

March 5, 1968

P. KOLLSMAN
PROCESS OF PRODUCING HIGHLY REACTIVE
COMPOUNDS BY METATHESIS

3,372,101

Filed Oct. 8, 1962

2 Sheets-Sheet 1

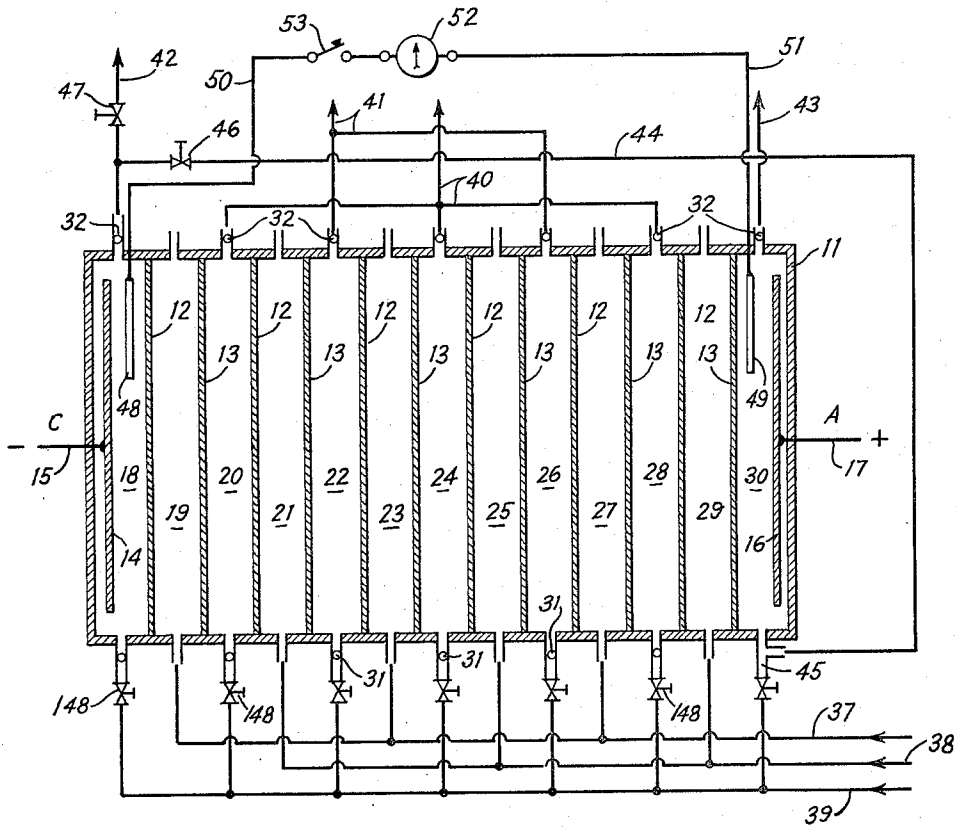


Fig. 1

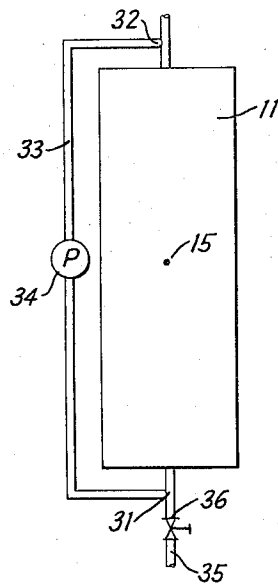


Fig. 2

INVENTOR.
Paul Kollsman
BY Howard G. Russell
his ATTORNEY

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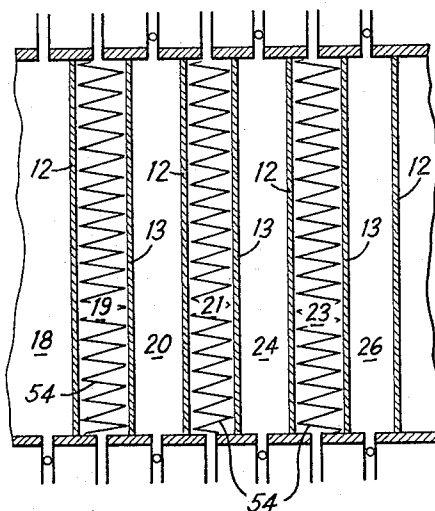


Fig. 3

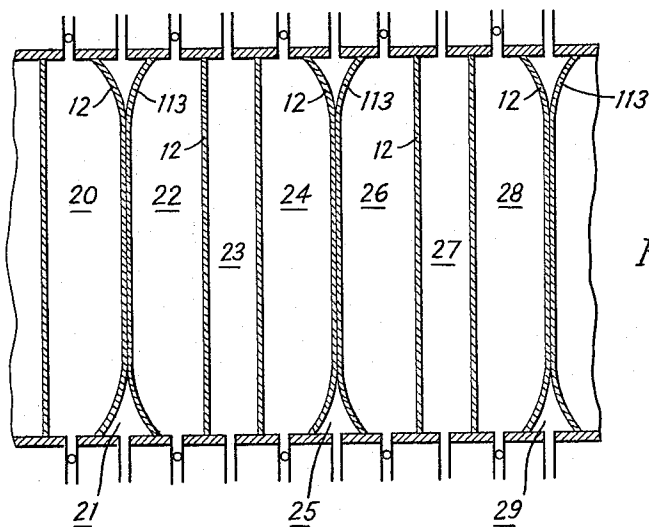


Fig. 4

INVENTOR.
Paul Kollsman
BY
Howard B. Russell
his ATTORNEY

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3,372,101

**PROCESS OF PRODUCING HIGHLY REACTIVE
COMPOUNDS BY METATHESIS**

Paul Kollsman, 100 E. 50th St.,
New York, N.Y. 10022
Filed Oct. 8, 1962, Ser. No. 228,867
2 Claims. (Cl. 204—130)

This invention relates to the treatment of compounds composed of anionic and cationic constituents for the purpose of economically upgrading the source materials by producing product compounds which are more highly reactive than the compounds from which they are produced.

