultrathermostat is then started. In the beginning it is necessary to start the 500 watt heater to bring about a rather quick heating. This was usually for a period of 10 minutes, after which the ultrathermostat was run as such and the friction of the pump was utilised to cause a steady change in the bath temperature. The heat thus produced was found enough to bring about the desired rate of heating.

The stirrer was kept on, while the heating was done. The speed of the stirrer to remove vertical temperature gradient was found to be about 1000 r.p.m.

Before recording any data, the set up was kept running for 90 minutes so as to enable the sample in the float chamber and the water in the bath to attain the thermal equilibrium.

A cathetometer and two stop watches were employed to record the distance and the time of motion respectively of the float while sinking, from which the velocities were calculated at different temperatures.
The velocities and the corresponding temperatures being ascertained a plot was then made of the velocity of the float vs. temperature, which resulted in a straight line. This line was interpolated to zero velocity which gave the value of the equilibration temperature.

The equilibration temperatures of five samples of known \( D_2O \) content were found out and plotted against their mole\% \( D_2O \).

Any sample to be analysed was put in the float chamber and its equilibration temperature found out. The corresponding value of the concentration of the sample was obtained by the use of the calibration curve.

Attempts were made to get data for the calculation of the velocities of the float while it was rising, but reproducible results could not be obtained, because of the difficulty encountered in the regulation of the fall of the temperature.

**IX. Mass-Spectrometer**

Some of the samples were got analysed by mass spectrometer from Germany.

**III. Preparation of the Catalyst**

Nickel was employed as a catalyst in the present investigation. The Ni was supported on Kieselguhr, the composition of the supported catalyst being maintained at a ratio of the Ni: Kieselguhr as 30:70. The raw catalyst had already been prepared as under.
A. Treatment of Kieselguhr:

The kieselguhr used was supplied by the British Drug House. To remove its iron content and organic impurities, it was refluxed for an hour with concentrated HNO₃, cooled, filtered and washed free of acid. After drying it for nearly 6 hours at 110°C, it was finally calcined at about 375 to 400°C for six hours in a muffle furnace for the removal of impurities like alumina.

B. Precipitation of the Catalyst:

175 g of the kieselguhr treated as detailed above, was mixed with 420 cm³ of the nickel nitrate solution containing 75 g of nickel. The nickel content of the stock solution was assessed by the "dimethyl glyoxime" method. The solution was then diluted to a volume of four litres with distilled water and heated to 80°C.

A solution of potassium carbonate (Baker's Reagent) was also prepared by dissolving 200 g of the material in one litre of distilled water and was heated to 80°C. This solution was then added in small amounts to the nickel nitrate solution, while the kieselguhr was kept in suspension by constant stirring. The nickel carbonate precipitated on kieselguhr in the above manner, was allowed to settle and the clear solution was decanted off after cooling it down to the room temperature. The precipitate was washed free of nitrate content by various washings done by hot distilled water. The wash water was discarded by decantation.

The moist cake thus obtained was partially dried at 60°C and the soft cake was passed through a sieve of 3 mm mesh size.
The catalyst was then further dried at 60°C, the final drying being conducted at 100°C for a period of four hours.

The catalyst particles were then sieved to get particles of -3mm +2mm mesh size, where as the fines were employed in the present investigation. The bulk density of this catalyst was found out after keeping it at a temperature of 110°C for a period of 24 hours, and the value found was 0.417 g/cm³.

C. Decomposition of the Catalyst:

The raw catalyst prepared as mentioned above was then decomposed at 500°C to give NiO as:

\[ \text{NiCO}_3 \rightarrow \text{NiO} + \text{CO}_2 \]  \hspace{1cm} (162)

The completion of the reaction was checked by knowing the amount of carbon dioxide liberated. The decomposition was carried out under an inert atmosphere of nitrogen. The oxide thus formed was then reduced by hydrogen at 375°C, the control of reaction was made by weighing the amount of water produced.

D. Experimental Set-up:

The sketch of the apparatus used for the decomposition and reduction of the catalyst is shown in the form of a flow sheet in Figure (4). The set up primarily comprises of a catalyst chamber which is enclosed in a furnace, and the arrangements for the measurements of the amount of carbon dioxide and water produced during decomposition and reduction of the nickel compounds respectively. The reduction tower consists of a 5 cm diameter 0.1. pipe
94 cm long furnace length, having a valve and a flange on the inlet side and fitted with two flanges with a gate valve in between the outlet side. The gate valve is employed to make it easier for the catalyst to be taken out without opening the flange.

