3. LITERATURE SURVEY
I. ISOTOPIC SEPARATION

A. General:

The earlier investigations suggested that any property dependent on mass could be utilised for achieving isotopic enrichment. F.W. Aston(24) first tried distillation and diffusion on Neon isotopes and reported partial success. Slight separation was also observed by D.W. Harkins and S.L. Madersky(25) by using such methods.

The principles being used at present for the isotopic enrichment are the following:

i) Equality of the thermal kinetic energy of the molecules at a given temperature.

ii) Difference in centrifugal effects on isotopes.

iii) Electromagnetic forces.

iv) Interatomic and intermolecular forces.

i) Thermal Kinetic Energy of the Molecules:

The average kinetic energy of the light and the heavy molecules is the same at a particular temperature, i.e.

\[ \text{K.E.} = \frac{1}{2} m v^2 \]  

where K.E. is the kinetic energy, \( m \) the mass and \( v \) the velocity of the molecule. As is evident from the equation, the molecules of the different masses will have different velocities. The separation of the isotopes making use of this difference will be inversely proportional to the square root of the masses of the isotopes. As the difference in mass is very small, the method yields very low magnitude of separation per stage.
ii) **Separation By Centrifugal Forces:**

Gravitational forces or centrifugal forces are proportional to the mass of a particular substance. In a very high vacuum, isotopes of an element would fall with the same acceleration. However, a combination of gravitational and intermolecular forces bring about a separation under certain conditions.

iii) **Separation by Electromagnetic forces:**

Electric and magnetic fields offer better control than gravitational forces and are therefore very effective in isotopic separation.

iv) **Separation by interatomic and intermolecular forces:**

In general, these forces are governed by outer electrons in the atoms and not by nuclear masses. However, at the time of the formation of a new molecule through the agency of these forces, the mass effect comes into play. The energy levels of different isotopic molecules are changed differently. Such effects are responsible for slight difference in the chemical behaviour of isotopes.

**II Methods of Separation:**

They can be divided into two categories:

A. Physical Methods,
   - B. Chemical Methods.

A. Physical methods utilise the difference in the physical properties of the isotopes. The methods in current use are

1) Distillation,
2) Gaseous Diffusion,
3) Thermal Diffusion,
4) Sweep diffusion or Mass diffusion,
5) Electromagnetic Methods,
6) Nozzle Method,
7) Electromigration method.
B. Chemical methods depend upon the slight variations in the chemical properties of isotopes. The commonly used ones are

i) Electrolysis

ii) Chemical Exchange.

A. Physical Methods of Isotope Separation:

i) Distillation: F.W. Aston\(^{(24)}\) did not achieve any measurable separation of neon isotopes by fractional distillation from charcoal cooled in liquid air. F.A. Lindeman\(^{(26)}\), after some experiments concluded that the method could not be used for isotopic fractionation. Keenan and Van Dijk\(^{(27)}\), by rectification of neon near its triple point produced fractions with atomic weights of 20.091 and 20.574 from the normal neon of atomic weights 20.183. H.C. Urey\(^{(18)}\) and his collaborators obtained their first indication of deuterium through distillation of liquid hydrogen.

By calculation on the basis of Debye's Theory, it is found that all differences of isotopic properties disappear when \(kT\) becomes large as compared with the separation of quantized energy levels. K.F. Hertsfeld and E. Teller\(^{(28)}\) have discussed the problem of the difference in vapour pressure of isotopes.

H.C. Urey and M.H. Wahl\(^{(29)}\) found that the separation factor for the oxygen isotopes in the distillation was 1.089 at 11.25° falling to 1.062 at 46.2°C. Specially efficient columns are therefore necessary in such cases. The same have been developed in recent years, which are capable of separating isotopes with very small vapour pressure differences. As the relative volatility decreases with increasing temperatures, the columns have to be worked under reduced pressures.
The highest value of relative volatility has been observed for H₂ - HD system, where it is 1.5, so that the method offers good prospect for the separation of hydrogen isotopes.

Table 1 gives relative volatility of other substances.

**Table - 1**

<table>
<thead>
<tr>
<th>Components</th>
<th>Temperature °C</th>
<th>Relative Volatility</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O, HD₂</td>
<td>25</td>
<td>1.050</td>
</tr>
<tr>
<td>H₂O₁₆, H₂O₁₈</td>
<td>25</td>
<td>1.008</td>
</tr>
<tr>
<td>N₂₁₄, N₁₄, N₁₅</td>
<td>-209</td>
<td>1.006</td>
</tr>
</tbody>
</table>

For economic utilization of this method for systems with such low relative volatility values, it is essential to use a number of columns in series and to operate them with minimum hold up and pressure drop and to utilize waste heat efficiently.

The method has been commercially employed for D₂O manufacture and has been studied successfully for Hg, Cl₂, Zn, Ne and oxygen.

ii) Gaseous Diffusion: The velocity of diffusion of a gas through porous medium is, by Graham's law, inversely proportional to the square root of its molecular weight. The pore size of the material must be smaller than the mean free path of the molecules. In 1932, G. Hert (31) enormously increased the efficiency of the
process by incorporating porous tubes in a series of mercury diffusion pumps. A 50-pump system gave practically pure Ne$^{20}$ and complete separation of H$^2$ and D$^2$.

The ideal separation factor for such process is

$$\alpha = \sqrt{M_2/M_1}$$

(4)

where $M_2$ and $M_1$ are the molecular weights of the isotopic compounds. This separation factor is applicable for instantaneous diffusion only. If the diffusion is continued till appreciable amount of gas has diffused through, the separation factor decreases. If the same is continued indefinitely, the separation factor goes on decreasing till the concentration of isotopes on the two sides of the barrier becomes the same.

The method has been commercially employed for the production of U$^{235}$. The separation factor for this system is 1.0043, which is extremely small. This method, however, finds application because of the fact, that its capacity can be appreciably increased by increasing the size of the individual units, whereas in the case of other methods like mass-spectrograph, thermal diffusion, etc., the increase in capacity means the increase in the number of units. The process suffers from the disadvantage of having large number of stages because of extremely low separation factor.

iii) Thermal Diffusion: This method was first suggested by the theoretical investigations of J. Niskog (32) and later by S. Chapman (33), both theoretically and experimentally. If a gas mixture (34) is subjected to a temperature gradient, a diffusion process sets in, resulting in the enrichment of lighter gas in the hotter zone. Opposed to this effect, works the ordinary
diffusion, tending to produce uniform distribution.

A new principle was introduced by Clausius and Dickel\(^{(35)}\) in that they utilised the temperature gradient necessary to produce the thermal diffusion also to bring about a thermal convection whereby the hot gas was carried in the opposite direction to the cold gas thus multiplying the effect of separation due to thermal diffusion. In their apparatus, an electrically heated vertical wire disposed axially in a cylindrical tube served as the hot surface whereas the tube itself acted as the cold surface. Between the two, the gas mixture, at a suitable pressure, was subjected to get separation due to thermal diffusion and in addition, due to the thermal siphon effect, the gas rising at the hot surface carried the lighter constituent in excess upwards and the gas falling at the cold surface similarly concentrated in the heavier constituent.