Compounds which occur plentifully in a natural state are normally stable and substantially non-reactive. Their economic value is correspondingly low. This invention provides a process for converting stable raw material into less stable and more highly reactive products. For example, calcium sulfate and sodium chloride are inexpensive, stable materials in ample supply. The invention permits conversion of these two source materials into calcium chloride and sodium sulfate, each of which is commercially more valuable because of its higher reactivity.

The invention involves treatment in a multichamber electro dialysis cell and resembles in some respects the known process of metathesis. It differs, however, from the known processes in that electrical energy must be expended to force the ions of the source materials into other chambers to form the products and, further, in that the products, if left without the influence of the current-producing direct potential, will revert into the source compound form. In a sense, electrical energy is stored in the products, or the process may be termed an "uphill" movement of the ions involved, forcing them to move in a direction in which in the absence of the applied direct potential and current they would not move.

The critical distinction between ordinary electrometathesis in a multichamber membrane cell and the present process is ascertainable as follows:

It may be assumed that a conventional metathesis process is being carried out in a multimembrane cell by application of a direct potential, resulting in a flow of direct operating current through the cell. It may then be assumed that the operating current is interrupted and that a pair of non-polarizing test electrodes is inserted in the cell, one test electrode in one electrode chamber and the other test electrode in the other electrode chamber. Then a galvanometer connected between the test electrodes will indicate the flow of a test current which is in the same direction as the operating current.

If a corresponding test were made in connection with the practice of the present invention, the direction of the test current would be opposite the direction of the operating current.

The test electrodes may, as is readily seen, be inserted into intermediate chambers of the cell. One test electrode may be in one endmost source compound chamber and the other test electrode may be put in the other endmost source compound chamber. Or the test may be made across the minimum unit of cells required for producing a product. In that case, one test electrode would be in one source compound chamber which is followed by a product chamber, a source compound chamber, another product chamber and another source compound chamber containing the second electrode. In all these instances the present invention is characterized by a reversal of the current direction.

In comparing the properties of the source compounds with those of the product compounds produced by the present invention, one or more of the following properties will be noted:

When mixed, the product compounds generally react

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to revert into the source compounds from which they were formed.

The sum of the heats of formation of the source compounds is always higher than the sum of the heats of formation of the products produced therefrom. This appears to be characteristic and indicative of the storage of electrical energy in the product and of the directional relationship of the test current and the operating current above described.

The products have a higher degree of ionizability than the source compounds. Generally their solubility is also higher. Further, the source compounds generally have a lower dissociation constant than the product compounds.

The source compounds are generally less ionizable than the products, hence the product solutions have relatively a higher conductivity.

A weakly basic source material is convertible into a highly basic product, for example ammonium hydroxide into sodium hydroxide.

A weakly acid source material is convertible into a strong acid, for example acetic acid into hydrochloric acid.

A source material may be highly volatile whereas the products are not.

Thus, volatile solutes may serve as source materials such as solutions of gases in solvents, for example CO_2 in water or NH_3 in water. In this connection, the process may be carried out under superatmospheric pressure conditions to maintain greater amounts of gas in solution.

Where the purity of the product is an important factor, it is preferred to operate with ionic concentrations in the source solutions lower than those existing in the membrane pores and in the product chambers of the apparatus.

In cases where the product compounds are so highly soluble as to require no solvent addition to prevent precipitation, the product solutions consist preferably entirely of ions and accompanying solvent moved from the source liquid chambers through the membranes.

In certain instances it may be necessary to add just enough solvent to the product chambers to prevent precipitation. Another way of preventing precipitation is operation at elevated temperatures.

The process is applicable to all compounds capable of dissolving in a solvent and dissociating therein to form an ionized solution. The ions may be inorganic, or organic. The solvent may be of inorganic or organic nature. Polar solvents of high dissociating power and high dielectric constant are preferred. Examples of such solvents are water, acetic acid, alcohols, acetone, ammonium hydroxide, liquid ammonia or carbon dioxide.

The source compounds from which products are formed according to this invention are generally solutes, for example NaCl , but the solvent may or may not enter into the process. When it does, for example by solvent decomposition under polarizing conditions, additional product forming constituents become available. Thus, for example, an aqueous NaCl solution may yield H and OH in addition to the Na and Cl ions. In that case the source compound is considered to comprise both solute and solvent. Thus the same aqueous NaCl solution supplied to different deionization chambers of a cell operating under non-polarizing and polarizing conditions, respectively, represent two different source compounds.

Source compounds normally require the presence of a solute, since pure solvents are nonconductive for practical purposes.

Nevertheless, a pure solvent may be employed as a source compound in a special arrangement in which the deionizing chamber is of practically zero thickness, due, for example, to contact of the bordering membranes as shown in FIG. 4. Alternately the deionizing chamber may contain a spacer of ion exchange material for establishing a continuous solid electrically conductive bridge between

the bordering membranes, as shown in FIG. 3. In either arrangement an electric current is capable of passing through such a chamber to which solvent may be supplied from the outside. Solute ions pass into the deionizing chamber through its bordering membranes from the neighboring product chambers. Thus, in effect, solute and solvent are present in the deionization chamber, but solute and solvent come from different sources, one from the neighboring product chambers, the other from an outside source. Both are decomposed, the solvent by operation under polarizing conditions.

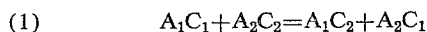
In order to illustrate the practice of the invention it may be assumed that an ample supply of gypsum is available and that it is desired to produce a commercially more valuable product therefrom.

One may then proceed as follows:

Example A.—The heat of formation of gypsum, CaSO_4 is first determined as 335.72 Kcal.