Arrangement was also provided through the inlet flange for the introduction of a thermocouple lead for the accurate measurement of the temperature. An iron constantan thermocouple was employed for recording the temperature. The temperature of the tower was controlled by a sunvic control.

The gases, nitrogen and hydrogen, from their respective cylinders were freed from their oxygen contamination by passing through an alkaline pyragallol solution wash bottle. Separate arrangements were provided for the passage of the two gases, through separate stop-cocks. A by-pass for the gases had also been provided, which was generally connected to a marjote system to stop the back flow of the alkaline pyragallol solution from the wash bottle.

The same purification system was utilized for both the gases. After removal of oxygen traces by alkaline pyragallol, the gases had to pass through a calcium chloride tower where the moisture of the gases was removed. A mercury seal was connected to the purification system through the T-piece, so that the gases could bubble out when ever the back pressure of the system increased due to the choking etc. The dust taken up by the gases from the calcium chloride tower was caught by a dust catcher, which was a
straight glass tube containing cotton wool. The manometer was provided on the inlet side to have an idea of pressure in the system. The quantity of the gas passing through the system was measured through a rotameter of 2-50 litres per hour range.

Immediately after the outlet of the reduction tower, there was provided a double walled condenser to remove any water that was formed during the reaction. The arrangement, however, was used only while the decomposition of the catalyst into NiO and CO₂, where quite significant amount of water was let off when the temperature was raised to 500°C. The water produced during reduction of NiO to metallic nickel was weighed after absorbing it in calcium chloride, contained in a U-tube with the ground glass junctions. Provision was there in the set up to put another calcium chloride tube when the first one was taken out for weighing.

Sintered-glass bottom absorption towers were employed for absorbing carbon dioxide. KOH solution of known normality was added to this flask. The amount of CO₂ absorbed was found out by means of titrations. This procedure was adopted because of the difficulty encountered in observing small changes in weight of these towers, which weighed, as a whole more than 700 g each. With the help of different stop cocks, the potash bulbs could be completely cut off and the gas by passed. This arrangement was used when the system was to be put under some inert atmosphere by means of a marfotte system. A mercury seal acted as a safety releaser on the outlet side. A CaCl₂-tower and a manometer were also provided to remove any water vapour from potash bulbs and to measure the pressure of the system.
A system for taking out the gas samples for analysis was provided at the end, so that the sample gas had to pass through the whole of the equipment, before being sampled. This was used just before the reduction when it was necessary to be sure that the system was free of oxygen etc. Hay's analysis apparatus was employed for the analysis of the gas for oxygen content.

E. Procedure for Reduction:

A weighed quantity of 375 cm$^3$ of the catalyst were taken in the reduction tower. The catalyst was introduced from the outlet side by the dismantling of the flange. It was brought to position by making use of a long iron rod of $1/2''$ diameter, fixed with disc of slightly smaller diameter than that of the catalyst tower. The catalyst was so arranged that it was located entirely within the furnace. Connections were then made of the ends of the reaction chamber with the gas inlet and outlet sides. For the decomposition of the NiO$_2$ to NiO and CO$_2$, the furnace was slowly heated till the temperature of the tube reached a value of 200°C, while nitrogen gas was passed at a rate of about 5 liters per hour, to carry out the gases or the water vapour. The gas from the outlet side was bye passed from the potash bulbs. Most of the absorbed water that still stuck to the catalyst was removed from the catalyst by this arrangement. Temperature of the reduction chamber was then slowly raised to 500°C and was maintained at that value by means of a sunvic control. The decomposition took place at this elevated temperature when the gases were passed through one of the potash bulbs. The solution of the bulb was titrated after every half an hour. When one bulb was being used for taking the
sample, the other bulb was put in line. The heating was continued until there was practically no more carbon dioxide evolved. The amount of carbon dioxide produced with time is presented in Figure (5). The decomposition process took about 12 hours.

The reduction tower was then cooled to 375°C (at which the reduction was carried out), under a current of nitrogen. The simmerstat control was then adjusted to this temperature, and a current of purified hydrogen gas was then passed through the system at a rate of nearly 8 liters per hour to reduce the catalyst. Water, formed as a product of reaction, was absorbed in a calcium chloride U-tube which was weighed every hour till the weight was constant. The apparatus was not put out of commission, while the weighing was being done, but the outlet gases were passed through an alternate calcium chloride tower. The constancy of the weight indicated the completion of the reduction of the catalyst. The increase in the weight of the tube with time has been presented in Figure (5). For the reduction of the catalyst it took about 48 hours.