The constant of thermal diffusion is not a simple factor involving molecular weights only but takes into account the forces of attraction and repulsion between isotopic gas molecules and their interaction in the transfer of momentum upon collision.

iv) Centrifuging: The possibility of separating isotopes by centrifugation was suggested by F.A. Lindemann and F.W. Aston\(^{(36,37)}\), in 1919 and the theory was critically discussed by R.S. Mulliken\(^{(38)}\), S. Chapman\(^{(39)}\), W.D. Harkins\(^{(39)}\) and others. Earlier investigators met with practically no success in achieving enrichment by this method due to convection, and the method was left off as impracticable. However, with the development of the convection free vacuum
type ultracentrifuge \(^{(40)}\) in 1934, the method was tried again and the experiments met with success \(^{(41,42)}\). In most of the useful experiments evaporative centrifuge method suggested by H.S. Mullikan \(^{(38)}\) was employed to separate Cl\(^{37}\) and Cl\(^{35}\) isotope in CCl\(_4\). The method consists in partially filling a hollow centrifuge rotor with a liquid compound containing the element, whose isotopes are to be separated. The centrifuge is then set in motion to high speed. The substance containing the isotopes evaporates near the periphery of the spinning rotor, diffuses along the centrifuge radius against the centrifugal field and passes out through a hollow shaft. The fraction drawn off along the axis contains mostly the lighter isotopes, while the residue in the rotor contains mostly the heavier isotope.

J.W. Beams \(^{(43)}\) tried the method and found the experimental results to be in good agreement with those from the theory, for equilibrium conditions. R.F. Humphreys \(^{(44)}\), using the same type of evaporative centrifuge for the separation of Bromine isotopes extended the theory to non-equilibrium conditions. It was clear from the theory that the separation factor for such method was proportional, among other factors, to the depth of the rotor. Accordingly, methods of spinning long tubular rotors were developed and used with greater degree of success \(^{(41)}\).

The method has recently been studied by J.W. Beams, L.B. Snoddy and A.R. Kuhltham \(^{(45)}\) for the enrichment of uranium isotopes in uranium hexa fluoride. The results have been reported to be in substantial agreement with the general theory of K. Cohen \(^{(46)}\) and his collaborators.
v) *Sweep Diffusion (Mass Diffusion)*: The method was initially suggested by C. Hertz (47) for the separation of gases, by the diffusion in the current of an auxiliary vapour. The process has been thoroughly investigated by C. O. Waid (48). Enrichment is achieved due to the different rates of diffusion of the compounds in steam or other separating agent. The mixture to be separated is fed on one side of the mass diffusion screen, while the vapour is fed on the other side. The components possessing the higher diffusion coefficients diffuse preferentially in the separating agent and collected as heads where as the ones with lower diffusion coefficients remain behind and are collected as tails. The auxiliary vapour is condensed from each fraction after the stage. If the difference in the diffusion coefficients is low, a cascade system of mass diffusion stages is to be employed.

To have a greater degree of separation, use is made of the mass diffusion column. This apparatus utilizes the principle of mass diffusion in a true counter current column. The condensable vapour in this case is caused to flow through the mixture from one wall of the column to the other where it is continuously condensed throughout the entire length of the column. The portion of the mixture being separated, which is caused to flow along the wall at which the separating agent is charged, becomes enriched in the components with higher diffusion coefficients; a second portion of the mixture, which is caused to flow in the opposite direction along the wall at which the separating agent is condensed, is enriched in components having lower diffusion coefficients. This column, if long enough, could in principle, effect complete separation of the components of the feed without the use of cascade of columns.
Theory for the functioning of both types of columns has been developed by M. Benedict\(^{49}\). The theory, when checked with the experimental results secured by C. G. Maier\(^{48}\) stands in good agreement.

Because the sweep diffusion is a thermodynamically irreversible process, it is characterized by a relatively large energy requirement.

Table 2 gives the comparative efficiencies of the three diffusion processes.

**TABLE 2**

<table>
<thead>
<tr>
<th>Process</th>
<th>Efficiency ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal diffusion</td>
<td>0.2</td>
</tr>
<tr>
<td>Mass diffusion</td>
<td>1.5</td>
</tr>
<tr>
<td>Gaseous diffusion</td>
<td>11.0</td>
</tr>
</tbody>
</table>

vi) Nozzle Method: The method was first developed by F. W. Becker, H. Eier and H. Burghoff\(^{50}\), and is based upon the principle of pressure diffusion in a free expanding jet stream. The gaseous mixture of the isotopes is fed to a convergent nozzle under a definite pressure and molar rate, where it emerges in the form of an expanding jet. Due to different diffusion rates, partial separation of the isotopes is achieved. The gas in the peripheral portion is enriched in the lighter isotope whereas in the core portion, the percentage of the heavier of the isotopes is increased.
The peripheral portion is separated from the core portion by means of a diaphragm. The separation effect is defined as

\[ C_A = \frac{n_M (1 - n_K)}{n_K (1 - n_M)} - 1 \]  

(5)

where \( n_M \) and \( n_K \) are the mole fractions of the lighter component of a binary mixture in the peripheral portion and the core portion respectively. The separation factor is of the same order of magnitude as that of gaseous diffusion.

W. W. Becker (51) and co-workers studied this method for the separation of argon isotopes and obtained good results.

The method has further been extended (52) for the separation of uranium isotopes using uranium hexafluoride as the feed material. The energy consumption as worked by the authors is a bit higher than the gaseous diffusion, but production capacity is comparatively higher.

The method suffers from the disadvantage of high suction volume of the compressors, but the avoidance of the porous membranes which is apt to ensure high degree of reliability, appears to be an advantage attached to the nozzle method.

vii) Electromagnetic Method: Mass spectograph is one of the earliest means of isotope separation and is still used for the purpose. This method utilises the effect of electrostatic and electromagnetic fields on the motion of the individual gaseous ions. A collimated beam of ions, accelerated by electric field is deflected by a magnetic field. The ions of different masses are deflected to a different degree, as the deflection is determined
by the ratio $e/m$ where $e$ is the charge and $m$, the mass of the ion. The different ions are collected through different suitable collecting slits.

The isotopes of $\text{Li}^7$, $\text{B}^{10}$, $\text{B}^{11}$, and $\text{C}^{13}$ have been obtained by the mass spectrographic method in amounts of 20 to 30 g. (53). In 1940, A.O. Neir produced the first microgram quantities of $\text{U}^{235}$ by this method.

The advantage of this method is the high separation but suffers from the disadvantage that only minute quantities can be prepared.

B. Chemical Methods:

1) Electrolysis: The method was first suggested by J. Kendall and B.D. Crittenden (53) for the separation of isotopes. It was practically confirmed by E.W. Washburn and H.C. Urey (19), who observed that samples of water from electrolysis cells were enriched in heavy water content. G.N. Lewis (20) and co-workers produced pure heavy water by prolonged electrolysis of water.

Many investigations were carried out for finding out the separation factors for the process, but the results were generally not reproducible. The cathode material, current density and the temperature of electrolysis have been found to be having significant influence on the separation factor.

