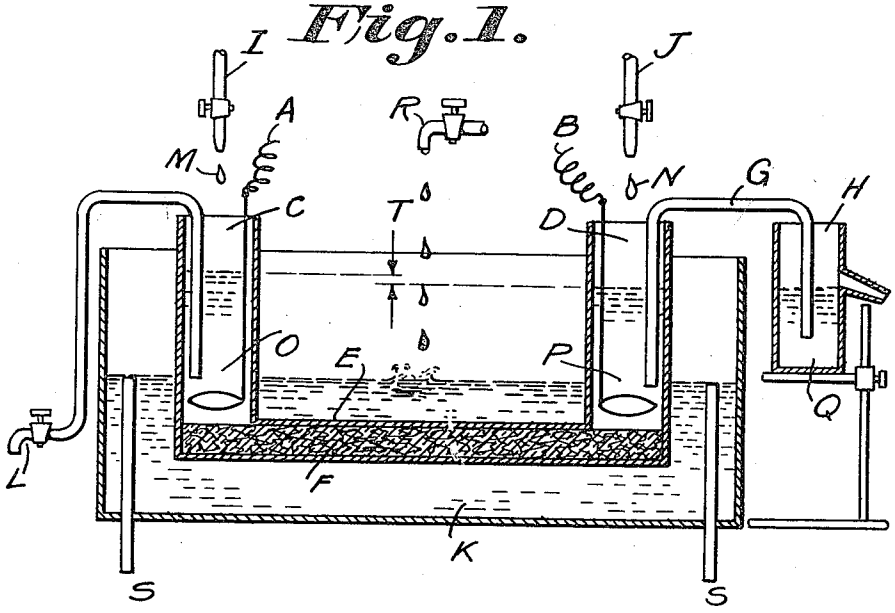
July 14, 1953 S. L. MADORSKY ET AL 2,645,610

PROCESS FOR THE SEPARATION OF ISOTOPIC IONS

Filed Feb. 25, 1942

Fig. 1.



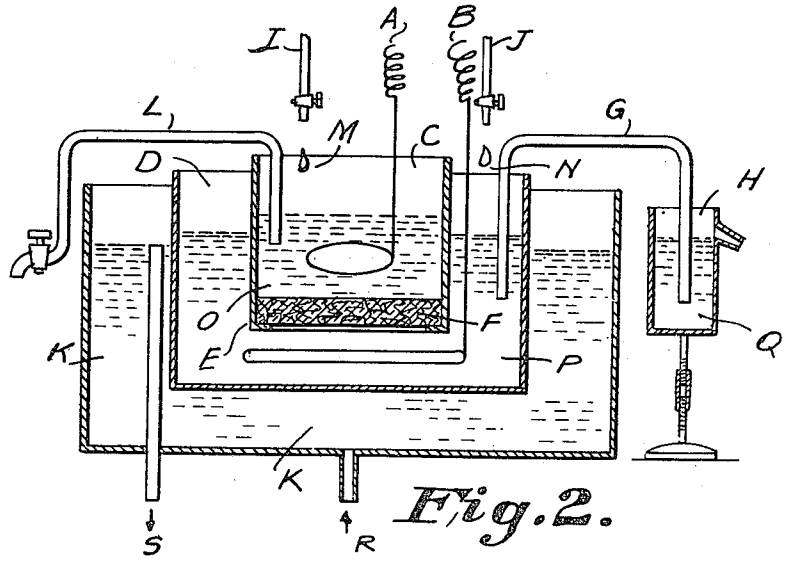


Fig. 2.

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PROCESS FOR THE SEPARATION OF ISOTOPIC IONS

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Application February 25, 1942, Serial No. 432,185

1 Claim. (Cl. 204—1)

(Granted under Title 35, U. S. Code (1952), sec. 266)

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The invention described herein may be manufactured and used by or for the Government of the United States without the payment of any royalty therefor.

This invention relates to the art of separating substances and aims generally to improve the same.

In particular the invention provides a method of beneficiating mixtures of isotopes and like substances capable of ion transport, applied in a new manner rendering it possible to separate isotopes (that is, increase the content in an isotope mixture of one isotope relative to another) and to similarly separate other substances having different ion mobilities.

The method in its preferred form is one in which charged particles in a fluid medium are transported in an electric field in a direction opposite to the flow of the dispersion medium. These charged particles can be the ions of the isotopes of a given element, the ions of a mixture of elements or compounds, as well as charged groups of atoms differing in the velocities of their electrical transport. It is preferable but not essential that the stream velocity be intermediate between the velocities of the ions to be separated. It is also preferable that the composition and concentration of liquid electrolyte solutions which may be employed remain unchanged throughout the operation. It is essential that the system embody provisions to prevent remixing of the separated components.

The method by which our invention can be applied to the separation of isotopic ions can best be shown by specific examples. It must be recognized that various details will necessarily vary for different isotopes and different ion combinations, however, the basic principles involved will remain the same in all cases.

