Nov. 22, 1938. W. A. WEBB 2,137,430

PROCESS FOR THE CONCENTRATION OF ISOTOPES

Filed May 15, 1934

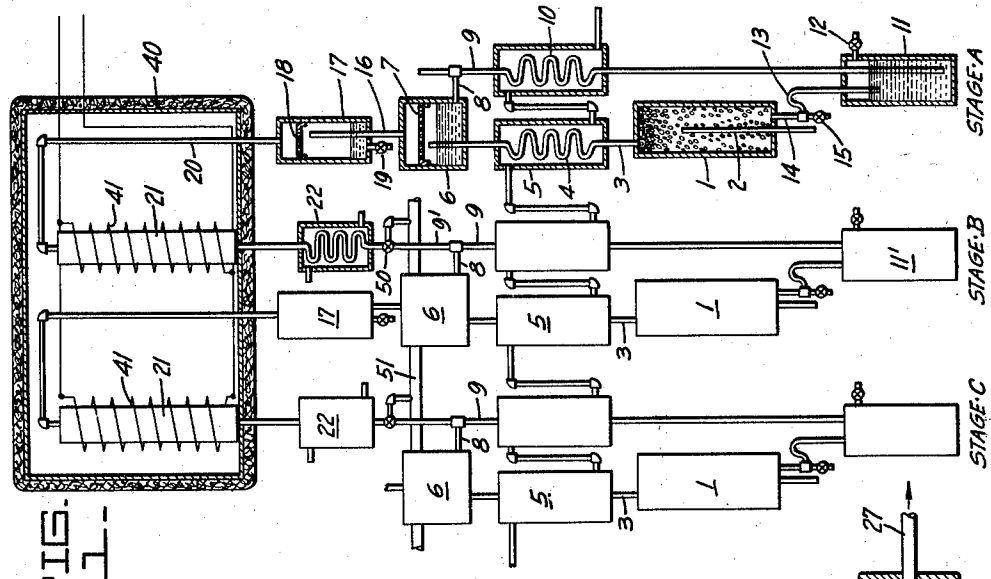


FIG. 1.

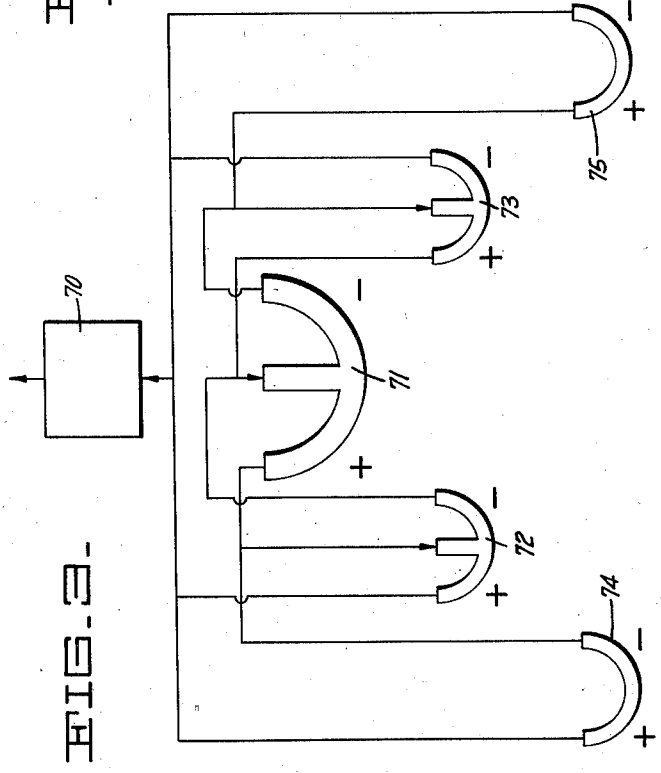


FIG. 3.

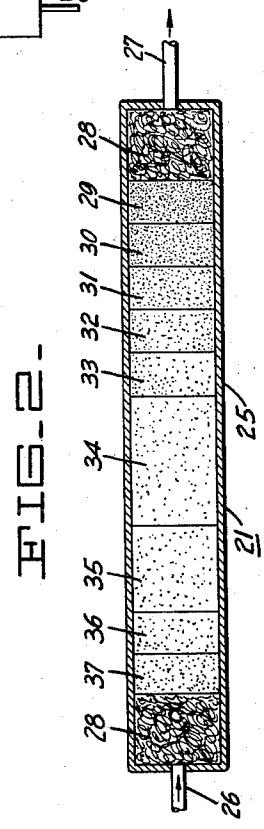


FIG. 2.