J.Horiuti and G.Okamoto (54) found that the separation factor at metal cathodes with normal sulfuric acid and $\text{D}_2\text{O}$ as electrolyte were divided in two groups; from 6-7 with Ni, Au, Ag, Ca and
Pt and a value of 3 with Sn, Hg, and Pb. The existence of such two groups of electrodes with different separation factors has been supported by the data of F. Walton and J. H. Wolfenden (55).

The separation factor normally increases with increasing current density and decreases with increasing temperature.

Despite the large separation factors in electrolysis of water, it can be only used economically where cheap electric power is available. Because the process is irreversible, the thermodynamic efficiency is low. But combined with catalytic exchange, the process forms an economic basis for the production of D2O.

ii) Electromigration: S. C. Modorsky and S. Strauss (56) have described the partial separation of chlorine and copper isotopes by counter current electromigration through packed columns. A. Klemm (57) has calculated the transfer velocity ratio of isotopic ions as a function of their difference in mobility, hydration and dissociation. Using electromigration in molten salts (thallium chloride), A. Klemm (58) et al obtained a change in the Tl203/Tl205 ratio corresponding to a difference in migration rates of 0.4%.

An interesting extension of electrolytic migration to utilise a simultaneous concentration of chemical exchange has been proposed by H. Martin (59, 60). In this process, a counter current flow of charged particles is caused to occur with respect to uncharged or oppositely charged particles by means of an electric current.

Theory suggests that a relatively high concentration of isotopes may be produced by this method.
iii) Chemical Exchange: The method came into development as a result of theoretical calculations done by H.C. Urey and D. Rittenberg (61) who showed that the equilibrium constants for the exchange reactions in isotopes differed from unity. With successful enrichment of hydrogen by this method, systematic exploration of several other isotopes were made theoretically by H.C. Urey and L. Greiff (14). For example the equilibrium between liquid water and gaseous carbon dioxide, viz.,

\[
\frac{1}{2}^{16}O_2 + 2 H_2^18O \longrightarrow CO_2^{18} + 2 H_2O^{16}
\]  

was shown by calculation to yield a separation factor of 1.047 at 0°C, favouring the concentration of $^{18}O$ in the carbon dioxide.

For nitrogen isotopes, use was made of the exchange reaction between ammonia gas and ammonium ion, the latter in solution as nitrate.

\[
N^{15}H_3 (g) + N^{14}H^+ (sol) \longrightarrow N^{14}H_2 (g) + N^{15}H^+ (sol)
\]  

The process involving the above reaction has been adopted commercially by Eastman Kodak Company (30).

The concentration of $^{34}S$ by chemical exchange between sulfur dioxide and bisulfite ion (62) has been put to further investigations by E.P. North (63). This work has suggested that increasing the temperature may have a favourable influence through rate increase, which more than compensates for any decrease in equilibrium constant value with increasing temperature. W.I. Byod (64) reports similar results with $^{18}O$. He studied the exchange between
carbon dioxide and dissolved bicarbonate ion at temperatures up to 120°C and pressure up to 150 pounds per square inch.

Table 3 gives a list of the equilibrium constants for some of the typical reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant at 298.1 K</th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N^{15}H_3 (g) + H^{14}H_4^+(aq) = H^{14}H_3(g) + N^{15}H_4^+(aq)$</td>
<td>1.033</td>
<td>1.023</td>
<td></td>
</tr>
<tr>
<td>$S^{34}O_2(g) + H^{32}O_2^-(aq) = S^{32}O_2(g) + HS^{34}O_3^-(aq)$</td>
<td>...</td>
<td>1.012</td>
<td></td>
</tr>
<tr>
<td>$HC^{12}N(g) + C^{13}N^-(aq) = HC^{13}N(g) + C^{12}N^-(aq)$</td>
<td>1.026</td>
<td>1.013</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constants for most of the reactions involving isotopes other than that of hydrogen are relatively low. $C^{13}$ and $O^{18}$ isotopes are being concentrated by the Howdry Process Corporation in America.
III. HEAVY WATER

A. Methods of Preparation:

1) Distillation of hydrogen: The sample of hydrogen enriched in deuterium, in which H.C.Urey, F.G.Brickwedde and G.N.Murphy\(^{(18)}\) discovered this isotope in 1932, was obtained by the fractional distillation of liquid hydrogen.

The method was developed with preliminary plant design by duPont Company, working in collaboration with H.C.Urey\(^{(65)}\).

Studies carried out by K.Clausius and K.Starke\(^{(66)}\) in Germany, also showed the promise latent in the process.

The serious problems encountered in the employment of the process for heavy water manufacture were\(^{(67)}\) the following:

a) The removal of nitrogen as it chokes the heat exchanger of the plant.

b) Suppression of the conversion of ortho to para hydrogen which if allowed to occur completely releases heat equal to 440 cal. per g.mole.

c) Lower relative volatilities for H\(_2\)-HD mixtures than originally anticipated. The ratio of the vapour pressures of ortho hydrogen and HD, which are the key components in the distillation tower, at 25 psia and -419.4°F, is 1.59 against the relative volatility value of 1.39. This is because the hydrogen vapour at this temperature and pressure deviates from the perfect gas and the activity coefficient of HD in liquid hydrogen is 1.075. This can be inferred from the measurements of the dew point of H\(_2\)-HD mixtures\(^{(68)}\), which shows positive deviation from the Rault's Law.

ii) Distillation of Water: The separation factor for the process has been expressed by H.C.Urey\(^{(6)}\) in terms of vapour pressures of H\(_2\)O and D\(_2\)O by

\[
\alpha = \frac{n_{H_2O}}{n_{D_2O}}
\]

(8)
where $\eta_{D_2O}$ is the vapour pressure of $D_2O$ and $\eta_{H_2O}$ is the vapour pressure of $H_2O$. The above formula takes the following assumptions for its derivation:

a) Liquid and vapour phases from ideal solutions.

b) The vapour pressure of HDO is the geometric mean of the vapour pressures of H$_2$O and D$_2$O.

c) The equilibrium constant for the reaction

$$H_2O + D_2O \xrightarrow{\text{vapour}} 2\text{HDO}$$

in the vapour phase has the value of 4.

d) This equilibrium is maintained in the liquid. R. L. Combs, J. M. Googin and H. A. Smith (69) studied the distribution of deuterium and hydrogen between liquid and vapour phases and found the observed separation factor in close agreement with the one predicted by the above equation.

Because (67) of the increase in the value of $\alpha$ with reduction in pressure, there is a strong incentive to operate a water distillation plant at subatmospheric pressures. This, however, necessitates larger towers for handling a given mass flow rate of vapour at lower pressures.

With $\alpha = 1.05$; $x = 0.000149$ and the product of hundred percent purity, minimum moles of steam required per mole of $D_2O = 141,000$. For a practical plant with optimum number of stages, around 200,000 moles of steam must be provided per mole of heavy water produced.

Despite these severe conditions in regard to requirements, the process has received considerable attention because of the simple equipment used.
iii) **Chemical Exchange Process**: The method generally finds application as a means of deuterium recovery during electrolysis process. The deuterium in electrolytic hydrogen which cannot be recovered by electrolysis can be economically recovered by this method. Use is made of the reversible reaction:

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

The equilibrium constant for this reaction in the vapour phase varies from 4.19 at 0°C to 2.43 at 125°C. Deuterium is thus transferred from hydrogen to water without burning, thereby increasing the heavy water production without sacrificing the hydrogen production.