Chemical handbooks contain extensive heat of formation tables listing a vast number of compounds and CaSO_4 is readily located therein.

The next step may be the selection of one or two suitable main products. It is evident that one must have a Ca component, the other a SO_4 component. The heat of formation table serves as a convenient guide and from the SO_4 listings Na_2SO_4 may be selected. This now points to the need for a companion source compound comprising a Cl component. It should be relatively inexpensive and readily available. For the purpose of the example NaCl is chosen. This fixes the second product compound as Na_2SO_4 on the basis of the formula



wherein

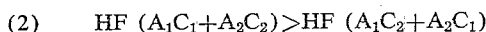
A are anionic components

C are cationic components

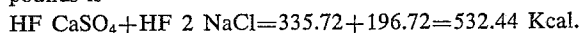
A_1C_1 and A_2C_2 are source compounds

A_1C_2 and A_2C_1 are product compounds

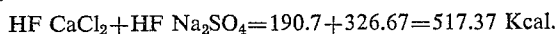
A characteristic of the present inventive process is that the sum of the heats of formation (HF) of the source compounds must be greater than the sum of the heats of formation of the products, thus



The sum of the heats of formation of the source compounds is



The sum of the heats of formation of product compounds is



The requirement of Formula 2 is therefore met.

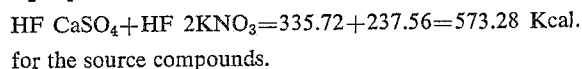
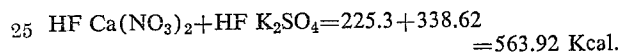
Particulars of the process are given below.

Following is an excerpt from a table beginning on page 1807 of the Handbook of Chemistry and Physics, 42nd Edition, The Chemical Rubber Publishing Co., Cleveland, Ohio. The excerpts are limited to Ca, Na and SO_4 compounds to illustrate the foregoing example.

Ca Compounds:	HF, Kcal.
CaBr_2 -----	162.2
CaCl_2 -----	190.7
$\text{Ca}(\text{OH})_2$ -----	236.1
CaF_2 -----	286.26
$\text{Ca}(\text{NO}_3)_2$ -----	225.3
$\text{Ca}(\text{ClO})_2$ -----	181.6
CaI_2 -----	128.6
$\text{Ca}(\text{ClO}_2)_2$ -----	326.88
CaCO_3 -----	287.93
CaSO_4 -----	335.72
K Compounds:	HF, Kcal.
KOH -----	102.01
KCl -----	104.30
KNO_3 -----	118.78
K_2SO_4 -----	338.62

SO_4 Compounds:	HF, Kcal.
$\text{Al}_2(\text{SO}_4)_3$ -----	714.46
$(\text{NH}_4)_2\text{SO}_4$ -----	277.66
NH_4HSO_4 -----	240.43
BaSO_4 -----	345.28
K_2SO_4 -----	338.62
CuSO_4 -----	178.7
H_2SO_4 -----	189.75
FeSO_4 -----	217.23
PbSO_4 -----	214.6
MgSO_4 -----	301.08
Na_2SO_4 -----	326.67
NaHSO_4 -----	265.19
ZnSO_4 -----	229.51

Example B.—The following example is again based on CaSO_4 as one of the source compounds. $\text{Ca}(\text{NO}_3)_2$ is chosen as the principal product compound, pointing to the need for a companion source compound yielding NO_3 . KNO_3 is chosen which would make the second product K_2SO_4 .



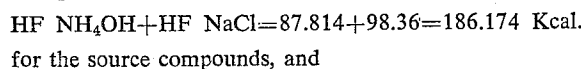
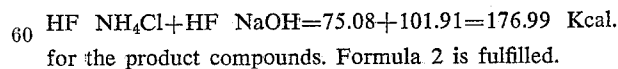
for the product compounds.

Formula 2 is again fulfilled. For the purpose of this example the heat of formation table of the aforesaid Handbook of Chemistry and Physics was again consulted, but no additional excerpt is given, as the principle was sufficiently illustrated in Example A.

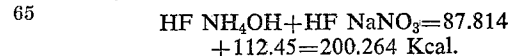
Example C.—Aqueous ammonia NH_4OH is available as a source compound having a heat of formation of 87.814 Kcal. Possible products and the required companion source compound are determinable from the heat of formation table of which the following is an excerpt.

NH_4 Compounds:	HF
NH_4 acetate -----	150.25
NH_4Br -----	64.708
NH_4Cl -----	75.08
NH_4F -----	111.71
$(\text{NH}_4)_2\text{CO}_3$ -----	223.4
NH_4NO_3 -----	87.93
$(\text{NH}_4)_2\text{SO}_4$ -----	277.66
OH Compounds:	HF
NaOH -----	101.91
KOH -----	102.01
LiOH -----	116.4
$\text{Ca}(\text{OH})_2$ -----	236.1
$\text{Mg}(\text{OH})_2$ -----	223.4
$\text{Zn}(\text{OH})_2$ -----	158.4

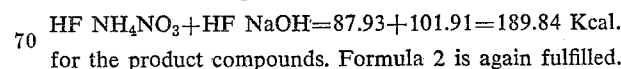
Principal product NH_4Cl . Second product NaOH. Companion source compound NaCl.



Example D.—Starting again with NH_4OH as a source compound, NH_4NO_3 and NaOH are chosen as products, NaNO_3 serving as companion source compound.



for the source compounds and



In the computation and comparison of the heats of formation the number of source compounds is always equal to the number of the product compounds. In a cell having a great number of chambers a source compound,

or a product, is counted as often as it occurs in a chamber. If, for example, NaCl solution occurs in three deionization chambers, it is counted three times.