INVENTOR.
Wells A. Webb
BY
ATTORNEY.

Patented Nov. 22, 1938

2,137,430

UNITED STATES PATENT OFFICE

2,137,430

PROCESS FOR THE CONCENTRATION OF ISOTOPES

Wells A. Webb, Berkeley, Calif.

Application May 15, 1934, Serial No. 725,711

2 Claims. (Cl. 204—9)

The present invention relates to the recovery of isotopes, and has for its principal object the provision of an improved apparatus and method for effecting their separation.

It is now known that certain elements exist in isotopic forms of different atomic weight, and extensive studies are being carried on to determine the chemical and physical properties of the heavier isotopes, the rarity of which, heretofore, has permitted them to escape detection. Examples of these heavy isotopes are found in hydrogen, which is now known to have at least one isotopic form having an atomic weight of two, and in oxygen, which is now known to have at least one isotopic form having an atomic weight of eighteen.

In order to effect separation of the various isotopic forms of what has heretofore been assumed to be a single element, it is, of course, necessary to rely on some difference in the physical or chemical behavior of the several forms either in elemental or compound form. Several techniques for such separation have been proposed which include differential diffusion of gaseous forms through metallic or other membranes, fractional distillation of liquefied gases and liquid compounds, and fractional electrolysis of various compounds. The first technique depends upon the fact that the lighter isotopes diffuse through membranes more readily than the heavier, the second, upon slight differences in boiling points, and the third, upon the fact that compounds of the lighter isotopes are more readily decomposed by electrolysis than the heavier.

The improvements of the present invention are principally directed to the method of separation by fractional electrolysis although certain of their principles are equally applicable to other methods. Briefly summarized, the objects of the invention are as follows:

The provision of a method and apparatus for obtaining gradually increasing concentrations of the isotopes in a series of concurrently operating stages of a concentrator;

The provision of a method and apparatus for concurrently concentrating isotopes of a plurality of elements and separating the maximum concentrations of each;

The provision of a method and apparatus in which, during a process of isotope concentration, additional material of equal isotopic concentration may be introduced into the material undergoing concentration;

The provision of controlling means whereby the concentration of material introduced, as above, is maintained equal to that of the material undergoing concentration, thus avoiding loss of efficiency by dilution;

The provision of a method and apparatus whereby isotope concentration may be effected in a batch of material without change in its volume;

The provision of an electrolyte particularly adapted for the electrolytic concentration of isotopes;

The provision of electrodes particularly adapted for the electrolytic concentration of isotopes;

The provision of an improved form of cell for the electrolytic concentration of isotopes;

The provision of an improved device for recombining evolved gases resulting from the electrolytic decomposition of material; and

Other objects which will appear more fully in the following specification, read with reference to the accompanying drawing forming a part thereof, in which:

Figure 1 is an elevation of a series of cells for the electrolytic separation process;

Figure 2 is a diagrammatic section of the catalyzer; and

Figure 3 is a diagram of ancillary apparatus for the separation of concentrated mixed isotopes.

In the following description, the recovery by electrolysis of the heavier isotopes of hydrogen and oxygen from water will be described, as a convenient example of the application of the invention, it being understood that it is equally applicable to other substances containing one or both of the heavy isotopes. The hydrogen isotope having an atomic weight of two, will be referred to as deuterium, and under the chemical symbol "D".

The present invention contemplates the recovery of deuterium from a substance, such as water, which contains a very small percentage of it, by electrolytic decomposition. It has been pointed out that such compounds of the lighter isotope are more readily decomposed by such action than those of the heavier isotope, deuterium, and a concentration formula may be

calculated for given constant temperatures, current densities, and other factors hereinafter noted, as follows:

$$\frac{D}{Do}=\frac{H^{\alpha}}{H_o^{\alpha}}$$

Where

Ho is the amount of water containing ordinary hydrogen, before electrolysis;

Do is the amount of water containing deuterium, before electrolysis;

H is the amount of water containing ordinary hydrogen, after electrolysis;

D is the amount of water containing deuterium, after electrolysis; and

α is a factor representing the difference between the rate of electrolytic decomposition of the hydrogen oxide and the deuterium oxide, the factor being less than unity in the above formula, since the deuterium oxide decomposes less readily.