The exchange has to be catalysed to increase its rate. As the catalysts so far known to have been developed lose activity appreciably in liquid water, use has to be made of gas phase catalytic reactor. Attention is now being paid to the development of the catalysts which function in the liquid state.

Herteck and Suess\(^{(67)}\) proposed the method in 1941 and developed a supported Ni-catalyst which caused the exchange reaction to take place at an acceptable rate below 100°C, where the equilibrium constant was favourable.

A Ni chromia-catalyst and a platinum catalyst supported on activated carbon was developed by H.C.Urey and H.S.Tylor\(^{(67)}\) respectively.

The exchange reaction has been used in Trail Plant which produces 1100 lbs. of 99.8% D\(_2\)O per month.
iv) **Dual-Temperature Separation Technique**: The method was suggested by A. Farkas in Germany and V.K. Rideal in England\(^{(70)}\).

The separation of isotopes by dual temperature exchange process is based on the variation of the exchange equilibria with temperature, and the separation efficiency is a function of the temperature differential which can be maintained in the system. This necessitates the employment of two towers. In the hot tower, the gas is enriched and the depleted liquid goes to the waste, whilst in the cold tower the enriched gas is in its turn denuded of the heavy isotope and can be recycled. The cold liquid contains the desired heavy isotope and can be taken off between the two towers.

The fact that the water is the only raw material and that only a limited amount of hydrogen gas is required in the closed circuit is an advantage.

Other reactions that can be used in the dual temperature technique are

\[ \text{a) } \text{HDS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{HDO} \]  

\[ \text{b) } \text{DCl} + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HDO} \]  

These two methods, however, suffer from the disadvantage of the corrosive nature of the reactants.

v) **Adsorption**: The selective adsorption and desorption of hydrogen and deuterium has been widely investigated. H.S. Taylor, A.J. Gould and W. Bleaky\(^{(72)}\) found that hydrogen enriched in deuterium could be obtained by adsorption and desorption of electrolytic hydrogen on porous adsorbents as silica gel and active charcoal. The operation was carried out under conditions of very low temperature, the adsorbent being cooled by liquid...
air. They reported a fivefold increase in the deuterium content, over that present in the sample of hydrogen taken up for the investigation. Subsequently, a number of investigations were carried out by different investigators over a wide temperature range and very low pressure of desorption of the order of a fraction of a millimeter \( \mu \) and different adsorbents. The method has not yet been developed for industrial scale purposes.

vi) **Biological Methods**: Certain biological systems, e.g., algae are capable of hydrogen isotope discrimination and it might be possible to employ this in a process to provide material enriched in heavy water content. If algae are grown in water and they are supplied with suitable quantities of nutrient, carbon dioxide and energy of sunlight, the photosynthesis reaction takes place:

\[
\begin{align*}
\text{n CO}_2 + \text{n H}_2\text{O} & \quad \longrightarrow \quad (\text{CH}_2\text{O})_n + \text{n O}_2 \\
\end{align*}
\]

which has been shown to utilize \( \text{H}_2\text{O} \) more readily than \( \text{D}_2\text{O} \) with a separation factor of approximately 2.5. Thus, if two-thirds of a given volume of water is used up in this manner, i.e., removed in the continuous harvesting of algae, the residual water is then of twice the natural concentration.

vii) **Miscellaneous Methods**: There are a number of methods mentioned in literature, which though theoretically are capable of affecting isotopic enrichment, give very low separation factors.

The fractional crystallisation of water and the centrifugation of gases have been suggested, but no details are known about any industrial use of these techniques. Methods like
preferential gas absorption, active metal water reactions, liquid-liquid extraction and electromagnetic techniques have still to be developed.

viii) Electrolysis: On the decomposition of water by electrolysis, there has been observed a preferential release of hydrogen, thereby leaving the residual cell liquor enriched in the deuterium content.

a) Theories of D₂O separation by electrolysis: Overvoltage influence upon the rates of evolution of the two isotopes has been held responsible for the electrolytic separation. H. Erying and A. Sherman (74), from purely kinetic considerations, predicted a separation factor of 4. A number of theories based upon different mechanisms of overvoltage have been put forward.

a₁) Bell's Theory: H.P. Bell (75) applied Gurney's treatment of overvoltage to the relative rates of discharge of the two isotopes on the basis of the following reasoning. Out of the three steps, vis.:

1. The mobility of isotope ions
2. The rate of neutralization of the two ions by electrons
3. The rate of combination of H and D atoms on the electrode;

the step 1 was discarded because of the independence of the separation on the pH of the electrolytes (77). The step 3 was considered to have no influence on the separation because of the independence of the separation factor of the cathode material (78). Therefore, the Gurney's mechanism of overvoltage i.e. the slow
step being passage of electrons over a potential barrier, the slowness, therefore, of the reaction between $\text{H}_2\text{O}^+$ or $\text{H}^+$ with electrons to produce the atom, was considered to be applicable.

The relative rates of discharge of the isotopes, as obtained from Gurney's treatment are expressed by:

$$\log \alpha = \frac{[ (E_o)_x - (E_o)_y ]}{\gamma kT} \quad (12)$$

where $E_o = \text{the energy of neutralisation of the hydrated ion in its lowest energy state of an electron, } \gamma = \text{a correction factor little greater than unity and } x \text{ and } y \text{ are the two isotopes and } \alpha \text{ the separation factor.}$

The variation of $\alpha$ with temperature as predicted by this theory is

$$\frac{d \log \alpha}{dT} = -\alpha / T \quad (13)$$

This equation predicts a decrease in efficiency of about 35% over the temperature range from 0°C to 100°C.

The separation factor should be independent of current density and of the cathode metal, facts not realised in practice. The value of $\alpha$ should fall exponentially with the rise of temperature, a conclusion from this theory which cannot explain the behaviour of Hg and Sn as cathodes.

2) Theory of Horiuti and Okamoto; J. Horiuti and G. Okamoto (54). During their investigations, found that the cathodes studied by them fell into two groups; cathodes like, Ag, Sn, Ni, Pt, Au, Cu, and Pb (in alkali) yielded separation factors of 6-7, whereas Hg, Sn and Pb (in acid) gave values of $\alpha$ in the neighbourhood of 3.
The temperature coefficient of the separation factor $\alpha$ was observed to be large and negative for the first group, whereas the value of the same was zero or positive for the second group's cathodes. The authors considered that the electrolytic discharge of hydrogen proceeds through different paths with the two classes of cathodes; in each case the primary step being the neutralisation of the hydrogen ion, thus:

$$H_2O = H^+ + Me \rightarrow H_2O + H - Me.$$  

The absorbed hydrogen atoms can then react to form molecules in two ways, either:

1. $2 Me - H \rightarrow 2 Me + H_2$ or
2. $Me - H + H^+ - OH_2 \rightarrow Me + H_2 + OH_2$

The first process is assumed to operate at cathodes of group I and is called the catalytic mechanism; the second the electrochemical mechanism is ascribed to the cathode of group II.