Care was taken not to allow the reduced catalyst to come in contact with the atmosphere and hence, was heated under a slow stream of purified dry hydrogen gas. The catalyst was kept under cooled conditions for a period of one week. During this period, the catalyst was kept under hydrogen atmosphere by means of a Mariotte system.

IV. Equipment employed for electrolysis:

The equipment in which the experiments for the electrolysis were conducted is shown in Figure (7). The figure mainly
FIGURE 5. AMOUNT OF CO$_2$ FORMED DURING DECOMPOSITION OF CATALYST VS TIME IN HOURS.
FIGURE 6. AMOUNT OF WATER FORMED DURING REDUCTION OF CATALYST VS TIME IN HOURS.
consists of two electrolytic cells, gas saturator, catalytic chamber, burner and different condensers in which ice cold water was circulated.

A. Electrolytic Cells

A three limbed electrolytic cell was employed during the investigation. The two side limbs were formed out of a 26 mm o.d. Pyrex tube and were both provided with ground glass junctions. The two electrodes were housed, one in each side of these limbs. The middle limb (a 30 mm tube) was connected to the main cell tube through a stop cock, and acted as a store for the electrolyte. The cell proper had another stop cock through which the electrolyte after electrolysis was over, could be drawn out. Just below the ground glass junctions, were provided two side tubes, for the passage of hydrogen and oxygen - the products of electrolysis. The cell was fixed on a wooden frame. The electrodes used were semi-circular form and were made out of the strips of nickel plate. They were pointed at the ends and were nearly 10 cm in length. The surface area of the electrodes was \( \frac{43}{4} \) cm in each case from one side. The electrodes were made out of nickel crucibles available. The main electrodes were connected to nichrome wires so as to be extended to the ground glass junctions where they were fixed in position through rubber tubes.

Another cell of exactly the same design (not shown in the diagram) was also used during some of the runs. The two were connected in parallel in such a manner that either one or both of the cells could be operated as a single unit.
Fig. 7.
The cells were held in position in cooling baths, which were rectangular glass tanks of thirty liters capacity. In one of the cells, tap water was directly used for the cooling purposes after being measured, whereas in the second cell, the cooling water was the outlet water from the condensers of the system. The level of water in the cell bath was kept constant by taking out the water from the bath by means of a suction pump.

The double walled coolers 6 and 7 were supplied for cooling hydrogen and oxygen respectively. The condensers were connected to the hydrogen and oxygen lines by means of T pieces, the open ends of which were fixed with stop cocks. This arrangement was made to draw out the water that had come as a result of evaporation during electrolysis. The oxygen-side condenser was left open to the atmosphere to let off the gas, whereas the hydrogen-side condenser was connected further with the gas saturator. Cold water was passed through the condensers, for which they were connected in series, so that the water at low temperature after cooling the hydrogen would cool the oxygen thereby condensing the major portion of the water carried by the gases as a result of evaporation.

Hydrogen condenser was connected to the gas saturator through stop-cock 8, and a coil. The coil brings the cooled gas to the room temperature. The gas saturator was a bubbler 125 mm long and 40 mm diameter and was filled up to a height of 30 mm with glass balls. The saturator was fixed with a calibrated funnel through a stop-cock, for feeding the sampler bubbler. The inlet gas tube dipped well into the glass beads so that the gas on coming up
should be completely saturated with water sample. The outlet gas side was directly connected to the catalyst chamber through an insulated (lagged) tube having a stop cock. The saturator was housed in a 2-liter capacity beaker having paraffin oil in it. The temperature of the saturator could be raised by means of a 200 watt heater fixed in the bath. The temperature of the bath could be maintained at any particular temperature by means of a sunvic control, through which the heater was connected. The temperature of the bath was read by means of a thermometer which could read up to \( \pm 0.50^\circ C \). The bubbler temperature was read by means of a thermometer and was assumed to be the same as that of the bath for calculating the amount of water carried away by the samples.