Under the conditions set forth in the following description, a value for α of about .143 has been obtained, from which it follows that if 1000 grams of water containing .25% D_2O is reduced to 100 grams of H_2O plus an unknown quantity of D_2O, the concentration of deuterium thus effected may be calculated as follows:

$$D=\frac{H^{\alpha}Do}{H_o^{\alpha}}=\frac{100^{.143}\times 2.5}{997.5^{.143}}=1.8$$

which shows that in a final liquid weight of 101.8 grams there will be 1.8 grams of deuterium oxide, or a concentration of 1.77% as compared with a concentration of .25% at the beginning. This concentration obviously may be increased by further procedure along this line.

To expedite such progressive concentration, the present invention contemplates the concurrent electrolytic decomposition of a plurality of batches of water containing different concentrations of deuterium oxide, and provides the apparatus shown in Figure 1 which may be used for this purpose.

The apparatus

This apparatus comprises a circulatory system containing a quantity of water having an electrolyte in solution and consisting of a cell 1, the wall of which serves as an anode, and which has a cathode 2 located therein.

Decomposition of the electrolyte solution produces a mixture of the gaseous products of the decomposition with a portion of the solution, which mixture passes upwardly through a tube 3 through cooling coils 4, surrounded by a jacket 5 through which a cooling medium is passed, and into a separator 6 having means such as a baffle plate 7 therein to insure separation of the mixed gases from the liquid.

From the separator 6, the liquid returns to the cell 1 through tube 8 connected to tube 9 which passes through cooling coils 10 similar to coils 4 and correspondingly jacketed and cooled. From these coils, the liquid passes into a reservoir 11 having a cock 12 by means of which the air pressure in the reservoir may be regulated to maintain proper liquid levels in the system. Also connected to this reservoir 11 is a tube 13, adjustable so that its end may be maintained below the level of the liquid in the reservoir, and connected with the cell 1 by means of tube 14 having a cock 15, by means of which the cell may be drained. The evolved gases, acting to raise the liquid in tube 3, maintain the liquid in this system in constant circulation, cooling and mixing it adequately.

From the separator 6, the mixed gases pass into tube 16 and through a trap 17 provided with a baffle plate 18 and a drain cock 19, which trap is preferably provided for the purpose of separating any foam escaping from the separator. From this trap, the mixed gases are conveyed, by tube 20, to a recombining means 21, hereinafter described in detail, which effects a chemical recombination of the gases and feeds the resulting liquid and/or vapor into a condenser 22, of conventional form, whence the liquid is conveyed by a tube 9' to the reservoir 11' of an adjacent circulatory system or "stage" corresponding in construction and operation to the system just described. It will be evident that as many of these systems may be thus interconnected as are necessary to effect the degree of concentration desired.

The separation of the isotopes may be considerably expedited by the use of an electrolyte which does not contain the element sought to be separated in its composition. If, for instance, potassium hydroxide, is used as an electrolyte in the concentration of deuterium, the KOD concentration of the KOH will increase as rapidly as the D_2O concentration of the H_2O and, if a full yield is to be obtained, it will be necessary to free the deuterium from the potassium salt by bubbling carbon dioxide through the electrolyte

$$(2KOD+CO_2\rightarrow K_2CO_3+D_2O)$$

or by equivalent means. This extra operation may be avoided by using a hydrogen free electrolyte such as sodium or potassium carbonate, in a concentration giving the minimum electrical resistance.

It has been found that the separation factor α may be favorably affected by the use of a cathode material requiring a relatively high overvoltage in operation, and since the objective is not a maximum evolution of gas for a given amount of current, but rather a maximum separation of the isotopes, it is desirable to use a material such as lead, aluminum or other material requiring a comparatively high overvoltage for the cathode.

Certain of these metals, aluminum for instance, are attacked by alkaline electrolytes, but since the reaction is checked by cooling the electrolyte solution, and since such cooling also affects the separation factor α favoraby, it is evident that the cooling of the solution is desirable for the double purpose of inhibiting electrode decomposition and favorably modifying the separation factor.

Where it is desired to concentrate only one of a plurality of isotopes present, the factor α as to this isotope may be favorably affected by increasing the current density at the electrode evolving it, as by using a rod of comparatively small area for such an electrode, as compared with a cylindrical chamber, forming the cell wall, for the other electrode.