The existence of two groups of metals with different separation factors has been confirmed by the data of H.F. Walton and J.H. Wolfenden (25).

25) H. Eyring, S. Glasstone and K. Laidler's Theory: A mechanism is suggested by them based upon their new theory of overvoltage, which in turn is based upon the absolute reaction rate theory of chemical reactions. This theory relates the current density $I$ at an electrode to the overvoltage $V$ by the expression:

$$I = I_0 \exp \left( \frac{\alpha VF}{RT} \right) \quad (14)$$

where $I_0$ is a constant for a given electrode representing the
current passing in each direction at a reversible potential and $\alpha$ is the fraction of the added potential $V$ operating between the initial state and the activated state of the system. It is suggested that the slow process may consist of the transfer of a proton from a water molecule in solution to another water molecule attached to the electrode surface. The theory explains not only the magnitude of the separation factor and its variation with cathode material, but also accounts for the variation of separation factor with temperature.

b. Factors Influencing Separation Factor:

b.) Material of the cathode: Earlier investigations carried out by B. Topley and H. W. Spring (78) indicated that the separation factor is not appreciably influenced by the electrode material. Bell based his theory by interpreting the data of the above authors that $\alpha$ is independent of the material of the electrodes. A close examination of the data of the above investigators which is presented in Table 4, illustrates that different metals used as electrodes yield different separation factors.

**Table 4**

Separation factors for various conditions of electrolysis.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Separation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>0.5N KOH</td>
<td>7.2 - 7.4</td>
</tr>
<tr>
<td>Platinum</td>
<td></td>
<td>6.5 - 7.6</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.5N H₂SO₄</td>
<td>5.7</td>
</tr>
<tr>
<td>Iron</td>
<td>0.5N KOH</td>
<td>6.9 - 7.6</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td>Copper</td>
<td></td>
<td>6.8</td>
</tr>
<tr>
<td>Silver</td>
<td></td>
<td>5.3 - 5.8</td>
</tr>
</tbody>
</table>
A.Eucken and K.Bratsler (80) carried out a comprehensive investigation of the influence of the cathode material on the separation factor, by special attention to the history of the material. The results reported were, however, erratic; separation factor for platinum between 3.4 and 14.7; for gold 3.1 and 17.6; for Ag 4.1 - 9.1 and for lead 4.0 to 9.8 being found. Horiuti and Okamoto (54) carried out experiments with Ag, Ni, Pt, Au, Pb, Sn, and Hg with \( \text{H}_2\text{SO}_4 \) and \( 6\% \text{D}_2\text{O} \) and observed that the electrodes fell in two groups - the first five having a separation factor of 6-7 and the others of nearly three. H.F.Walton and J.H.Wolfenden (55) carried out investigations under carefully controlled conditions, excluding all contaminations from the cathode and using current densities of 1 mill amp/cm\(^2\), and confirmed the findings of J.Horiuti and G.Okamoto (54).

b\(_2\) Shape of the Electrodes: T.H.Oddie (81) concluded from his investigations that the separation factor during electrolysis is independent of the nature of the electrodes. The same has recently been confirmed by Kalman et al (82) who carried out the electrolysis of water under various conditions of electrode size and shape and showed that the separation factor is not influenced by the electrode nature.

b\(_3\) Temperature of Electrolysis: The influence of the temperature of the electrolysis on the separation factor has been observed by quite a few of the investigators. D.H.Rank (83) attributed the lowering of separation factor with increasing temperatures to the higher evaporation rate. He developed an equation relating the rate of evaporation and the electrolytic separation factor as
If $\delta_1$ and $\delta_2$ represent the amount of $H^1$ and $H^2$ evolved per mole of hydrogen produced and $C_1$ and $C_2$ are the respective concentrations of the two kinds of hydrogen in the electrolyte expressed as mole fractions, $\epsilon$ is the hydrogen lost by evaporation of water per mole of water electrolysed. H.F. Walton and J.H. Wolfenden with rigorous exclusion of grease, oxygen and other contamination studied the temperature dependence of $\alpha$ with Hg and Ag, whereas in case of Ag the value of $\alpha$ fell from 7.0 at 15°C to 4.4 at 98°C, but the same increased in case of Hg. T. Noguti attributed the lowering of separation factor to pronounced corrosion at higher temperatures and was successful in keeping a constant separation factor by continuously cleaning the electrodes. J.H. Wolfenden and H.F. Walton carried out investigations on electrodes of Hg, Sn, Ag, Ni, and Pt and found in general that the effect of temperature on separation factor can be expressed by the expression

$$\alpha = \exp \left( \frac{\Delta F}{RT} \right)$$

(16)

where $\Delta F$ is the difference in activation energy for the two isotopes at some stage in the cathode discharge. Peculiar behaviour was, however, noticed in case of Hg and Sn. The separation factor increased in case of Sn, but in case of Hg, it increased up to 55°C but then fell again. Their data is presented in Table 5.
D.F. Mason, R.H. Biddick and C.A. Boyd applied the ultrasonic radiations to the polished platinum cathode in an electrolytic cell and found the effect of temperature on the separation factor was less under such conditions. This has been explained to be due to the rapid removal of the discharge gas by the ultrasonic radiations, preventing the surface catalysed exchange reaction between the discharge gases and the electrolyte.

Martin Hone and C.F. Hiskey investigated the isotopic separation at mercury cathodes and found that at current density $10^{-4}$ amp/cm$^2$, it decreases from 3.83 at 0°C to 3.71 at 96.5°C, whereas with a c.d. of $3.0 \times 10^{-2}$ amp/cm$^2$, it increases from 2.96 at 0°C to 3.31 at 96.5°C.

b) Effect of current density: T. Noguchi in his investigations on the effect of current density on the separation factor observed that the latter is virtually unaffected by the current density. T.H. Oddie, however, noticed that $\alpha$ increases with increase in current density, after correcting for the evaporation and spray losses. Increase in the current density decreases $\alpha$ in case of cathodes like Hg., Sn, Ag and Ni but increases

### Table 5

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Hg</td>
<td>3.3</td>
</tr>
<tr>
<td>Sn</td>
<td>3.0</td>
</tr>
<tr>
<td>Ag</td>
<td>6.0</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
</tr>
<tr>
<td>Pt</td>
<td>-</td>
</tr>
</tbody>
</table>

The table above shows the influence of temperature on the separation factor for different metals. The separation factor decreases with increasing temperature for Hg and Sn, whereas it increases for Ag and Ni.
it slightly with Pt, the effect decreases with increasing temperatures. The extent of decrease of \( \alpha \) at 15°C has been reported by H.F. Walton and J.H. Wolfenden to be as 75 for a 20 fold increase in current density (from \( 3 \times 10^{-5} \) to \( 6 \times 10^{-4} \) \( \text{amp/cm}^2 \)). At 95°C, the same authors reported no change in the value of \( \alpha \) with the same variation in current density. Martin Rome and C.F. Hickey (87) working with Hg cathode found that the variation in separation factor was to the extent of \( \frac{1}{3} - \frac{1}{3} \) for 20 fold increase in the current density \( (10^{-4} \text{ to } 2 \times 10^{-3} \text{ amp/cm}^2) \) at all observed temperatures. However, Kalman et al (82) have recently reported the independence of separation factor on current density.