The stop cock between the bubbler and the catalyst chamber was mainly meant for cutting off the catalyst chamber side from the cell side, so that each could be separately put under a mariotte system. The two sides could not be kept under the same mariotte system because of the bubbler which practically cut off one side from the other. Then comes the exchange tower in which the reaction between hydrogen and water vapour takes place in the presence of nickel catalyst. The tower was a glass column 1050 mm long and 38 mm in diameter, fused with a number 32 ground glass junction. The tower was filled with glass beads up to a height of 90 mm over which the catalyst in the reduced condition, was filled.

The tower was surrounded by a heating element consisting of Kanthal strip, the total resistance of which was 45 ohms. 220 AC was fed through a variac of maximum output of 5 amperes and the current fed to the heating element was measured. On the side of
the reduction tower at the top, an Iron Constantan thermo-couple was introduced to the lower half of the tower for the measurement of the temperature during the exchange reaction. The temperature was recorded by means of a Haskins pyrometer, the range of which had been extended. The thermocouple was calibrated upto 150°C.

Provided along with the side of this thermocouple tube was another side tube through which the catalyst in the reduced condition was fed under inert atmosphere conditions.

The condenser for HDO was of coiled type which was connected in series, with oxygen condenser.

The condenser in the Dewar's flask was 200 cm long and was made out of a 30 mm inside diameter tube. The coils were provided for more than half of the length of the tube and a side tube permitted the outlet for the depleted gas. The Dewar's flask was filled with ice water mixture to condense all the HDO sample.

The Dewar's flask could be raised or lowered by placing it on a platform, the elevation of which could be manually changed through pulleys and locking arrangement.

Connected to the HDO trap through two glass coils was the burner. Provided between the trap and the burner was also a wide tube filled with glass pieces. This helped in not allowing the mixing of the air and hydrogen by offering a spring effect. The coils too, served similar purpose.

**B. Hydrogen burner**

The burner employed to convert the dry hydrogen into water was made out of 24 mm I.D. tube. Oxygen of air was used in the combustion because of its constant isotopic composition.
The burner was divided into two chambers by means of a constriction. The air used for combustion entered the lower chamber while the hydrogen entered through a narrow tube vertically below the glowing nickel wire and is fused through the lower portion of the burner. The burner is provided with a B-10 ground glass junction at the top, where the arrangement for the coil is housed. A Pyrex tube of 180 mm length (including the scale limbs) and drawn into a Y shape at the end was used to carry the platinum leads for the burner. The platinum wire was fused to the two limbs. The nickel wire coil used for the hydrogen combustion was connected to the platinum wires. Two nichrome (18 g) wires were used to make the connection between the filament and the copper leads. Eight volts were applied for glowing the burner.

A side tube at the top of the burner permitted the products of combustion to go out. A condenser was used to condense the water formed which was allowed to drip in a collector. A Dewar's flask and a condenser were provided to cool and recover the final quantity of water left off by the burner condenser.

C. Air Supply:

Dry air was used in excess after its rate being measured by a rotameter.

D. Bye-Pass:

To operate the cells without making use of the catalyst chamber etc., a bye pass was provided, which took the gas directly to the hydrogen burner, the coil being placed in position before the burner.
E. Water Flow System:

All the condensers were connected in series. Tap water after its rate being measured by means of a flowmeter and its temperature measured, was made to flow through a properly lagged glass coiled condenser, which acted as a heat exchanger. After this preliminary cooling, the water, was allowed to flow through a cooling bath. The cooling bath was a 300 mm round box having a copper coil of 200 mm in it. Arrangements are provided for measuring the temperature of inlet water and outlet water. The cooling vessel was housed in a rectangular wooden box of a little larger size, the intervening space being filled with cotton waste. The cold water from the cooler was fed to the hydrogen cooler, oxygen cooler, HDO condenser and burner water condenser, all of which were connected in series. The water from the last condenser still at a much lower temperature than that of tap water was fed to the heat exchanger (already explained) where it is precooled the tap water. This was then used to cool the bath of second cell to attain quite low temperature.

F. Mercury Seals:

Two mercury seals on the two sides of exchange tower were provided to see the excess pressure and if so, to control this. Arrangements were also provided for putting the mariotte sytem, as well as flushing the whole of the equipment with any gas.

The pressure of the cell, apart from being noted from the difference of level in the two extreme limbs, was also measured by means of a manometer.
V. Experimental Procedure:

Three different procedures were employed during the present investigation for different kinds of runs, i.e.