Example I.—The separation of ^{39}K and ^{41}K by the electrical transport of K^+ ions against a counter-flow of an aqueous solution of K_2SO_4. When K_2SO_4 is dissolved in water, it disassociates into ions according to the equation:

$$K_2SO_4 \rightarrow 2K^+ + SO_4^-$$

These ions in turn are believed to become hydrated by attracting to themselves a number of water molecules. The actual ions transported are therefore believed to have the form:

$$(K.nH_2O)^+ \text{ and } (SO_4.nH_2O)^-$$

Hereafter, when K^+ or SO_4^- are mentioned, the actual ions, whether or not these are regarded as solvated ions, are meant. When a direct electric current is applied to two electrodes immersed in an aqueous solution of K_2SO_4, K^+ ions migrate towards the cathode. During the electrolysis hydrogen is liberated at the cathode and oxygen at the anode, the K^+ and SO_4^- remaining in solution at the cathode and anode respectively. In consequence, in a stationary electrolyte body in absence of special provision, the cathode compartment will become alkaline due to the transport of K^+ ions into it and the simultaneous transport of SO_4^- ions out of it. Concomitant with this action at the cathode, the anode compartment in absence of such provisions will become acid due to the transport of SO_4^- ions into it and simultaneous transport of K^+ ions out of it. Since the K^+ ions consist of a mixture of light and heavy isotopes $^{39}K^+$ and the $^{41}K^+$, both isotopes are transported towards the cathode. In this application of our invention it is extremely desirable for the solution to flow in the direction from cathode to anode at a rate preferably intermediate between the velocities of the $^{39}K^+$ and $^{41}K^+$ ions, of which the former is faster than the latter.

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It is also preferred for continuous operation that the composition and concentration of the solution remain unchanged.

(*a*) These conditions may be realized in practicing this invention by the continuous or intermittent addition of H_2SO_4 and H_2O to the cathode compartment at such a rate that the composition and concentration of the original electrolytic solution are controlled in a desired manner or remain unchanged. At the same time KOH and H_2O may be added to the anode compartment at such a rate that the composition and concentration of the original electrolytic solution are controlled in a desired manner or remain unchanged. The anode compartment may be equipped with a constant level overflow device. In the preferred arrangement, there is established a flow of electrolyte thru the system in the cathode-to-anode direction, and the velocity of this flow for best operation is held at about some weighted mean of the migration velocities of the slow and fast moving isotopes, the weighting being dependent on the stage of advancement of separation. In the particular example given, the velocity of flow approaches nearer and nearer the average velocity of $^{39}K^+$ ions as the separation advances, in the absence of withdrawals. When the concentrated isotope is being withdrawn from the cathode compartment the stream velocity will not necessarily be the weighted mean of the isotope velocities. The rate of intermittent or continuous withdrawal should not be so great as to reduce the stream flow to a rate less than that of the $^{41}K^+$ ions. Under these prescribed conditions it will be seen that the faster moving $^{39}K^+$ ion will make head-

way against the electrolyte stream and move towards and into the cathode compartment while the slower moving $^{41}K^+$ ions will be carried out of the cathode compartment and will be carried by the stream in the cathode-to-anode direction.

In this invention the loss of the concentrate in the cathode compartment is minimized by reducing remixing by turbulence and diffusion to a minimum. This may be accomplished in any desired manner, and in our preferred embodiment is accomplished by separating the cathode and anode compartments by some porous packing, such as sand, fritted glass, porous Alundum or any other porous or granular electrically nonconducting material, which will permit the electrical transport of ions and the flow of electrolytic solution while quieting the flow through the separating zone. It is believed desirable, for best efficiency, to have the packing of a character providing interstices having minimal areas of relatively uniform small size, of the order of half a millimeter or less.

The theoretical criteria are that the minimal sections should be small enough to reduce remixing to a substantial degree, the ultimate being to a degree comparable to diffusion in static liquids, and large enough to enable flow of the electrolyte through the packing without requirement of excessive heads.

The uniformity of size of minimal areas is believed desirable because, by Poisieulle's law, fluid flow varies as the fourth power of the radius, while the ion migration varies as the square of the radius. It would thus appear that non-uniformity of minimal areas would accommodate a disproportionate amount of the counter-flow in the larger interstices, resulting in excessive counter-flow in the larger areas, and insufficient counter-flow in the smaller areas, with respect to the rate of ion mobility.

It will be observed that as the rate of counter-flow is not essentially required to be held at the weighted mean of the rates of ion mobility, there is a substantial tolerance of minimal area sizes, particularly where the length of packed column is considerable. However, it is desirable to reduce the length of packed column in order to increase the electrical efficiency of the system, i. e., reduce the power consumption, and therefore it is desirable to correspondingly reduce and make more uniform the interstices; the pore size being made as small as possible commensurate with free flow of the electrolyte without excessive head; and the frit being made as short as possible while reducing back diffusion to a value approximating diffusion in stagnant liquids. The use of a cooling means to reduce the effect of thermal diffusion is also desirable.