The incidental concentration of heavy oxygen which takes place during deuterium concentration is undesirable unless the heavy oxygen be afterward separated out of the yield, as hereinafter described, because it effects an increase in the density of the yield which may be erroneously attributed to the presence of a larger concentration of deuterium. By controlling the relation of the current density on the two electrodes as

above described such incidental concentration of heavy oxygen may be minimized.

The catalyzer

In effecting the recombination of evolved hydrogen and oxygen, heretofore referred to, it is desirable to lessen the force of the reaction, which under ordinary circumstances would be explosive. The present invention contemplates the provision of a novel form of catalyzer for this purpose, such as that shown in detail in Figure 3.

The catalyzer comprises a tube **25**, preferably of metal, such as brass, and sealed at both ends except for the access provided by inlet tube **26** and outlet tube **27**. Adjacent these tubes stuffings **28** of fibrous or other material through which the gases and vapor may pass freely are preferably provided, and the remainder of the tube is filled with inert material such as sand, of an 8 to 10 mesh size through the interstices of which the gases and vapors may pass in intimate contact with the surfaces of the particles. These particles should be free from sharp points and protuberances which might be heated disproportionately during the reaction and thus cause the reaction to be accelerated to an explosive degree. Upon the surfaces of these particles, platinum or an equivalent catalytic agent is deposited in concentrations varying from a minimum at the inlet end of the tube to a maximum at the outlet.

Such deposition of platinum upon sand may be effected by dissolving platinum in aqua regia, soaking clean sand in the solution and heating the wet sand to effect decomposition of the chlorplatinic acid leaving metallic platinum uniformly deposited upon the sand particles. The remaining solution then may be diluted and additional sand soaked therein and heated as before, in order to secure successive deposits of smaller platinum concentration.

For a catalyzer tube of three quarter inch inside diameter, satisfactory concentrations of platinum on sand have been secured as follows. First, enough clean sand to fill one inch of the tube was soaked in a solution of .0371 gram of platinum in 1 c. c. of aqua regia, and, after heating, this sand was placed in the portion **29** of the tube **25** adjacent the outlet tube **27**. Next, an equal amount of platinum was dissolved in 2 c. c. of aqua regia, and enough sand to fill another inch of the tube was similarly treated with this solution and placed in the portion **30** of the tube **25**. Next an equal amount of platinum was dissolved in 10 c. c. of aqua regia and sand similarly treated therein was used to fill the next inch **31** of the tube **25**. Next an equal amount of platinum was dissolved in 25 c. c. of aqua regia and sand similarly treated therein was used to fill the next inch **32** of the tube **25**. Next an equal amount of platinum was dissolved in 37 c. c. of aqua regia and sand similarly treated therein was used to fill the next inch **33** of the tube **25**. Next, an equal amount of platinum was dissolved in 50 c. c. of aqua regia and sand similarly treated therein was used to fill the next three inches **34** of the tube **25**. Next an equal amount of platinum was dissolved in 100 c. c. of aqua regia and sand similarly treated therein was used to fill the next two inches **35** of the tube **25**. Next, an equal amount of platinum was dissolved in 200 c. c. of aqua regia and sand similarly treated therein was used to fill the next inch **36** of the tube **25**. Finally, an equal amount of platinum was dissolved in 300 c. c. of aqua regia and sand similarly treated therein was used to fill the next inch **37** of the tube **25**. The foregoing is, of course, an empirical determination of concentrations which will produce an operative device, and it is evident that departures from the exact concentrations set forth may still be well within the scope of the invention which contemplates a catalyzer of the characteristics hereinafter set forth.

In operation, it is desirable to mount the tube **25**, as shown in Figure 1, in an insulated housing **40** which may contain a plurality of such catalyzers, and to preheat it to an efficient operating temperature by means of electrical resistance coils **41** or equivalent means. Some heat is generated by the reaction, and hence the insulation should be designed to maintain the tubes at an operating temperature of about 200° C. either with or without external heating from the means **41**.