A. Differential Electrolysis,
B. Differential Electrolysis cum Catalytic Exchange Tower,
C. Integral Electrolysis.

A. Differential Electrolysis:

Only one cell i.e. Cell (1) was employed during these runs. 375 cc of 15% KCH solution of water having 0.024-15 heavy water content obtained by the distillation of bitterns were used as electrolytes. A constant current of 6 amps was passed through the system. Tap water was used for cooling and the temperature of electrolysis was maintained between 25-27°C. The surface condition of the electrodes was not found to change with time and the results were fairly constant.

The cell was run in six hours intervals during which time, 11.8 cc of the water were electrolysed. The electrolytic hydrogen saturated at the temperature of the electrolyte was cooled to 5° in the hydrogen cooler, where it left off most of its water content. Little carry over was observed due to spray during the investigations. The relatively dried hydrogen was then by passed by closing stop cock 8, and by opening stop cocks 9 and 10 to the burner. Excess air was passed through the burner to bring about complete combustion. The water thus formed and present in the form of vapours was recovered through Leibig condenser and the rest through an ice cooled condenser put in a Dewar's flask.
The water collected from the burner was analysed for its isotopic content and the concentration of cell liquor calculated by means of Deuterium balance and the separation factor was thereby calculated.

The amount of water electrolysed in 6 hours was replenished at the end of this period, thereby keeping a constant amount of electrolyte in the cell. The concentration of the feed was kept constant, throughout the runs. Two runs of this nature were carried out of 927 and 150 hours respectively.

The water collected at the hydrogen and oxygen coolers was fed back to the cell.

B. Differential Electrolysis Cum Catalytic Exchange.

The cell was run in exactly the same manner as that of differential electrolysis with the only difference that the feed supplied to the cell was of variable Deuterium content. To have a source of variable Deuterium content feed the catalytic exchange tower was introduced into this system. The exchange tower also helped in recovering a certain amount of Deuterium from the electrolytic hydrogen.

The hydrogen produced and stripped off its water content, instead of being bypassed to the burner, was passed through the bubbler, the temperature of which was kept at 85°C, by means of the sunvic control. The temperature of the bubbler was so adjusted as to evaporate the same amount of water as was being electrolysed.

The water and hydrogen mixture was passed through the catalyst bed, where the exchange reaction occurred:

\[ \text{HD} + \text{HOH} \rightarrow \text{HDO} + \text{H}_2 \]
The temperature of the catalyst chamber was maintained at 120°C at which the exchange reaction was allowed to proceed. The value of $K$ at this temperature was 2.43.

The outlet from the catalyst chamber was passed through a coiled condenser and then through another condenser surrounded by ice water mixture, where the HDO sample was collected.

The depleted hydrogen sample, after passing through the coils and the bubbler containing glass pieces, was burnt in the burner.

The values of separation factor and $K$ were calculated. The procedure as outlined above was followed in runs 3 and 4. Such runs ensured a continuous supply of changing feed concentration.

C. Integral Electrolysis

To have a high rate of electrolysis, two cells working as one unit were employed. 3.56% KOH solution was employed as an electrolyte. 375 and 380 cm$^3$ of the electrolyte were used in each cell respectively. The amperes were so adjusted that the run for both the cells should finish at the same time. The amperes passed through the cells 1 and 2 were 6.60 and 4.5 respectively.

The electrolysis was conducted till the electrolyte was merely touching the bottom of the electrodes. This left 75 cm$^3$ of electrolyte in cell 1 and 65 cm$^3$ in cell 2.

The samples from the burner as well as from the cell were analysed. Different separation factors for the individual cells were then also found out.

Six such runs have been conducted giving the rate of electrolysis as $\sim 2$ g/hr. No catalytic exchange was used during these runs.
D. Performance of the Column

A comparison of the amount electrolysed and the amount of water collected in the burner, as well as the amount of water evaporated and collected in the ADO trap is necessary for checking up the reliability of the data obtained in the set up. The data of run three of a typical differential cum catalytic exchange tower have been given in Table 8. The data have also been presented in the form of a curve. The comparison indicates that the recovery is above 98% in both the cases. Typical calculations of the separation factors and the values of \( \gamma \) have been given in the chapter on results and discussion.

**Table 8**

Table showing the water balance from burner and Dewar's Flask.

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<th>Sl. No.</th>
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<th>Water added to Evaporator</th>
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<th>Theoretical Water Collected (( \gamma ))</th>
<th>Dewar's Flask (( \gamma ))</th>
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(continued..)
FIG 9 SKETCH OF ELECTROLYTIC CELL.
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<th>Water added to Evaporator (g)</th>
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