A simple design of the apparatus necessary for the separation of ^{39}K and ^{41}K isotopes is shown in Figures 1 and 2, in which—

Fig. 1 is a diagrammatic longitudinal section of one illustrative embodiment; while

Fig. 2 is a similar section of another. Corresponding parts are designated by the same letters in both figures. In these illustrations A is the cathode, B the anode, C the cathode compartment, D the anode compartment, E the connecting compartment, F the porous medium to prevent remixing, G and H constant level means, I the acid inlet, J the alkali inlet, K a cooling means, and L a means for withdrawing the light isotope concentrate from the cathode compartment. Letter M refers to the required solution of H_2SO_4 in water, N to that of KOH in water, O refers to the cathode zone in which the ^{39}K isotope is being concentrated, P to the anode solution, which serves as a supply of fresh K^+, and Q to the overflow liquid. Where water is used as the cooling means K, the system may comprise a cooling water inlet R and suitable overflow pipes S.

In operation, when a negative potential is applied to A, with respect to B, K^+ ions will be transported in the D-to-C direction while SO_4^- ions will be transported to the C-to-D direction. In the preferred operation of the method inlet means I is then regulated to admit H_2SO_4 at such concentration and rate as to keep the concentration and pH of O in its original state. At the same time inlet means J is regulated to admit KOH at such concentration and rate as to keep the concentration and pH of P in its original state. Additions of small amounts of methyl orange solution, either separately or with the H_2SO_4 and KOH solution, to the cathode and anode compartments serves as a means to control the pH in the two compartments. Concentrations of H_2SO_4 and KOH solutions are computed on the basis of concentration of K_2SO_4 in the electrolyte being used and on a knowledge of hydrolysis and velocities of K^+ and SO_4^- ions.

The rates of addition of H_2SO_4 and KOH are computed on the basis of the amount of direct current applied. Since F is a material of fine porosity, solution O will have a higher head, T, than P. In consequence, the solution flows from C-to-D, the velocity of the flow preferably being maintained at about the weighted means of the average rates of migration of $^{39}K^+$ and $^{41}K^+$ ions. The length of tube E, filled with porous material, is not critical, lengths of a few millimeters and of 120 centimeters have been used successfully. In practice, short tubes, filled with fine-grained materials are preferable to long tubes filled with coarse-grained materials. The direct current flowing between A and B can be varied between wide limits; however, it should not be so low that the rate of diffusion from cathode to anode and vice-versa becomes comparable to the rate of transport; neither should the current be so high that the electrolytic solution boils or becomes turbulent.

In one embodiment carried out by the inventors the apparatus used was similar to that shown in Fig. 1. Connecting tube E consisted of a glass tube, 2.2 centimeters inside diameter and 122 centimeters long, fitted with a cathode and an anode compartment and other parts, as shown in Fig. 1. The apparatus was packed with a fine-grained sand, in the neighborhood of 60 mesh or less, and filled with solution of K_2SO_4 containing 1 equivalent of K_2SO_4 to 50 equivalents of H_2O. The restituent solutions of H_2SO_4 and KOH contained each 1 equivalent of the acid or base to 25 equivalents of H_2O and a small amount of methyl orange. The apparatus was immersed in a bath of flowing water maintained at a temperature of about 35° to 40° centigrade. A direct current of 0.5 ampere at about 825 volts was applied between platinum electrodes. Aqueous H_2SO_4 solution was added at the rate of about 8.74 cubic cms., per hour, and aqueous KOH solution at the rate of about 8.57 cubic cms., per hour, these rates being those which just maintained neutrality, i. e., pH of 3 to 4, as indicated by fading of the methyl orange indicator added to the cathode and anode compartments. The resulting overflow amounted to a little less than the

sum of these figures due to evaporation from the electrode compartments and receiver. From these figures, the flow rate through the connecting tube E, based on a calculated free cross-section of 14.35%, amounted to about 16.0 linear centimeters per hour. For comparison, the calculated average mobilities of $^{39}K^+$ and $^{41}K^+$ in the described field gave a weighted mean value of 16.07 centimeters per hour.

Samples were withdrawn from the cathode compartment at intervals of about 50 hours and analyzed for their relative content of ^{39}K and ^{41}K by the mass spectrograph. The experiment was discontinued after an operation of 335 hours. The results are shown in the table below in terms of ratio of $^{39}K/^{41}K$, the original ratio being 14.2:1.

Cathode Sample No.	Time from beginning of Experiment, hours	Ratio $^{39}K/^{41}K$ in Sample
1	0	14.20
2	25	14.70
3	102	15.20
4	152	15.70
5	204	16.20
6	243.5	16.65
7	294	17.00
8	335	17.40

The ratio in Sample 1 corresponds to 93.44% ^{39}K and 6.55% ^{41}K (the percentage of the isotope ^{40}K being negligible); and that in Sample 8 corresponds to 95.57% of ^{39}K and 5.42% ^{41}K. Thus, the ^{41}K in this run was reduced nearly one-fifth.