Mixed gases entering through the inlet tube **26** first impinge upon the surfaces of the sand particles in the portion **37** of the tube **25**, but the platinum concentration there is so low that the temperature rise engendered by the reaction is insufficient to accelerate the reaction to an explosive rate. Any concentration below this limit will be satisfactory, the particular concentration hereinbefore set forth being given merely as an operative example. As the mixture of the gases and water vapor passes along the tube **25** toward the outlet tube **27**, successively increasing concentrations of platinum are encountered, but the gases are also increasingly diluted by water vapor which tends to slow the reaction so that in no case is it accelerated to an explosive rate. The concentration of platinum adjacent the outlet tube **27**, however, is sufficient to insure effective combination of substantially all of the hydrogen and oxygen present.

A catalyzer of the proportions described above has been used to recombine the gases evolved from water by a 50 ampere current, without accelerating the reaction to an explosive rate.

The process, and operation of the apparatus

In the final stages of concentration for the purpose of obtaining deuterium oxide in as pure a state as is possible, the apparatus shown in Figure 1 is preferably operated with an equal current in each cell so that the volume of liquid in each cell system or stage except the last, shown at the right in this figure, remains constant, due to the fact that it receives as much liquid from the catalyzer of the adjacent system as it decomposes.

This avoids the necessity for distillation of the electrolyte solution, which becomes desirable whenever major changes in its volume takes place. In the stages or systems in which the volume remains constant, no such distillation is necessary, since the equality between input and output automatically retains the electrolyte concentration at the optimum value originally set. As the volume of liquid is reduced in the last stage A which receives no input, it is desirable to distill the liquid at intervals to remove enough electrolyte to prevent supersaturation of the solution.

In this type of operation it will be evident that the isotope concentration of stage B will be built up during operation by electrolytic passing off of the lighter isotope to stage C and by the reception of liquid from stage A having a substantial isotope concentration. At the commencement of operation the isotope concentration of the liquid in stage B should be equal to that received via the catalyzer from stage A. As the catalyzer's output increases in isotope concentration due to the volume reduction taking place in stage A, the

electrolytic action in stage B will concurrently build up its own isotope concentration to finally equal the initial concentration of stage A.

In a similar manner stage C and the remaining subordinate stages will each increase in isotope concentration so as to equal the initial isotope concentration of the next rightward stage by the time stage A has been reduced in volume to the point where such concentration attains the maximum desired.

When this point is reached, the liquid is drained from stage A by means of the cock 15, and distilled. This is the deuterium oxide yield. Stage B now becomes stage A for further operations, the former stage A being filled with new water of the concentration proper for its alphabetical position in the stages, and its catalyzer output shut off from original stage B by means of two-way valve 50, and diverted into header 51 for any desired purpose. To facilitate such operation of the apparatus, the several stages are preferably arranged in an endless chain rather than in line, as shown for convenience in the drawing.

The foregoing type of operation may, of course be used for all concentration work, but is particularly desirable in the more concentrated stages because it avoids the losses incident to frequent distillations of the electrolyte solution.

The apparatus may also be operated so as to obtain a reduction in the volume of liquid in each stage, this effect being obtained by connecting the electrodes of the several stages in parallel and controlling the current input to each cell by a rheostat, by the proportioning of the electrodes or by both such means.

When operating in this way, the liquid in stage A will be reduced in volume from, say, 100 c. c. to 10 c. c. while the liquid in stage B, subjected to a correspondingly heavier current will be reduced from 1000 c. c. to 100 c. c. and that in stage C, subjected to a correspondingly still heavier current, from 10,000 c. c. to 1,000 c. c. The current increase for each successive stage must be great enough, of course, to provide for the redecomposition of water received from the catalyzer of the adjacent stage in addition to effecting the proportionately greater volume reduction planned for the stage. Figure 1 may be taken only as diagrammatic for this type of operation since it will be evident that the circulatory systems of the several stages must be proportioned in size to the volumes of liquid to be handled, which may, of course, be in any desired ratio to each other.

A lesser volume reduction may be effected in this method of operation by feeding recombined gases from stage A to stage C, from stage B to stage D, and from stage C to stage E, lettering the stages in the order in which they become "yield" cells. In this way, the liquid in stage C is reduced in volume during its operation as stage B before it functions as stage A, and hence the isotope concentration of stage C is more easily brought into equality with the concentration of the isotope in the gases evolved from stage A.

This plan of operation possesses the advantage of effecting a proportionately greater concentration within fewer stages than that heretofore described, and is therefore more useful in the early concentration procedure than in the final purification.