In computing the heats of formation, the heat of formation of the hypothetical product is included which would be formed of the residual anions and cations of the two deionization chambers nearest the electrodes. If the deionization chambers lie adjacent the electrode chambers, then the ions in question are those entering into the electrode chambers, for example H at the cathode and Cl at the anode. If, on the other hand, deionization takes place in the electrode chambers proper, then the ions forming the hypothetical product are those ions of the anolyte and catholyte which do not pass into the adjacent product chambers.

FIG. 1 is a diagrammatic elevational view of an electro dialysis cell for practicing the invention;

FIG. 2 is an end view of the apparatus shown in FIG. 1; and

FIGS. 3 and 4 are diagrammatic illustrations of modified cells.

The cell housing 11 is subdivided into individual chambers by cation membranes 12 and anion membranes 13 arranged in alternating sequence. In one terminal chamber a cathode 14 is provided from which a lead 15 leads to a suitable source of direct current (not shown), and the other terminal chamber contains an anode 16 with a lead 17. The indicated polarity of the electrodes and membranes makes chambers 19, 21, 23, 25, 27, and 29 deionization chambers and chambers 20, 22, 24, 26 and 28 concentration chambers. Chambers 18 and 30 are electrode chambers.

Each chamber has an inlet port at the bottom and an outlet port at the top. These ports are unnumbered for the sake of clarity. Means are provided for circulating the liquid in the individual chambers within the chambers at a rate in excess of the inflow and outflow rate. For this purpose a bottom circulation port 31 and a top circulating port 32 are provided for each chamber connected by a circulating duct 33 (FIG. 2) and a pump 34, there being an individual pump 34 and duct 33 for each chamber. A make-up duct 35 and valve 36 permits addition of liquid to each concentration chamber.

A second source liquid supply duct 37 is manifolded to deionization chamber 19, 23 and 27. A first source liquid supply duct 38 is manifolded to deionization chambers 21, 25 and 29. A further liquid supply duct 39 is manifolded to concentration chambers 18, 20, 22, 24, 26, 28 and 30.

The chambers are 50 mm. wide, 300 mm. high and 3 mm. thick. The membranes are "Nepton" membranes CR-61 and AR 111-A. CR-61 membranes are essentially styrene divinyl benzene copolymer with sulfonic ion exchange groups, a cation exchange membrane (patent to Clarke 2,731,411). The AR 111-A membrane is an anion exchange membrane, is essentially a styrene divinyl benzene vinyl pyridine membrane.

The electrodes 14, 16 are platinum.

A first outflow duct system 40 manifolded to concentration chambers 20, 24 and 28 is provided for the first product and a second outflow duct system 41 manifolded to chambers 22 and 26 is provided for withdrawal of the second product. Outflow ducts 42 and 43 extend from the electrode chambers. The total liquid capacity of each chamber including circulating duct 33 and pump 34 is 300 cc.

Provision is made for conducting cathode chamber effluent into the anode chamber. A duct 44 extends from duct 42 to the cathode chamber inflow duct 45. Duct 44 is controlled by a valve 46. A further valve 47 permits closing of duct 42. Valves 148 are provided in the inflow ducts to the concentration chambers.

A pair of non-polarizing test electrodes 48, 49 are connected by leads 50, 51 comprising a switch 53 to a gal-

vanometer 52. When the switch is closed a circuit is established between the electrodes and the galvanometer indicates the direction of the current which, this being a characteristic of the invention, is opposite the direction of the operating current flowing between main electrodes 14, 15 through the cell.

The test electrodes 48, 49 are shown in chambers 18 and 30, respectively. The test electrodes need not be spaced thus far apart. It is sufficient to space them three intermediate chambers apart. Thus they may be installed in chambers 18 and 22, or chambers 22 and 26, for example.

Test 1.—CaSO₄ was solvated in water to form a saturated solution and NaCl was solvated in water to form a 0.2 N solution. NaCl solution was supplied to chambers 19, 23 and 27 and CaSO₄ solution was supplied to chambers 21, 25 and 29. All other chambers were originally filled with water. Circulation rate of pumps 34: 200 cc./min. Potential 19 volts.

After 30 minutes tests indicated the presence of NaOH in chamber 18; CaCl₂ in chambers 20, 24 and 28; Na₂SO₄ in chambers 22 and 26 and H₂SO₄ in chamber 30.

Operation was continued and the outflowing circulating streams passing through ports 32 were adjusted to 0.8 by addition of water at 35, 36 prior to reentry of the circulating liquid into the product chamber.

After 48 hours of operation the liquid passing through duct 42 was 0.8 N NaOH, the liquid passing through duct 40 was 0.8 N CaCl₂, the effluent of duct 41 was 0.8 N Na₂SO₄ and the outflow through duct 43 was 0.8 N H₂SO₄.

After carrying out the test CaCl₂ solution and NaSO₄ solution were mixed and produced a precipitate of CaSO₄ and a solution of NaCl.

Test 2.—A test was conducted with saturated aqueous CaSO₄ solution as in test 1, and an aqueous 0.18 N KNO₃ solution as the companion source solution. Potential 20 volts. Make-up water was supplied to limit the normality of the liquid outflow of the concentrating chambers 18, 20, 22, 24, 26, 28 and 30 to 0.7 N.

Results: After 48 hours of operation duct 42 yielded 0.7 N KOH, duct 40 yielded 0.7 N Ca(NO₃)₂, duct 41 yielded 0.7 N K₂SO₄, and duct 43 yielded 0.7 N H₂SO₄.

The cell was then operated for 48 hours at a temperature of 85° C. with the inflow of make-up water reduced to produce concentrations of the product solution in excess of the normal solubility of the products at room temperature. Resulting products were: From duct 40: 3.2 N Ca(NO₃)₂ with a trace of Na₂SO₄; duct 41: 2.1 N K₂SO₄ with a trace of Ca(NO₃)₂.

Operation at elevated temperatures is desirable in the commercial practice of this invention because a product, such as salt, may be recovered in its solid state by cooling of the product solution leaving the salt depleted cold product solution available for reuse in the process.