Mathematical analyses by the inventors hereof are borne out by the observed results, which, it will be seen from the above table, show a virtually straight line change of ratio with time (i. e., an asymptotic approach toward 100% ^{39}K and 0% ^{41}K), within the range of the table. The theory held by the inventors in this regard with respect to the net ion transport at any given plane in the transport zone, but to which, of course, the inventors are not to be restricted, may be expressed as follows:

1. Ion transport of positive ions away from the anode is a function of the concentration and the ion mobility.

2. Transport of positive ions back towards the anode in the counterflow system is a function of the concentration in the stream and diffusion.

1*a*. Thus it can be shown that the forward transport of the light isotope ions due to the electric current is given by

$$\frac{I^+}{FA}\left(\frac{C_1X_1}{C_1X_1+C_2X_2}\right)$$

where I^+ is the positive ion current, F is the faraday, A is the free cross-sectional area, C_1 and C_2 are the concentrations, and X_1 and X_2 are the mobilities of the light and heavy isotope ions respectively.

2*a*. At the same time the back transport of light isotope ions due to the undercurrent flow of electrolyte is

$$\frac{I^+}{FA}\left(\frac{C_1}{C_1+C_2}\right)$$

while that carried back by diffusion is

$$D\frac{dC_1}{dZ}$$

where D is the diffusion coefficient and

$$\frac{dC_1}{dZ}$$

is the concentration gradient.

3. At equilibrium the forward transport is just balanced by the backward transport. In consequence, the equilibrium expression is

$$\frac{I^+}{FA}\left(\frac{C_1X_1}{C_1X_1+C_2X_2}\right)=\frac{I^+}{FA}\left(\frac{C_1}{C_1+C_2}\right)+D\frac{dC_1}{dZ}$$

4. This expression upon integration gives for the overall separation factor S

$$lnS=\frac{I^+L}{FAD(C_1+C_2)}\left(\frac{X_1-X_2}{X_2}\right)$$

where L is the length of the tube and (C_1+C_2) is the normality of the solution in equivalents per liter.

5. From these expressions it can be shown that the optimum rate of isotope separation is obtained when the system is operating at half equilibrium; as well as supporting the observations that very small differences in ion transport rates may be put to work to give considerable separation by ion transport.

In other words, these and similar analyses indicate that it may be desirable to carry the concentration with a given batch of material, approximately half-way from the starting percentage toward 100%, or 0% as the case may be, and then use the enriched material as make-up material for another run to carry the concentration half way from that point onward, etc. Otherwise expressed, K (in the form of KOH) having 93.44% ^{39}K may desirably be fed to an anode compartment until ^{39}K in the solution drawn off at the cathode reaches about 96.7% ^{39}K. Thereafter K (in the form of KOH) derived from the solution previously drawn from the cathode end, or from other cathode compartments, and hence comprising up to 96.7% ^{39}K may desirably be used to feed an anode compartment until a concentration of about 98.4% ^{39}K is reached at the cathode; then solution comprising up to 98.4% ^{39}K may desirably be employed as make-up to feed another unit of operation, etc., all without departing from the principles of this invention.

Referring in more detail to the specific experiment described above, in that case detailed data was as follows:

Voltage ---------- 825
Amperage ---------- 0.5
Length of tube ----------cm-- 122
Inside diameter ----------cm-- 2.2
Cross-sectional area of unpacked tube-cm^2-- 3.8
Weighted mean velocity of K^+ (per Glasstone, "Phys. Chem.," Van Nostrand, N. Y., 1940, p. 895)$=(6.6\times10^{-4})$ cm./sec., for a gradient of one volt per cm., length of path; (as volts/cm.=825/122=6.76) weighted mean velocity $^{39}K^+$ and $^{41}K^+=(6.6\times10^{-4})$ (6.76) cm./sec.=16.07 cm./hour.

Solutions:

Concentrations:

Electrolyte-- 1 equivalent of K_2SO_4 to 50 molecules H_2O.
Acid-------- 1 equivalent of H_2SO_4 to 25 molecules H_2O.
Alkali ------ 1 equivalent of KOH to 25 molecules H_2O.

Rates of addition:

Acid---- 9.314 g. per hour H_2SO_4 solution=8.74 cc./hr.
Alkali -- 9.451 g. per hour KOH solution=8.57 cc./hr.

Now, since the velocity of K^+ is 16.07 centimeters per hour, we know that under the controlled conditions the rate of counterflow, i. e., of the flow

against the K^+, must also approximate 16 centimeters per hour. Also from the above, the effective free cross-sectional area of tube in this experiment was

$$\frac{8.74}{16}=0.546 \text{ cm.}^2$$

or 14.35% of the total cross-sectional area.

