1. OBJECT AND SCOPE.
The significance of pure heavy water in the generation of electric power from nuclear fuels hardly needs emphasis. A study of nuclear properties of neutron moderators indicates that heavy water achieves better neutron moderation than any other known usable material. Because of its being a liquid and its other favourable physical properties, it finds application as a coolant moderator within permissible limitations. It can be employed for the above purpose with natural uranium as fuel in either heterogeneous or homogeneous reactors. The latter fact has been mainly responsible for augmenting its importance many fold as a principal component in reactor design.

Its uses in small quantities for the correct formulation of reaction mechanisms in various fields and as a tracer element in metabolism studies in Biochemistry are also well known.

Perhaps the most recent anticipated application of heavy water is in the large scale production of electric power through the process of fusion.

The economy of power produced from approximately all nuclear fuels all over the world has a definite bearing on the cost of production of heavy water. (1) This is evident from the fact that a large percentage of the investment on a nuclear power plant is spent on the moderator alone. A cheap supply of this substance is liable to offer cheap power supply through the process of fusion also.
As it is, the cost of production of heavy water is far from low. The factors mainly responsible for it are the lack of enough technical development of the various processes of separation and its low natural abundance. It is present in all natural waters to an extent of about one part of it in 6900 parts of the latter (i.e. about 0.0145 mol% of D₂O). Though this concentration remains fairly constant all over the world, some variations have, however, been reported. Some glaciers have been found to contain higher deuterium content than normal. Similar variations in composition have also been observed in samples from certain lakes and between the sea and rain water. Such inconsistencies with abundance values can be explained by the physical conditions prevailing at the location of the source. The geographical location, relative humidity, wind direction and the history of the source are some of the factors that assist in proper interpretation of these fluctuations.

However, the variations noticed in concentration are so small in magnitude that they fail to produce a significant effect on the production cost of heavy water by making use of one source of feed water in preference to the other. Nevertheless, if a new source, significantly enriched in deuterium content is found, it would prove very valuable, as the cost of production of pure heavy water would be proportionately decreased.

Possibilities were explored therefore, to find a new source of feed water comparatively more enriched in deuterium content through operations like distillation and evaporation on a large scale occurring in nature, brought about through the
agencies of wind and sun. Such a search resulted in the undertaking of investigations on 'Bitterns' the mother liquor left after the marine salt production. As a very large quantity of water is evaporated by solar heat during this process in a semi batch manner, a certain amount of enrichment could be expected. Due to the fact that the evaporation occurs at relatively lower temperatures, conditions are established similar to vacuum distillation (4) which is specially suitable for separation of isotopes due to higher relative volatility values.

Calculations regarding the evaporation ratio during solar salt production indicate a value between 50 and 70, which suggests significant enrichment of the heavier isotope in "Bitterns."

Separation of salts from Bitterns was affected by complete evaporation and subsequent condensation of vapour by using copper still. The salt free samples thus obtained were further purified and subjected to isotopic analysis. The results indicated that these samples contained higher percentage of deuterium thereby confirming our expectations.

The water thus produced from bitterns was subjected to different operations for further enrichment. A number of methods have already been reported in literature for achieving enrichment (2,5), some of them having been employed for large scale production also. As most of the heavy water plants were erected during the war project, little attention was paid to the economy of its production. There is, therefore, a concentrated attempt to develop more economical processes for its production.
The more commonly used methods for enrichment are water distillation, hydrogen distillation and electrolysis. Apart from its low concentration in nature, its separation is rendered more difficult because of certain reactions which the heavy water in nature undergoes.

\[ \text{H}_2\text{O} + \text{D}_2\text{O} \rightarrow 2 \text{HDO} \]  

(1)

Due to the mass reaction of H\text{2}O, the major portion of deuterium oxide is present in natural waters as HDO. The properties of HDO are intermediate between those of H\text{2}O and D\text{2}O, which makes the process of separation more tedious.

Water distillation was one of the first commercially attempted methods for the isotope production. Because of the low relative volatility (1.017) for this system, the process suffers from the disadvantage of requiring a high reflux ratio and large number of theoretical plates. These result in enormous heat consumption per unit of product and the use of large number of fractionation towers.

Hydrogen distillation offers much higher values of separation factor than the distillation of water - HDO system, but the operation of the plant at extremely low temperatures (~24°K) and the prevention of the conversion of the ortho-hydrogen to the para form involve complications. More experience regarding materials of construction and the technical know-how for handling large amounts of hydrogen at extremely low temperatures is needed. Plants making use of this method are now running in Germany and France.
The exchange reactions utilise the equilibrium between water and a hydrogen containing gas. As a result of exchange the deuterium selectively concentrates in water component of the mixture. Steam-hydrogen reaction is being commercially utilised in Norway.

Most of the present supply of heavy water comes through the electrolysis of natural water using cascade system. The process requires a readily available, cheap supply of electric energy. The separation is achieved due to the small difference in the electrode potential between the hydrogen and deuterium, the former being lower. Though the separation factor is quite high in this case the irreversibility of the process increases the energy consumption.

The object of this investigation is to thoroughly study the effect of the type of mass transfer employed during electrolysis on the degree of enrichment achieved. Strong indications of the same had been found in our earlier investigations on the enrichment of heavy water during the marine salt manufacture by solar evaporation. The two possible types of operations have been called as the "Differential" and the "Integral" ones. In the Differential type of operation the amount of water disintegrated by electrolysis is replenished continually, whereas the Integral operation consists of the electrolysis of the large amount of feed to very small residues.

Studies have also been conducted to assess the influence of factors like temperature of electrolysis, current density, and corrosion on the separation factor, the ultimate object being
being to arrive at results which will indicate measures to be adopted for economic production of heavy water.

Recovery of deuterium from the off gas of electrolysis is achieved through the use of the exchange reaction,

\[ \text{HD} + \text{H}_2\text{O} \rightarrow \text{HDO} + \text{H}_2 \]  \hspace{1cm} (2)

Nickel catalyst on Kieselguhr is employed as a catalyst to increase the rate of reaction.

As the region of concentration under investigation was between 0.005 to 0.100 mol\(^3\) D\(_2\)O, ascertainment of the correct analytical data would have necessitated the use of a mass-spectrometer. In the absence of such an instrument, the temperature-float method was developed. The design of this method of analysis has been significantly simplified without affecting the accuracy of the method. The temperatures at which the known samples have the same density as that of quartz float of known density were found out and were plotted versus the concentrations of the standard samples to yield a calibration curve. Such temperatures of equilibration were also found out for samples of unknown deuterium content and the corresponding concentrations were read from the calibration curve.