b) Effect of concentration of \( \text{D}_2\text{O} \): The data of K.D. Applebeay and G.Odder (30) indicate that with Hg cathode and 5% \( \text{NaOH} \) solution, the separation factor varies from 5.2 at 3.76 \( \text{D}_2\text{O} \) to 5.56 at 29.5%, to 4.35 at 58.7% and 3.45 at 86.5% \( \text{D}_2\text{O} \). N.H. Trenner (81) also reports a lower separation factor factor in solution in approaching pure deuterium.

c) Effect of \( \text{pH} \) of the electrolyte: The value of \( \alpha \) has been reported to be independent of \( \text{pH} \) of the electrolyte by T.K. Oddie (81). A. Farkas (92), during electrolysis of mixtures of \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) in acid and alkaline solutions with \( \text{Pd} \) cathode observed the value of \( \alpha \) to be 6.6 and 4.4 respectively. M. Shiroma and Okamoto (54) noticed that the \( \alpha \) given by \( \text{Pb} \) cathode in alkaline solution was nearly 7 against the low value of 3 in acid solution. A.I. Brodski and M.P. Shrinikova (93) found that the separation factors determined for electrolysis for \( 100 \text{ cm}^3 \) of 0.2N salt solution in 0.15 \( \text{D}_2\text{O} \) between
Pt electrodes measuring the concentration of $D_2O$ in the residual liquor increase from 5.6 for KOH through $H_2SO_4$, KCl, NaCl, and $K_2CO_3$ to 10.6 for $Li_2SO_4$.

IV. ANALYSIS OF HEAVY WATER.

A. General:

H.C. Urey, F.C. Brickwedde and G.N. Murphy (18) were the first to make a quantitative estimation of deuterium in hydrogen gas by spectroscopic means. The measurements were based on the different wavelengths of the corresponding lines in the atomic spectra of light and heavy hydrogen.

Due to great difference in mass of hydrogen and deuterium their compounds differ significantly in their various physical properties. The numerous methods of analysis are based upon such differences. In general, the difference in any property of light and heavy water can find application for their isotopic analysis. The difference must, of course be sufficiently large for convenient measurement, and the precision of the measurement must be sufficiently great for the desired analytical accuracy.

Mass spectrometer utilizes the difference in mass of the two atoms. Differences in refractive index, freezing points, viscosity and vapour pressure between the two isotopes have been successfully employed for their isotopic determinations. The most widely used property for the purpose, however, is density. Since the difference in densities of light and heavy water amounts to nearly 10%, some of the most precise methods of analysis are based upon this difference. Of the various ways of determining the difference accurately, the principal ones are pycnometer method,
falling drop method and the float method.

B. Mass Spectrometer:

The analysis of hydrogen isotopes, employing a mass spectrometer was first worked out by W. Bleakney (94). Since then, the method has undergone various improvements. An electron beam produced by emitting electrons from a hot filament, and accelerating them by an electric field through defining slits, is directed through a region containing hydrogen at a pressure of about $10^{-4}$ mm Hg. It results in the formation of monoatomic, diatomic and triatomic hydrogen ions. The ions are drawn out of ionizing region by means of a negative potential and are turned into ribbon of ions by passing them through slits and accelerating them by electric fields. The ribbon of ions is dispersed into a mass spectrum by means of a magnetic field and the part of the spectrum of particular mass is isolated by means of parallel slits. The resolved ion beam of a given mass impinges independently on a collector plate, and the resulting current is detected and measured. A comparison of the magnitude of these individual currents, or the feedback potentials necessary to balance out the currents, gives the relative proportions of the isotopes.

1) Sample for Analysis: For mass spectrometric analysis of water, it is best to introduce into the mass spectrometer, a gaseous mixture of deuterium and hydrogen in which the concentration of D and H should correspond to the concentration of D and H in water being analysed. The water is changed into gas by distillation in vacuum over zinc granules at a temperature of 395°C.
D. Rittenberg and D. B. Sprinson\textsuperscript{(95)} emphasise that this temperature is critical. Above 400°C, the zinc melts and chokes the apparatus; at lower temperature, good conversion is not obtained. Johnson\textsuperscript{(96)} used zinc for relatively large samples of water in a glass tube 1 ft. long and 1 inch in diameter, and found best to operate the apparatus about 400°C in order to ensure decomposition of zinc hydroxide that might be formed.

ii) Presence of Ions: The ions observed will depend upon the amount of heavy isotope present. The mechanism of formation of triatomic ions is not known, though a number of suggestions have been made as to how triatomic ions could be formed. The effect cannot be ignored, for, as A. O. Nier\textsuperscript{(98)} points out, the ion beam current arising from triatomic ions may be as much as half the total ion beam current measured in the mass 3 position. When the relative abundance of deuterium is less than 1\%, it can be assumed that practically all the deuterium is bound as HD. Hence the masses compared are 2 and 3 only, whereas in deuterium gas containing very little hydrogen, the masses compared are 3 and 4.

The mass spectrometric analysis of deuterium in hydrogen gas is frequently complicated by discrimination and exchange effects. M. Orchin, J. Wender and R. A. Erredel\textsuperscript{(99)} have suggested the use of Grignard reaction with heavy water to generate methane and mono-deutromethane from the sample. These compounds can be analysed with good accuracy in the mass spectrometer.
C. **Infra Red Methods:**

When the hydrogen atoms of H$_2$O are replaced by deuterium, although the actual mass difference is small, the reduced mass of O-H bond is almost doubled, and since the force constant of the bond is unaffected, the stretching frequency is considerably lowered. Because of this large shift in frequency between O-H and O-D species, it is quite simple to identify infra-red absorption bands which are characteristic of each type of molecule and utilise them for the isotopic analysis of water.

Infra-red and ultra-violet absorption were used by H.S. Taylor and coworkers (100) for the analysis of deutromethanes. G.B. Kistiakowsky and R.L. Tichenor (101) employed infra-red absorption for the analysis of deuterium in DCl-HCl mixtures. V. Thornton and Condon (102) have reported a method for 1-5% range based upon the measurement of changes in the intensity of O-D stretching vibration at 3.98 μ. N.R. Trenner and R. Walker (103) improved the accuracy of the method by the use of thermostated absorption cells.

The method has recently been studied by J. Gaunt (104) for accurate and rapid determinations of deuterium both for laboratory and continuous plant monitoring. Use was made of a calibration curve and the average analysis time per sample is reported to be approximately three minutes. The data is found to be both repeatable and reliable. Separate calibration curve is necessary for each concentration range. The amount of sample required is 2-3 ml only.
D. Refractometric Method:

The significant difference between the index of refraction of ordinary water and deuterium oxide is used as the basis of isotopic analysis of water. The ordinary type of refractometer has limited application because of the need of high temperature control for obtaining accurate results. For an accuracy of 1 unit in the sixth decimal place in refractive index of aqueous solution, a necessity of \( \pm 0.01^\circ C \) temperature control has been reported.

A higher accuracy, however achieved with interferometer, because the temperature variation has not significant effect on the final results. The interferometer compares the refractive index of one liquid with that of another having very nearly the same composition and hence having almost the same temperature coefficient for the index of refraction.