For continuous withdrawal at maximum power efficiency, the withdrawal rate may desirably be set to maintain not to exceed half-equilibrium conditions as above described.

Thus in the detailed experiment above, in which ion transport is 16 centimeters per hour; free cross-section 0.546 cm.^{2}; and separation coefficient, calculated as the inverse square root of the ratio of ionic weights of the hydrated ions, viz: $\sqrt{41+8(18.02)/39+8\times(18.02)}$ is 1.0054; the withdrawal rate to maintain half-equilibrium amounts to the net gain in ion transport [(0.0054)(16 cm./hr.)(0.546 cm^2), which equals 0.04735 cubic centimeter per hour] divided by 2 (one-half of said gain being removed by withdrawal while the other half is dissipated by diffusion). Thus in the example given, for maximum power economy, 0.0236 cc./hr. of enriched electrolyte may be withdrawn at the cathode compartment. With the long frits employed equilibrium conditions lie at very nearly 100% of $^{39}K^+$, so the liquid withdrawn from this small system at 0.565 cc./day would be raised from, say 93.44% ^{39}K to about 96.71% ^{39}K, yielding a substantial output of greatly beneficiated material. A slower withdrawal rate will yield a lesser quantity of material at a higher equilibrium value, i. e., a greater enrichment, with decreased power efficiency; a faster withdrawal, a greater quantity of less enriched material.

In the foregoing, the example has assumed for the sake of simplicity, that the process was applied only for concentrating the light isotope ^{39}K in the cathode compartment.

(*b*) If, on the other hand, it is desired to concentrate the heavy potassium isotope in the anode compartment, instead of the light isotope in the cathode compartment, the spill-over at the anode is maintained as before, except that instead of introducing a fresh supply of KOH into the anode compartment, the overflow liquid from the compartment is treated to convert the K_2SO_4, which it contains, into KOH and this KOH is used again to neutralize the H_2SO_4 formed in this compartment. At the same time, H_2SO_4 is added as previously to the cathode compartment, except that fractions of solutions are withdrawn from the cathode compartment and equal amounts of a fresh solution of K_2SO_4 is added to this compartment at regular intervals, so as to maintain the original ratio $^{39}K/^{41}K$ in this compartment. Otherwise, the operation is the same as when the desired product is the light isotope ^{39}K, i. e., the K^+ is moving from anode to cathode, while the mass flow of the solution is countercurrent from the cathode to the anode. The product, whether light or heavy, is withdrawn from the cathode or anode compartment respectively at regular intervals.

(*c*) In the method just described, KOH enriched in ^{41}K is added at the anode compartment to neutralize the acid formed therein. The method may also be practiced by subtracting free SO_4^- ions from the anode compartment instead of neutralizing them therein. This may be effected, for example, by precipitating the excess sulfate ions in the anode zone as an insoluble sulfate. Thus, if the anode zone electrolyte is withdrawn and treated with $Ba(OH)_2$ the excess SO_4^- ions will be precipitated as $BaSO_4$, and the K_2SO_4 solution remaining may be reintroduced to the anode compartment, steps being taken to maintain the water balance, as by evaporation of water from the K_2SO_4 solution before or after its reintroduction to the anode compartment. As before the pH in the cathode compartment may be maintained by addition of H_2SO_4 and water, and for continuous operation accompanied by withdrawals from the anode compartment of solution enriched in ^{41}K, restituent K^+ ions may be added at the cathode compartment, as by addition of K_2SO_4, to maintain the original ratio of K_{39}/K_{41} therein.

(*d*) If desired, the maintenance of proper pH conditions may be effectuated by adding acid ions at the cathode compartment through the medium of an electrode formed of an appropriate metal salt, and the excess acid ions may be removed from the anode compartment by the use of a metal electrode forming a substantially insoluble salt with the acid. Thus in the case of K_2SO_4 a lead sulfate cathode and a lead anode may be used, producing a non-gassing system. After reduction of the cathode to lead, and oxidation of the anode to lead sulfate, the electrodes may be interchanged and the process continued as before. In concentrating either heavy or light isotopes with this arrangement, the entire system will automatically maintain a pH identical with the pH of the initial electrolyte and, when no withdrawal of concentrate is being made, only water need be added at the cathode compartment to produce the counterflow, and only the corresponding quantity of water need be removed from the anode compartment. Indeed water may be evaporated in an evaporation chamber connected with the anode compartment, and be thereafter condensed and returned to the system at the cathode compartment. During withdrawal of concentrate of lighter or heavier isotopes from the compartment toward or from which the ions migrate, respectively, make-up electrolyte solutions may be added at the opposite end of the system.

(*e*) As above mentioned, the practice of this invention is not limited to details applicable in the specific case of an aqueous solution of K_2SO_4, but contemplates modification of details of operation to suit other systems of solute and solvent, as will be apparent to those skilled in the art from the above and following examples, showing that this invention can be used to separate the isotopes, for example, of any element whose ions can be made to migrate against a countercurrent stream of electrolyte. Consider for instance:

Example II.—The concentration of the light isotope of uranium, ^{235}U.