Test 3.—First source solution: 0.4 N NH₄OH; second source solution: 0.4 NaCl in water. The cathode chamber effluent (duct 42) was used as anode chamber influent, and the anode chamber effluent passed through duct 43 without the addition of water at chamber 30.

Make-up water was added to chambers 18, 20, 22, 24, 26 and 28 to maintain a normality of 0.8 N in the outflows from chambers 20, 22, 24, 26, 28 and 30. Potential 17 volts.

After 48 hours of operation: duct 40 yielded 0.8 N NH₄Cl; duct 41 yielded 0.8 N NaOH; duct 43 yielded 0.8 N NaOH.

48 hours after reduction of make-up water inflow to less than one-half into chambers 20, 22, 24, 26 and 28, duct 40 yielded 2.6 N NH₄Cl and duct 41 yielded 2.1 N NaOH.

Test 4.—First source solution: aqueous 0.35 N NH₄OH; second source solution aqueous 0.15 N NaNO₃. Potential 18 volts. Valve 47 closed, valve 46 open, duct 45 closed.

After the first 48 hours of operation with addition of make-up water for cathode and product chambers to limit the normality of the outflowing liquids to 0.75 N, duct 40 yielded 0.75 N NaOH; duct 40 yielded 0.75 N NH_4NO_3 ; duct 41 yielded 0.75 N NaOH; and duct 43 yielded 0.75 N NaOH.

48 hours after reduction of make-up water inflow into the product chambers to less than one-half, duct 40 yielded 2.65 N NH_4NO_3 with a trace of Na and OH and duct 41 yielded 2.35 N NaOH with a trace of NH_4 and NO_3 .

In processing compounds forming ionic solutions of low electrical conductivity, low solubility such as BaSO_4 , or compounds having a low dissociation constant such as acetic acid, H_2CO_3 or NH_4OH , or in the processing of a variety of weak inorganic or organic acids and bases or weakly dissociated solvents, it is preferred to modify the above described apparatus by reducing the thickness of the chambers containing liquids of low conductivity to a point where the bordering membranes practically contact except for a thin film of liquid therebetween. Alternatively, electrolytically conductive spacers of ion exchange material, preferably of amphoteric nature, may be used through which the liquid flows in a substantially tortuous path. Such spacers may be used in the deionizing as well as in the concentrating chambers.

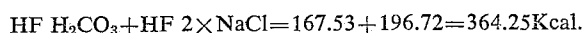
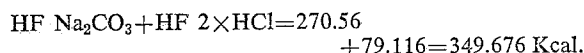
Modified cell.—Tortuous path spacers of 3 mm. thickness were installed in all chambers. The spacers were made by molding a mixture of equal quantities of fibers of 0.1 mm. thickness and 1 mm. length, the fibers consisting of quaternized and of sulfonated polyethylene-styrene copolymer, respectively, as described in my Patent No. 3,271,292, dated Sept. 6, 1966.

Molding took place at 320° F. and 1000 p.s.i. pressure with subsequent hydrolysis in aqueous solutions of 1 N HCl, 1 N NaOH and 1 N NaCl at 160° F.

Test 5.—Spacer equipped cell. First source compound: H_2CO_3 made by absorption of CO_2 in water to form a saturated solution. The solubility of CO_2 in water is 0.00145 and the dissociation constant of the resulting H_2CO_3 is 4.3×10^{-7} .

The H_2CO_3 solution is only weakly conductive.

Second source solution: aqueous 0.1 N NaCl solution. Product compounds to be formed: Na_2CO_3 and HCl.

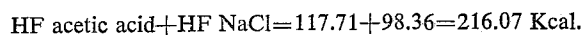
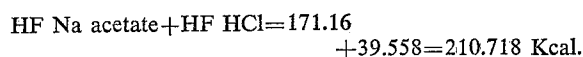


Catholyte effluent (42) was conducted through the anode chamber 30. Make-up water addition to chambers 18, 20, 22, 24, 26 and 28 at a rate to produce a normality of the effluent of 0.6 N. Potential 22 volts.

After 48 hours, duct 40 yielded 0.6 N HCl; duct 41 yielded 0.6 N Na_2CO_3 and NaHCO_3 , and duct 43 yielded 0.6 N Na_2CO_3 and NaHCO_3 .

The test was repeated at a potential of 36 volts. After 48 hours, duct 40 yielded 0.6 N HCl; duct 41 yielded 0.6 N Na_2CO_3 , and duct 43 yielded 0.6 N Na_2CO_3 .

Test 6.—Cell with amphoteric membrane spacers in all chambers. First source liquid: acetic acid dissolved in water to form a 0.8 N solution. Second source liquid: an aqueous 0.1 N solution of NaCl. Dissociation constant of acetic acid 1.76×10^{-5} .



Catholyte effluent 42 was used as anode chamber 30 influent. Make-up water addition to limit the effluents to a normality of 1 N.

Potential 21 volts. After 48 hours, duct 40 yielded 1 N

HCl; duct 41 yielded 1 N sodium acetate and duct 43 yielded 1 N sodium acetate.

Test 7.—Test 4 was repeated in a cell modified to contain an amphoteric membrane spacer 54 (FIG. 4) in chambers 19, 21, 23, 25, 27 and 29. Potential 16 volts. No addition of make-up water to the product chambers.

After 48 hours of operation, duct 40 yielded 2.9 N NH_4NO_3 and duct 41 yielded 2.55 N NaOH.

The products were of higher concentration and greater purity than those obtained in test 4.

Test 8.—Test 5 was repeated after saturating the water with CO_2 under 6 kg./cm.² pressure. The cell was maintained under a pressure of 7 kg./cm.². After 48 hours of operation, duct 40 yielded 0.6 N HCl; duct 41 yielded a mixture of 0.6 N of Na_2CO_3 and NaHCO_3 and duct 43 yielded an 0.6 N mixture of Na_2CO_3 and NaHCO_3 . The NaHCO_3 content was higher in relation to the Na_2CO_3 content than in test 5.