The principle of the refractometer is as follows:

Light from a source is made to fall on a screen through two small openings thereby forming interference fringes. The points where the light through both the slits reach in the same phase, form white bands, whereas dark bands are produced at the points where the path difference is exactly a half wave length. With a monochromatic source, the white bands are of the colour of the incident light, and the dark bands are black. If a transparent material is introduced in the path of one of these beams, the light waves of these beams are retarded by an amount which depends both upon the thickness and the refractive index of the material. The lengthening of the optical path is given by: 

\[ \text{Lengthening of optical path} = 2 \times n \times t \]
\[ \Delta p = l \left( n - n_0 \right) \]  

where \( \Delta p \) = path difference, 
\( l \) = thickness of material 
\( n \) = refractive index of material 
\( n_0 \) = refractive index of the surrounding medium

As a result, the position of the central white band is shifted. The shift counted in the form of the number of fringes follows the relationship

\[ N = \frac{\Delta p}{\lambda} \]  

where \( N \) is the shift number of fringes, and \( \lambda \) the wave length of the light.

The instrument commonly used in the analysis of heavy water has been explained in detail by L.H. Adams (105). The reproducibility of the analysis made by this instrument is found to be 0.01 to 0.02 mole percent of deuterium.

E. Thermal Conductivity Method:

The method originally designed for the determination of the ortho hydrogen to para hydrogen ratio in a particular sample was applied by A. Farkas and L. Farkas (106) for the isotopic analysis of hydrogen. It is based upon the difference in the specific heat of the three types of gas molecules \( \text{H}_2 \), \( \text{HD} \) and \( \text{D}_2 \).

Quantities of the order of \( 2 - 3 \) \( \text{cm}^3 \) of the gas at N.T.P. are required for one analysis. A Farkas (107) reports that the methods can be employed successfully only if the deuterium
content of the gas sample is above one mole percent. The
accuracy of the method has been reported to be ±0.1 mole percent.

The apparatus is calibrated against standard samples of
the gas. These samples are prepared by the quantitative mixing
of the hydrogen and deuterium gas and equilibrating over a hot
nickel wire.

G.R.Cleno and G.A.Swan (108) have described a method wherein
water samples are used instead of hydrogen. Use is made of the
difference in thermal conductivity between vapours of H₂O and D₂O
are in equilibrium with the corresponding ices at a constant tempera-
ture.

F. The Nuclear Magnetic Resonance Method:
This method reported by E.M.Vladimiresky et al (109) is
based upon the difference of the magnetic moments of the nuclei
of the hydrogen and deuterium, which makes it possible to measure
the amplitude of the resonance of hydrogen and deuterium without
mutual interference. Measurements are done by comparing the
amplitudes of the signals from the standard sample and the
sample being investigated.

G. Density Methods:
1) Pycnometer: E.H.Washburn and E.R.Smith (110) used
modified pycnometer for measuring small differences in density for
the analysis of heavy water samples. Two silica pycnometers of
the same size approximately, and of nearly the same shape and
weight were employed. Each pycnometer had a single capillary
having a reference mark of less than 0.01 cm. width. The volume
of each pycnometer upto reference mark was found out with an
accuracy of 0.1% whereas the capillary volume was found by
calibration with mercury. Two pycnometers, after filling one
with standard water and the other with the sample, are brought
to the same temperature and their levels above the mark are
noted by a cathetometer. Difference in weight of the two is
determined by putting them in opposite pans of the balance. The
same is repeated after exchanging the samples in the pycnometers
and the difference in density calculated from the above data.

\[
d - d_0 = \frac{(m_2 - m_1) + d_0(\Delta v_1' - \Delta v_1'') - (\Delta v_2' - \Delta v_2'')}{v_1 + v_2}
\]

where

- \(d\) = density of the sample being studied.
- \(d_0\) = density of the standard sample.
- \(m_1\) = difference in masses after the first filling,
- \(m_2\) = difference in masses after the second filling,
- \(\Delta v_1', \Delta v_1''\) = volume of water above the reference mark in the
capillary of pycnometer one in the first and
second filling.
- \(\Delta v_2', \Delta v_2''\) = volume of water above the reference mark in the
capillary of pycnometer two in the first and
second filling.
- \(v_1\) = volume of pycnometer one to the reference mark.
- \(v_2\) = volume of pycnometer two up to the reference mark.

A bulb volume of 50 cm³, and a capillary diameter of about
0.1 cm have been reported to be suitable for precision work. The
density after being corrected for O¹⁸ content of water is inter-
preted in the form of deuterium percent. An alternate method for
avoiding this correction involves normalising of the sample with
sulfur dioxide before the determination of the density. difference
K. W. Vladimirska and B. M. Smasyevich (109) have recently compared
the density method with the mass spectrometric method and have reported that the density method gives results 0.002± 0.004% lower than that obtained by other methods.

ii) Gradient Tube: The method was first developed by Linderstorm-Lang K and coworkers (111) for the heavy water analysis and is based upon Fick's principle, according to which, when one liquid is layered over another of greater specific gravity with which it is miscible, a linear gradient of density develops in the region of the juncture of the two. The density was determined by comparing the equilibrium position of 1 mm³ drop of the sample with that of a standard sample, in a heterogeneous mixture of bromobenzene and kerosene forming a linear gradient of densities. The advantage of the process lies in the use of extremely small amount of the material needed for the determination and the insensitivity of the accuracy to the convection currents.

iii) Falling Drop Method: H.B. Barbour and W.F. Hamilton (112) were the first to illustrate that the method could be used for the accurate determinations of the specific gravity of a liquid. A drop of the fluid under investigation is allowed to fall through a column of liquid or a mixture of liquids immiscible with the fluid. After some time, the sphere of fluid achieves a terminal velocity, which, to a first approximation, is governed by Stoke's law

\[ v = \frac{2gr^2 (d_1 - d_0)}{9 \mu} \]  

where
- \( v \) = terminal velocity of the falling drop,
- \( r \) = radius of the sphere, \((\text{mm})\)
- \( g \) = acceleration due to gravity,
- \( d_1 \) = density of the sphere,
- \( d_0 \) = density of the medium, and
- \( \mu \) = coefficient of viscosity of the medium.
When the viscosities and density of the medium are constant, the terminal velocity of the sphere depends upon both the radius and the density of the drop. With a properly constructed pipette, the radius of the drop can be kept sufficiently uniform, so that the rate of fall of the spherical drop is a measure of its specific gravity.