(*a*) The isotopes of uranium can be separated by our invention from solutions of its salts, such as UO_2Cl_2; UO_2SO_4; $UO_2(NO_3)_2$; etc. Using, for example, an aqueous solution of $UO_2(NO_3)_2$, the apparatus can be essentially either that described in Fig. 1, or that in Fig. 2, or any other design based on similar principles. Some modifications as to details are necessary, however, when applying our method to this system of solute and solvent. In the case of uranium solutions, which are colored yellow, concentration and rate of addition of the acid (in this case, of a solution of HNO_3) to the cathode compartment, can be controlled by means of a liquid boundary which

forms in the cathode compartment, above the packing, between the $UO_2(NO_3)_2$ solution below and the HNO_3 solution above. A stationary boundary, i. e., one which does not move down or up, is an indication of the proper concentration and rate of the inflowing acid. The NO_3^- which accumulates in the anode compartment is neutralized by the addition of an excess of solid uranium trioxide, UO_3, or uranyl hydroxide, $UO_2(OH)_2$, to this compartment.. A sufficient amount of H_2O is also added to this compartment to maintain the concentration of the electrolytic solution in the original state. The ^{235}U concentrating in the cathode compartment, is withdrawn at regular intervals or continuously, as desired.

In this connection, precautions should be taken to prevent the deposit of oxide of uranium on the cathode which would upset the operation of the system. Various preventive measures may be taken. For example, one may prevent deposition of the uranium oxide, as by heating the cathode sufficiently to cause the uranium oxide to remain in solution. Again, one may prevent the uranium-carrying ion from coming in contact with the cathode, as by surrounding the cathode with a uranium free cathode zone restituent, herein the HNO_3 solution, which may be localized or segregated further from the uranium carrying ion by the use of a porous partition or cup between the cathode and the uranium carrying solution.

As before, the concentrations of restituents are calculated on the basis of the dilution of the electrolyte desired, the mobilities of the ion species involved, and the relative solvations of the positive and negative ions. The rate of addition of the restituents is then governed by the number of faradays current to be passed.

(*b*) In lieu of adding the anode restituents in the form of UO_3 or $UO_2(OH)_2$ in solid phase, with separately added water, the restituents may be added entirely in solution form, this solution being advantageously derived, for example, by dissolving UO_3 in a carrier solution of salt identical with the electrolyte solution. This restituent-carrying solution may be standardized to contain a definite amount of UO_3 per cc. to facilitate the control of restituent addition, and the equivalent amount of water, required to be added at the anode to maintain the composition constant, can be either added separately, or mixed with the restituent-carrying solution in the proper proportion and all the anode restituent ingredients added as one solution at the rate required by the current passed. Part of the overflow liquid passing from the anode zone may be used as a source of restituent UO_3, and the remainder as carrier for the anode restituent.

Starting with $UO_2(NO_3)_2$ recrystallized several times to eliminate impurities which might upset the separation, and containing about 99.27% ^{238}U, about 0.72% 235 U, and negligible amounts of ^{234}U, we have successfully increased the percentage of ^{235}U by 2.8% in a relatively short application of separation according to our invention.

Example III.—Separation of difficultly separable elements. Our invention can be used effectively to continuously separate, for example, radium from barium, or rare earths from one another or any two elements having different effective ion mobilities.

Example IV.—Separation of mixtures of atomic aggregates. Our invention can also be used to continuously separate various atomic or molecular aggregates forming ions and having different ionic mobilities when in solution; or mixtures of various types of colloids which form charged particles when in solution and whose ion mobilities, under the influence of a direct current, are not the same for the various kinds of particles to be separated.

To summarize: (*a*) This invention rests on the principle that different isotope-ions have different average mobilities under the influence of an electric field. Thus the lighter isotope ion of potassium $^{39}K^+$ has greater average mobility away from the positive electrode in an electrolyzing system than does the heavier ion $^{41}K^+$.

(*b*) In a freely communicating system, thermal convection and other agitation disturbs the system to such extent that any appreciable net separation of isotopes is unrealized.

(*c*) In accordance with this invention, steps are provided, such as cooling or the interposition of a porous body between the cathode and anode compartments, or both, which prevent such disturbances and even in a system in which no flow of electrolyte is maintained, this enables the above principle to effect slight net separation of isotopes, i. e., beneficiation of isotopic mixtures with respect to certain desired isotopes. Such separation, in a single batch electrolyte system, is not great, and such system, while within the purview of broad aspects of the invention, is thus not a preferred embodiment.