While the foregoing apparatus and process has been described with reference to the recovery of the hydrogen isotope, deuterium, the same means are applicable with very slight changes of proportion to the recovery of the oxygen isotope of atomic weight eighteen and to separation of other isotopes. In the case of the oxygen isotope, it is known that its abundance in nature is much greater than that of deuterium and it is therefore apparent that less volume reduction of the electrolyte solution will be necessary in its recovery. However, as its atomic weight difference from the commoner oxygen is proportionately less than the proportionate weight difference of the hydrogen isotopes, its separation factor in electrolysis is much more unfavorable, and many more stages will be required in apparatus for its recovery.

Both of these considerations favor the selection of the system in which the liquid volume remains constant up to the last stage.

Concurrent concentration of hydrogen and oxygen isotopes

In the light of the foregoing description, it will be seen that, during the concentration of deuterium oxide, some concentration of the heavier isotope of oxygen takes place incidentally, and vice versa. It is therefore possible to construct apparatus for the concentration of the two isotopes separately, in which such incidental concentration of the other isotope in one section is used to advantage in the other.

A diagrammatic illustration of such apparatus appears in Figure 3, in which cell systems designed to separate the evolved gases are shown as U-tubes, the direction of feed of the recombined gases is shown by arrow-headed lines, and catalyzers and electrical connections are omitted from the diagram for simplicity.

In this figure, 70 represents a stage of a system such as that shown in Figure 1; 71, 72, and 73 are intermediate cells designed to separate the evolved gases and to receive liquid produced by the recombination of gases evolved in other cells; 74 is the volume reducing cell from which the deuterium oxide yield is obtained; and 75 is the volume reducing cell from which the oxygen isotope yield is obtained. Cells 74 and 75 are also of the gas separating type.

After the yield is removed from cells 74 and 75, the liquid from cells 72 and 73 is transferred into these cells, respectively, and the liquid from cell 71 is divided into cells 72 and 73. Cell 71 is then refilled with the liquid from stage 70, and the apparatus of Figure 1 is reset so that the recombined gases from cells 72 to 75 will feed into the next full stage instead of into the one just emptied, which is filled with new water and is adjusted to discharge the recombined gases into the header 51.

In operation, it will be seen that light hydrogen evolved from cell 74 is recombined with oxygen and fed into cell 72; light hydrogen from cell 72, similarly recombined, is fed into cell 71; light hydrogen from cell 71, similarly recombined is fed into cell 73; and light hydrogen from cells 73 and 75 similarly recombined, is fed into stage 70.

Likewise light oxygen from cell 75, is recombined with hydrogen and fed into cell 73; light oxygen from cell 73, similarly recombined, is fed into cell 71; light oxygen from cell 71, similarly recombined is fed into cell 72; and light oxygen from cells 72 and 74, similarly recombined, is fed into stage 70. From stage 70 on, the operation is as described in connection with either mode of operation of the apparatus shown in Figure 1.

The effect of this operation is to concentrate both the hydrogen and oxygen isotopes in the stages leading up to stage 70, and then to sepa-

rate the isotopes by means of cells 71 to 75 inclusive which effect the final concentration. Since the flow of the light hydrogen isotope is to the right in this figure, it is evident that the maximum deuterium concentration will be found in cell 74, and since the flow of the light oxygen isotope is to the left in this figure, it likewise appears that the maximum concentration of the heavy oxygen isotope will be found in cell 75. The number of cells shown is, of course, merely illustrative and may be varied at will.

It will also be apparent that the process described is not dependent upon any particular apparatus, but may be carried out by manual transfer of the materials according to the procedure outlined. The apparatus disclosed, however, greatly facilitates the process by performing these transfers automatically.

I claim:

1. A process of concentrating isotopes by electrolysis comprising the steps of simultaneously decomposing a plurality of batches of material of differing isotope concentration, recombining the decomposition products of one of said batches to form material of different isotope concentration than the batch from which said products were derived, and introducing said recombined decomposition products into another of said batches having an isotope concentration substantially equal to that of the said recombined products, such introduction being effected while the batch into which the introduction is effected is undergoing decomposition.

2. A process of concentrating isotopes by electrolysis comprising the steps of simultaneously decomposing a plurality of batches of material of differing isotope concentration, recombining one of the decomposition products of one of said batches to form material substantially equal in isotope concentration to another of said batches, and introducing said recombined material into the latter batch while it is undergoing decomposition.

WELLS A. WEBB.