K. Vogt and W. F. Hamilton\(^{(113)}\) employed the method for the determination of the deuterium content of water and found the density with an accuracy of 1 to 2 parts per million. A mixture of bromobenzene and xylene was employed by these investigators as the medium. The use of binary mixture introduces complications due to the difference in vapour pressure of its components. Any evaporation results in the change in composition and thereby the density of the surface layer, giving rise to vertical currents. A. S. Keston et al\(^{(114)}\) avoided these difficulties by using o-fluorotoluene as the immiscible medium. They report the density value of 0.9996 at 26.8°C of the middle fraction of the o-fluorotoluene obtained from Eastman Kodak Co. The difference in the coefficients of thermal expansion of water and o-fluorotoluene permits the variation of the difference in their densities, by change of temperature. The accuracy of the method can be appreciably enhanced by decreasing the rate of fall through adequate control of the temperature. The above authors observed that a 7 mm\(^3\) drop of distilled water took 180 Sec. to fall through a distance of 15 cm. With this arrangement it was possible to compare two samples with a reproducibility of 1 ppm.
The correlation (96) between the specific gravity of the water sample and the falling time of a drop of the sample is obtained experimentally in graphical form. The basis of plot, as derived from Stoke's law gives

\[ d_1 - d_2 = C \left( \frac{1}{t_1} - \frac{1}{t_2} \right) \]

\[ t_1 = \text{time taken for sample 1} \]
\[ t_2 = \text{time taken for sample 2} \]
\[ d_1 = \text{density of the sphere} \]
\[ d_2 = \text{density of the medium} \]
\[ C = 9 \mu x / 2 g r^2 \]
\[ x = \text{falling distance.} \]

A plot is made of \((d_1 - d_2)\) versus \((1/t_1 - 1/t_2)\) for a set of standard waters, keeping either \(d_1\) or \(d_2\) the same. It is of importance to have the drops of the same size.

iii) Temperature Float Method: G. Pisati and N. Reggiani (115) were the first to employ the float for determining the specific gravity of sea water. The authors employed two methods of study. In one method, a float of constant specific gravity was employed and distilled water was added to the liquid till the float reached a state of equilibrium in the body of the liquid whereas in the other method, the same was achieved by the addition of platinum weights to the sinker. Nansen (116), during the course of his investigations on salinity of seawater in the north-polar basin, employed the second method of Pisati and Reggiani but brought about the final adjustment through slight variation in temperature. The method was used by A.W. Warreington (117) and accuracies of the order of one part in several hundred thousand were obtained.
T.W. Richards and Coworkers (118-120) modified the method by making temperature as variable and noting the exact temperature when a calibrated float is in equilibrium in the solution. The method was employed for the quantitative analysis of solutions with marked success by the above authors and was later used by Lewis and Mac Donald (121), Briscoe and Coworkers (122, 123) and Dole (124) for the isotopic determinations of heavy water.

The Temperature-Float method works on the following principle. The temperature at which a small quartz float has the same density as an unknown water sample surrounding it, i.e., the float neither sinks nor rises, is compared with the temperature at which the float has the same density as a standard water sample. This temperature difference along with the data on thermal expansion of quartz, D$_2$O and H$_2$O permits the calculation of the difference in densities of the two samples (125, 126). This difference can then be interpreted in the form of mol percent of heavy water.

a) Float: The material and design of the float have been reported to have significant effect on the final results. T.W. Richards and J.W. Shipley (118) advocated the use of a float with fish like shape, whereas H.J. Emeleus et al (122) preferred a slim cylindrical quartz float. Their float, about 25 mm long and 4 mm in diameter was found to be more sensitive to small differences in the density of the fluid.

Though Pyrex floats have been used by some authors, fused quartz forms an ideal material for the same because of its small thermal expansion, great elasticity, mechanical strength and extreme insolubility.
b) Purification of the Sample: The method demands extreme purity of the sample for analysis. Little or no isotopic fractionation should occur during the process of purification. Dole et al. (96) describe an evaporator which purifies water with negligible isotopic fractionation, within experimental error. The water, flowing in a steam heated coil in a controlled manner is evaporated by means of a stream of dry air and completely condensed. The method ensures complete evaporation and avoids the bubbles and bursting pockets of steam under the water surface thereby eliminating the formation of spray. However, volatile organic matter is not completely removed by this procedure and such samples have to be given preliminary purification.

6) Analysis of the Sample: The float is put in the sample in a float chamber. Test tubes 25 by 100 mm have been generally used as float chambers. The equilibration temperature was found by earlier investigators (96) through observing the movements of the float in a column of the sample in float chamber and measuring the temperature at which the float was stationary. Use was made of the dual tank thermostat (96) to maintain the temperature at the equilibration value for periods sufficient to follow the movement of the float. The outer small but well insulated tank is filled with water which is stirred vigorously. Mercury regulator and vacuum tube relay controls the temperature. The float chamber is placed in an inner bath consisting of a cylindrical battery jar also filled with water. The temperature of the inner bath is maintained constant up to ± 0.0003°C. by this arrangement.
It was observed by T.W.Richards and J.W.Shipley\(^{(118)}\) that a temperature variation of 0.001°C at the equilibration value is sufficient to reverse the motion of the float. Because of the sensitiveness of the measurement and the temperature gradient inherent with any thermostat, which makes the rigid control of temperature improbable, the determinations become tedious and time consuming and accurate results cannot be expected.

To avoid this method of directly observing the temperature of no motion by trial and error, later workers resorted to the determination of the same by calculating the float velocities at temperatures close to the equilibration value, plotting them versus temperature and interpolating the line to zero velocity. H.J.Emeleus et al\(^{(122)}\) have indicated that over a temperature range of the order of about 0.10°C the velocity of the float shows essentially a linear relationship with the departure from the equilibration temperature. R.J.Voskuyl, H.Davis and L.P.Saxer\(^{(127)}\) calculated the rate of rise or fall over a range of ± 0.010°C around the equilibration temperature.

Mention is made by J.Spanoen\(^{(128)}\), that the magnitude of the float velocity has got a definite bearing on the straight line relationship between the rate of motion of the float and the temperature. It is concluded thereby, that the velocity of the float is a linear function of the temperature if it does not exceed 0.04 mm/Sec.

The velocity of the float was calculated by observing the distance travelled through a cathetometer within certain time, whereas use was made of a platinum resistance thermometer for the measurement of temperatures.
There has been some disagreement regarding the outgassing of the sample before analysis. H. J. Emelius et al.\(^{(122)}\) and Merck\(^{(129)}\) observed quite a significant effect of the presence of dissolved air on the equilibration temperature at 20°C and below 20°C respectively, whereas T. Titani and N. Morita\(^{(130)}\) found no such effect on their final results.

The equilibration temperature difference between standard and unknown samples has been used to find out the density difference. The difference in deuterium content of the unknown sample and the reference water may be calculated from the difference in density at 25°C by means of the formula,

\[
\text{Mole percent D} = \frac{927.35 \Delta d}{1-0.0529 \Delta d}
\]

where \(\Delta d = (\text{density of the sample}) - (\text{density of pure water})\)

\(\Delta d = d - d_1\)

Use can be made of the following formula also\(^{(96)}\):

\[
P'' - P' = 927 \frac{(d'' - d_1)}{0.0529(d'' - d_1)} - \frac{(d' - d_1)}{1-0.0529(d'' - d_1)}
\]

where

- \(P'\) = mole percent deuterium in standard water.
- \(P''\) = mole percent deuterium in unknown water
- \(d'\) = density of standard water.
- \(d''\) = density of unknown water.

v) Pressure Float: The method was proposed by Lamb and Lee\(^{(131)}\) for producing a displacement of the float. The method involves the altering of the buoyance of the float by changing the pressure of the air above the liquid.

vi) Magnetic Float: In this case the movement of the float containing a small piece of soft iron in its bulb is controlled by means of an electric current sent through a properly placed electric circuit.