For example, when the ratio of the concentrations of $^{39}K^+$ to $^{41}K^+$ becomes greater in the cathode compartment in a single batch system, it becomes less in the anode compartment, so there is less and less $^{39}K^+$ to migrate compared to the $^{41}K^+$ and therefore less and less increase in the relative proportion of $^{39}K^+$ in the mixture of $^{39}K^+$ and $^{41}K^+$ reaching the cathode compartment. Thus after a time the ratio of $^{39}K^+/^{41}K^+$ in this migration stream approaches the ratio already built up in the cathode compartment, and when the decreasing ratio in the migration stream reaches that corresponding to the ratio in the cathode compartment, further electrolysis cannot increase the cathode compartment ratio, but will decrease it.

(*d*) In accordance with this discovery the invention, in its broader aspects not limited to physical transport of electrolyte during treatment, contemplates that electrolysis be terminated when the maximum concentration ratio in the cathode compartment is reached and before net ion-transport at a decreased ratio has reduced the cathode compartment concentration deleteriously.

(*e*) The invention further, in this broad aspect, contemplates maintaining substantially constant the ratio of isotopes (as the ratio of $^{39}K^+$ to $^{41}K^+$) in the anode compartment, thus preventing it from decreasing and preventing decrease of the migration ratio, so that the cathode compartment ratio can be brought up to the full value attainable by migration at the rate obtained from the original anode concentration ratio.

(*f*) The invention further contemplates, in this broader aspect, retreatment of batches to further increase their concentration using previously beneficiated material as the starting material for further improvement, so that by repeating treatment over and over again, comparatively great concentration ratio changes may be effected.

(*g*) In its preferred aspects, the invention con-

templates a fundamental improvement over the non-flowing batch treatment and provides a continuous process in which the electrolyte is flowed counter-current to the direction of migration or ion transport of the substances to be separated, at a rate substantially equal to the average rate of movement in ion transport of the materials to be separated. In the case of potassium, for example, $^{39}K^+$ ions move, on the average, a little faster than $^{41}K^+$ ions. This average speed is in each case, of course, a mean between certain ions moving more rapidly than others and certain ones moving more slowly. Thus, when the rate of counter-current flow is somewhat less than the average speed of $^{41}K^+$ ions, more of the slower $^{41}K^+$ ions would be swept back by the flow, than of the $^{39}K^+$ ions; and when the rate of countercurrent flow is somewhat greater than the average speed of $^{39}K^+$ ions, sweeping most of the K^+ ions back, more of the faster $^{39}K^+$ ions would successfully make headway against the flow than in the case of the $^{41}K^+$ ions. In this connection, our observations indicate that best efficiency is had with a rate of flow about equal to the weighted mean of the average rates of transport of the ions to be separated, and that the efficiency falls off more slowly with excess rate of flow than it does with too slow a rate of flow. Thus, while in the more preferred embodiments the rate of countercurrent stream flow is maintained intermediate the average velocities of the respective ions being separated; and while in the most preferred embodiments the stream velocity is held at about the weighted mean of the average velocities of the slow and fast moving substances; the invention is not limited in all its aspects, in this regard.

(*h*) The invention further contemplates as the best mode now known of practicing it, the combination of steps to prevent remixing of ions (see *c* above), the maintenance of the most advantageous concentration ratio at the electrode from which the ions flow (see *e* above), and the maintenance of an advantageous rate of flow of electrolyte counter-current to the direction of ion transport (see *g* above) which can be more nearly stabilized because of the elimination of one variable factor by *e* above.

(*i*) The invention, in its preferred form, involves addition of restitution constituents, herein called restituents, in such concentration, and at such ratio, as the maintain the composition of the electrolyte at the desired concentration and pH.

The correct compositions of the restituents can be computed from the Hittorf numbers of the various ions (which include the true transport numbers and the solvent of solvation being transported by the moving ions and thus increasing their effective mass and slowing their mobility as well as diluting the solution at the end of the system toward which the ions are transported).

As above noted an indicator or suitable test is used to govern the addition of restituents to maintain the desired pH and concentration. In maintaining the K_2SO_4 system at a pH of about 3 to 4 an indicator of methyl orange is suitable, as above described.

In starting with an electrolyte containing more or less than, say 50 molecules of water to an equivalent of K_2SO_4, the addition of restituent liquids correspondingly having 25 molecules of water to one of KOH and ½ H_2SO_4, respectively, will in a short time, a day or two at laboratory scale, adjust the composition to the desired 50:1 ratio, for the example given. The water of decomposition is replaced by the water of reaction of the KOH and H_2SO_4. In any event the system is self adjusting as to concentrations.

Equivalents of acid and alkali, as exemplified by KOH and H_2SO_4, determine the maintenance of neutrality to methyl orange in the examples. If it is desired in certain instances to operate with a pH other than this neutrality, the indicator or test used may be one suited to the pH desired to be maintained, and the addition of the restituent solutions will be governed to maintain the desired pH. Other indicators, refractive index, reflective index, absorption spectra, stratification, etc., are usable as indicators or tests in this connection, and may in certain instances be adapted for automatic control of the system.