Test 9.—Cell basically as used in test 1 modified to conduct the anode chamber effluent into the cathode chamber. Source compounds: 0.1 N aqueous solution of $(\text{CH}_3)_4\text{N}$ -formate and 0.1 N aqueous solution of acetic acid. Anode chamber effluent was conducted into cathode chamber. Acetic acid solution was supplied through duct 37 into chambers 19, 23 and 28 and $(\text{CH}_3)_4\text{N}$ -formate solution was supplied through duct 38 into chambers 21, 25 and 29. Solvent water was supplied to concentration chambers 20, 22, 24, 26, 28 and the anode chamber 30 in a quantity sufficient to produce an effluent concentration of 0.3 N. Potential 24 volts.

After 48 hours of operation, effluent from duct 40: 0.3 N $(\text{CH}_3)_4\text{N}$ acetate, and from duct 41 0.3 N formic acid. Duct 42 yielded 0.3 N formic acid.

Test 10.—Cell with membrane spacers as used in test 6. Source solutions: acetic acid dissolved in methyl alcohol to form a 0.2 N solution and NaCl dissolved in methyl alcohol to form a saturated solution. Methyl alcohol was used as a make-up liquid in a quantity sufficient to produce a product concentration of 0.3 N. Potential 22 volts.

Products: Duct 40 yielded 0.3 N HCl; duct 41 yielded 0.3 N Na acetate; duct 43 yielded 0.3 N Na acetate. It was also found that the HCl solution contained methyl chloride.

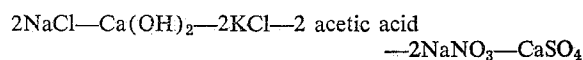
Test 11.—For the purpose of this test the manifolds were removed from the cell to maintain separate the several inflows and outflows to and from the chamber. The thickness of chambers 21, 25 and 29 was reduced to 0.5 mm.

A plurality of source compounds were selected to produce a plurality of products, in excess of two. The sum of the heats of formation of all source compounds was greater than the sum of the heats of formation of the products.

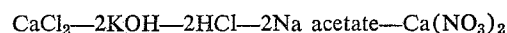
In the latter sum was included the heat of formation of the theoretical product compound formed by the cation of the source compound nearest the cathode and the anions of the source compound nearest the anode.

The process potential was again reversed with respect to the open circuit potential existing between the electrode chamber liquids as measured by non-polarizing electrodes.

Six source compounds:

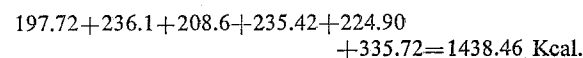


Product compounds to be formed:



Hypothetical product compound: Na_2SO_4 .

Heats of formation of source compounds:



Heats of formation of products:

$$190.7 + 204.02 + 79.17 + 342.32 \\ + 225.3 + 326.31 = 1367.82 \text{ Kcal.}$$

Compounds Ca(OH)_2 and CaSO_4 were supplied as saturated aqueous solutions. NaCl , KCl , acetic acid and NaNO_3 were supplied in the form of aqueous solutions of 0.6 N. Make-up water was supplied to the product chambers in quantities sufficient to maintain the product chamber effluents and the electrode chamber effluents at 1.1 N. Potential 18 volts.

Source compound solutions were supplied as follows: NaCl into chamber 19; CaOH_2 into chamber 21; KCl into chamber 23; acetic acid into chamber 25; NaNO_3 into chamber 27 and CaSO_4 into chamber 29.

After 48 hours of operation, the products were as follows: 1.1 N NaOH from chamber 18; 1.1 N CaCl_2 from chamber 20; 1.1 N KOH from chamber 22; 1.1 N HCl from chamber 24; 1.1 N sodium acetate from chamber 26; 1.1 N $\text{Ca(NO}_3)_2$ from chamber 28 and 1.1 N H_2SO_4 from chamber 30. In addition chamber 18 produced H_2 and chamber 30 produced O_2 .

Test 12.—The process was employed to convert LiCl into several different lithium products by combination with appropriate second source compounds. The apparatus of FIG. 1 was modified by removing the effluent manifolds 40, 41 and providing individual outflow ducts.

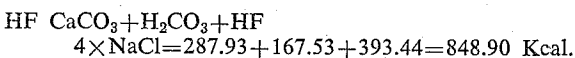
An 0.3 N aqueous solution of LiCl was passed through deionization chambers 21, 25 and 29. Aqueous 0.3 N solutions of sodium acetate, NaOH and NaBr were passed through deionization chambers 19, 23 and 27, respectively.

The cathode chamber effluent was conducted into the anode chamber through duct 44. Make-up water was added to the product chambers 20, 22, 24, 26 and 28 and to the cathode chamber 15 in a quantity sufficient to maintain the product chamber effluents and the effluent of the anode chamber at 0.8 N. Potential 14 volts.

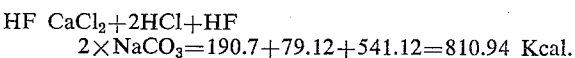
After 48 hours of operation the product liquid of chamber 20 was 0.8 N lithium acetate. Chamber 24 produced 0.8 N LiOH and chamber 28 produced 0.8 N LiBr . The product of chambers 22, 26 and 30 was 0.8 N NaCl .

Test 13.—Principal source compound limestone CaCO_3 . Companion source compound NaCl . Products CaCl_2 and Na_2CO_3 .

Limestone was dissolved in aqueous CO_2 solution to form CaCO_3 and H_2CO_3 .



for the source compounds.



for the product compounds.

For this test the cell was modified to reduce the thickness of the deionization chambers to 0.5 mm. Source liquids: saturated aqueous solution of CaCO_3 and H_2CO_3 and 0.8 N aqueous solution of the Na. Cathode chamber effluent passed through duct 44 into the anode chamber 30.