Rate of addition of the restituents determines the rate of counter-flow of the electrolyte. If acid is added too rapidly, the cathode compartment will become more acid because cations are not reaching it rapidly enough to neutralize the acid added. If the alkali is added too rapidly the anode compartment will become alkaline because anions from electrolysis are not reaching the anode compartment rapidly enough to neutralize the alkali added. The concentrations of the restituents determine the concentration of the electrolyte. The quantity of solutions to be added in a given time is determined by the faradays of current passed through the electrolyte. The addition of restituent solutions at just such rate as will restore the pH at their respective electrode compartments in the example given, automatically provides counterflow at the correct value with respect to the ion mobilities of the isotopes to be separated.

In the case of $UO_2(NO_3)_2$ in which there is a net transport of water from the anode to the cathode end, the addition of less water (i. e. more concentrated HNO_3) at the cathode end, and of more water at the anode end, as above set forth, automatically cuts down the counterflow rate by virtually the same amount as the water-transport cuts down the ion mobility, so here again addition of the properly calculated restituents at the rates appropriate to maintain the original composition, as indicated in any suitable manner, will automatically provide counterflow at the correct value with respect to the ion mobilities of the ions being separated.

(*j*) Visualized, the preferred embodiment of our invention may be likened to a treadmill, in which the ions to be separated are continually moving, at different rates, at the same time being continuously set back at a rate allowing only the lighter ions on the average to make progress against the rate of set-back, or causing only the heavier ions to be actually displaced counter to their direction of mobility, in the case of heavy isotope concentration. Regarded as an attenuation of travel, this preferred embodiment amounts virtually to a travel of infinite length.

(*k*) As is further apparent from the foregoing, the invention in its preferred aspects contemplates various modifications and refinements, severally and in various combinations. Thus, it includes provision of a mode of indicating the maintenance of the desired composition in the anode and cathode compartments (exemplified herein by addition of a chemical indicator and by stratification); it contemplates continuous or intermittent withdrawal of the aqueous or other medium in which ion transport has been pro-

moted both at the anode and at the cathode end of the system, for the purposes described; it contemplates that withdrawn material partially enriched in the desired constituent may be employed as a supply of materials to be separated in another stage according to the invention, as in refluxing or in batch retreatment; it contemplates concentration with respect to either the more mobile or the less mobile ions of like sign of the materials to be separated; and it contemplates provision of any means for obviating plating out of the material being separated, as, for example, operation in a medium supplying ions (such as the H^+ ions in the aqueous K_2SO_4 system) having a lower plating out potential toward the electrode used than the materials being separated, or isolation (as by stratification or the surrounding of the electrode by an isolating medium with or without an isolating cup in the uranium example), or by increasing the tendency of the material being separated to remain in solution (as by heating the electrode in certain instances).

(*l*) For ease of visualization, as above-mentioned, the system in its preferred form employing countercurrent may be likened to a treadmill (the countercurrent) on which the ions run in ion transport, the faster ions making progress against the treadmill, while the slower ions are held back or even carried in the opposite direction. As is also apparent from the foregoing descriptions, this invention may be employed for separating substances forming negatively charged ions of different mobilities in an electric field, and in such case identical descriptions will apply, reading "cathode" for "anode," and "anode" for "cathode" wherever these terms are used with respect to the direction of ion mobility and the direction of counterflow, other details of operation being adjusted accordingly.

The present invention obviously is not limited to the embodiments disclosed. Having described various preferred embodiments illustrating the invention, we claim:

A process for treating an aqueous solution of K_2SO_4 containing K^{39} and K^{41} ions in order to obtain a product beneficiated with respect to K^{39} ions which comprises passing a direct current thru an aqueous K_2SO_4 electrolyte from the anode zone thru a porous packing zone made from material selected from the group consisting of sand, fritted glass, and porous Alundum to a cathode zone thereby causing K^{39} and K^{41} ions to travel toward the cathode and the SO_4^- ions to travel toward the anode whereby the electrolyte in the vicinity of the cathode becomes slightly alkaline and the electrolyte in the vicinity of the anode becomes slightly acid, adding restituent aqueous sulfuric acid solution to the cathode zone to reduce the alkalinity caused by electrolysis, adding restituent aqueous potassium hydroxide solution to the anode zone to reduce the acidity caused by electrolysis, the volume of aqueous sulfuric acid solution that is added to the cathode zone being sufficiently greater than the volume of aqueous potassium hydroxide solution that is added to the anode zone to set up a flow of electrolyte that is counter to the direction in which the K^{39} and K^{41} ions are traveling due to electrolysis and which flow is at a velocity that is intermediate the rates at which the K^{39} and K^{41} ions are being electrically transported whereby K^{39} ions become concentrated in the cathode zone while K^{41} ions are swept back therefrom, and withdrawing K_2SO_4 electrolyte beneficiated with respect to K^{39} ions from the cathode zone.

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