Make-up water was added to chambers 18, 20, 22, 24, 26 and 28 to limit the outflows to 1 N. Potential 26 volts.

After 48 hours of operation duct 40 yielded 1 N CaCl_2 and HCl ; ducts 41 and 43 yielded 1 N Na_2CO_3 with a small amount of NaHCO_3 .

The product solution of CaCl_2 and HCl was then percolated through a bed of limestone to form aqueous CaCl_2 as a final product and CO_2 gas. CO_2 was dissolved in water under pressure to form aqueous CO_2 solution for dissolving limestone to serve as a first source liquid.

Test 14.—Test 13 was repeated with an applied potential of 10 volts. After 48 hours of operation, duct 40 yielded 1 N CaCl_2 and HCl , the HCl content being less than in test 12, ducts 41 and 43 yielded a mixture of

Na_2CO_3 and NaHCO_3 , the NaHCO_3 content being larger than in test 12.

Comment: The higher potential and the corresponding closer approach to polarization conditions in the relatively dilute source solution in test 13 appears to be conducive to the transfer of CO_3 anions rather than HCO_3 anions from the deionization chambers into the concentration chambers.

Test 15.—Operation under induced polarization conditions. The membranes of the cell were modified by placing on the membrane surfaces facing chambers 21, 25 and 29 a layer of a microporous plastic material known to the trade as "Mipor 14 PN" whose specification is as follows: Low density polyethylene, void volume 75%, pore size range 75–125 microns with particle retention of 10 microns, thickness 10 mils (0.010") or 0.25 mm. Cathode chamber effluent served as anode chamber influent without the addition of water at chamber 30.

Source solutions 0.02 N NaOH and 0.8 N NaCl . Make-up water added to chambers 18, 20, 22, 24, 26 and 28 to maintain a normality of 1 N at the respective outflows from chambers 20, 22, 24, 26, 28 and 30. Potential 36 volts. Cell pressurized at 3 kg./cm.².

After 48 hours of operation duct 40 yielded 1.0 N HCl and NaCl ; ducts 41 and 43 yielded 1.0 N NaOH .

Comment: The production of NaOH far exceeded the trace quantity supplied in the first source solution. The H ions in the acid product and most of the OH ions in the alkaline product appear to be the result of water decomposition of the solvated weakly alkalinized first source compound caused by the polarization at the membrane surfaces contacting the first source solution.

Test 16.—A repetition of test 15 modified by supplying an aqueous 0.01 N solution of HCl in place of the 0.02 N NaOH .

Results: From duct 40: 1.0 N HCl ; from ducts 41 and 43: 1.0 N NaOH and a trace of NaCl .

Test 17.—A repetition of test 16 modified by supplying, as source solutions, aqueous 0.04 N NaCl and aqueous 0.9 N NaCl . Potential 38 volts.

After 48 hours of operation duct 40 yielded 1.0 N HCl and some NaCl ; ducts 41 and 43 yielded 1.0 N NaOH and some NaCl .

The cell was operated under polarizing conditions of the first source solution, causing decomposition of the water, so that the following source ions were available for transfer through the membranes: Na , Cl , H and OH .

Test 18a.—The cell was modified by substitution of neutral "Mipor 13 PN" membranes 113 in place of the anion membranes of deionization chambers 21, 25 and 29, the arrangement being such that the neutral membranes would contact the adjacent cation membranes 12, thus forming deionization chambers 21, 25 and 29 of substantially zero thickness (FIG. 4). "Mipor 13 PN" membranes are low density polyethylene, void volume 70%, pore size range 75–125 microns with particle retention of 10 microns, thickness 25 mils or 1 mm.

Chambers 21, 25 and 29 received liquid only through the neutral membranes from the adjacent product chambers. The cathode chamber effluent served as anode chamber influent, and make-up water was supplied to chambers 18, 20, 22, 24, 26 and 28 to limit the normality of the effluent of chambers 20, 22, 24, 26, 28 and 30 to 0.7 N.

The membrane and chamber arrangement causes product solution from adjacent chambers to diffuse into deionization chambers and forms the source compound, whereupon the source compound solution is deionized in the hereinbefore described manner. Stated briefly, product becomes source compound.

Second source solution: aqueous 0.6 N NaCl . Potential 36 volts. Cell pressurized at 3 kg./cm.².

After 48 hours of operation: from duct 40: 0.7 N HCl and some NaCl ; from ducts 41 and 43: 0.7 N NaOH . The

first source solution consisted of the liquid in the polarized layer between the contacting membranes, i.e., dilute NaOH solution plus solvent decomposition products H and OH.

Test 18b.—Test 18a was repeated after omission of the neutral membranes and the cell was operated at atmospheric pressure and at a potential of 40 volts.

After 48 hours of operation, duct 40 yielded 0.7 N HCl and NaCl, and ducts 41 and 43 yielded 0.7 N NaOH and a small quantity of NaCl.

It is apparent that the first source solution consists of the liquid in the polarized layer at the surface of the cation membrane facing the anode, i.e., dilute NaOH solution plus decomposition products H and OH.

Test 19.—Cell modified by replacing the cation membranes of chambers 21, 25 and 29 by neutral "Mipor 13 PN" membranes, the membranes contacting the adjacent cation membranes to form deionization chambers 21, 25 and 29 of substantially zero thickness.

After 48 hours of operation, duct 40 yielded 0.7 N HCl and ducts 41 and 43 yielded 0.7 N NaOH and some NaCl. Again, the first source solution consisted of dilute HCl and decomposed water, H and OH.

Test 20.—A cell was constructed in which chambers 21, 25 and 29 were surface grooves in otherwise contacting "Nepton" anion (AR 111-A) and cation (CR-61) membranes. The grooves were 0.8 mm. wide, 0.2 mm. deep, and were spaced 10 mm. apart to form a grid pattern.

Water was supplied through these grooves from the membrane periphery. Aqueous 0.3 N NaCl solution was supplied to chambers 19, 23 and 27. The cathode chamber effluent was directed into the anode chamber as influent 30.

Make-up water was supplied to chambers 18, 20, 22, 24, 26 and 28 to maintain the respective effluents at 0.8 N. Potential 36 volts.

After 48 hours of operation, duct 40 yielded 0.8 N HCl; duct 41 yielded 0.8 N NaOH; duct 43 yielded 0.8 N NaOH.

Test 21.—Test 20 was repeated after discontinuing the solvent inflow into chambers 21, 25 and 29. After 48 hours of operation, duct 40 yielded 0.8 N HCl and a small quantity of NaCl; ducts 41 and 43 yielded 0.8 N NaOH and a small quantity of NaCl.

Test 22.—Test 20 was repeated in a cell fitted with "Amfion" cation membrane C-103 and "Amfion" anion membrane A-60 pairs molded together. These membranes are basically polyethylene-styrene copolymers, sulfonated and quaternized, respectively. The membranes were dried and bonded in a hydraulic press at 150° C. at a pressure of 400 lb./sq. inch to form two ply membrane structures. The bonded membranes were then hydrolized by successive immersion in 1 N aqueous solution of HCl, NaOH and NaCl at 80° C.

The hydrolized membranes were used in place of the contacting membranes of the preceding test 21.

After 48 hours of operation, duct 40 yielded 0.8 N HCl and a small amount of NaCl. Ducts 41 and 43 yielded 0.8 N NaOH and a small quantity of NaCl.

Test 23.—In the cell of test 7 an ion conductive spacer of ion exchange material, substantially equally conductive to anions and cations, was installed in chambers 19, 21, 23, 25, 27, and 29 to form an ion conductive bridge between the anion and cation membranes. The cathode chamber effluent was conducted into the anode chamber. Make-up water was added to all product chambers and to the cathode chamber to limit the normality of the effluents to 0.6 N.

Water was supplied to chambers 21, 25 and 29 and an aqueous solution of 0.5 N NaCl was supplied to chambers 19, 23 and 27. Potential 40 volts.

After 48 hours of operation, duct 40 yielded 0.6 N HCl and ducts 41 and 43 yielded 0.6 N NaOH.

Test 24.—Test 23 was repeated after discontinuing supply of water to chambers 21, 25 and 29.

After 48 hours of operation duct 40 yielded 0.6 N HCl and a small quantity of NaCl; ducts 41 and 43 yielded 0.6 N NaOH and a small quantity of NaCl.

What is claimed is:

1. The process of converting, under the influence of an electric current, a weakly acid compound composed of an anionic component A₁ and a cationic component C₁ into a strong acid compound, the process comprising, maintaining the weakly acid compound, in solution, in a certain deionization chamber of a multichamber electro dialysis cell in which the space between the electrodes is subdivided into chambers by membranes of two kinds arranged in alternating sequence, the membranes of one kind being permeable to ions of one polarity and passage resistant to ions of the opposite polarity, the membranes of the other kind being permeable to ions of said opposite polarity, the membranes of the two kinds being arranged in alternating order, making every other chamber a deionization chamber and making the chambers between the deionization chambers product chambers, there being at least three chambers of one kind and at least two chambers of the other kind; maintaining in at least another deionization chamber spaced from said certain chamber a solution of a companion source compound comprising a cationic component C₂ and an anionic component A₂, said other deionization chamber being spaced from said certain chamber by one product chamber, said companion source compound comprising one ionic component of the opposite polarity of the weakly acid compound in the adjacent deionization chamber produces a strong acid, and said companion source compound being so selected with respect to the product compounds to be produced that the sum of the heats of formation of the source compounds exceeds the sum of the heats of formation of the product compounds, one of the source compounds being a gas dissolved in liquid; maintaining in said one product chamber a conductive liquid; maintaining said cell under above-atmospheric pressure; applying an electrical direct potential across said membranes and chambers and the liquids therein; and withdrawing strongly acid product liquid from said one product chamber.
2. The process of converting, under the influence of an electric current, a weak base compound composed of an anionic component A and a cationic component C into a strong base compound, the process comprising, maintaining the weak base compound, in solution, in a certain deionization chamber of a multichamber electro dialysis cell in which the space between the electrodes is subdivided into chambers by membranes of two kinds arranged in alternating sequence, the membranes of one kind being permeable to ions of one polarity and passage resistant to ions of the opposite polarity, the membranes of the other kind being permeable to ions of said opposite polarity, the membranes of the two kinds being arranged in alternating order, making every other chamber a deionization chamber and making the chambers between the deionization chambers product chambers, there being at least three chambers of one kind and at least two chambers of the other kind; maintaining in at least another deionization chamber spaced from said certain chamber a solution of a companion source compound comprising a cationic component C₂ and an anionic component A₂, said other deionization chamber being spaced from said

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certain chamber by one product chamber, said companion source compound comprising one ionic compound of a certain polarity which with an ionic component of the opposite polarity of the weak base compound in the adjacent deionization chamber produces a strong base, and said companion source compound being so selected with respect to the product compounds to be produced that the sum of the heats of formation of the source compounds exceeds the sum of the heats of formation of the product compounds, one of the source compounds being a gas dissolved in liquid;
 5 maintaining in said one product chamber a conductive liquid;
 10 maintaining said cell under above-atmospheric pressure; applying an electrical direct potential across said membranes and chambers and the liquids therein;
 15 and withdrawing strongly basic product liquid from said one product chamber.

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15 HOWARD S. WILLIAMS, *Primary Examiner*.

MURRAY TILLMAN, JOHN H. MACK, *Examiners*.

G. E. BATTIST, E. ZAGARELLA, *Assistant Examiners*.