Product condenser
(fluorocarbons, etc.)

Hydrogen   Sodium
fluoride   hydroxide   Drier
condenser   reactor

33   32
26   29   30
18
19   21'   23'   25'
Coolant   27
20   22   24   28

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Mixture of
gaseous   Hydrogen
products   gas

17   14   Liquid air
          Hydrogen fluoride
          return

16   Charging inlet
10   11   15
5   7
6   8   9   Cathode
Anode
          4'   1
Cooling   Electrolysis cell
jacket
2   Liquid hydrogen fluoride
          solution containing
          organic starting compound

3   31
Coolant

                              Gas meter

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Outlet for
liquid products

Inventor
Joseph H. Simons
By
Carpenter Abbott Coulter & Kinney
Attorneys

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ELECTROCHEMICAL PROCESS OF MAKING FLUORINE-CONTAINING CARBON COMPOUNDS

Joseph H. Simons, State College, Pa., assignor to Minnesota Mining & Manufacturing Company, St. Paul, Minn., a corporation of Delaware

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This application is a continuation-in-part of my copending application Ser. No. 677,407 (filed June 17, 1946), since abandoned. The latter was filed as a continuation-in-part of the following prior applications which thereafter were abandoned in its favor: Ser. Nos. 384,729 (filed March 22, 1941), 569,265 (filed December 21, 1944), and 626,434 (filed November 2, 1945).

This invention relates to my discovery of a basically new process of making fluorocarbons and other fluorine-containing carbon compounds. The process is simple in operation, does not involve the use or formation of free fluorine at any stage, and has great versatility in enabling the direct production of many types of product compounds using organic starting compounds which are readily available and relatively inexpensive. It is an electrochemical process and its utility has been demonstrated by extensive pilot plant operations employing a 2000-ampere cell, as well as by many laboratory experiments.

This process was publicly disclosed in the oral presentation on September 15, 1948, at the Portland, Oregon, session of the 114th meeting of the American Chemical Society, of five papers authored by me and my assistants. Abstracts of these papers had been previously published in the advance "Abstracts of Papers" volume issued by the society (pp. 42–0 to 45–0). News items relating thereto and briefly describing the process have been published in the society's magazine Chemical and Engineering News, vol. 26, p. 2428 (Aug. 16, 1948) and pp. 2878–9 (Sept. 27, 1948). These papers were subsequently published in the Journal of the Electrochemical Society, vol. 95, No. 2, pp. 47–67 (Feb. 1949).

Briefly stated, this new and useful electrochemical process involves electrolyzing a liquid hydrogen fluoride (HF) solution containing a fluorinatable organic starting compound, at an electrolyzing potential which is insufficient to generate free fluorine under the existing conditions, but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate. A wide variety of organic compounds are soluble in anhydrous liquid hydrogen fluoride and provide adequate electrolytic conductivity. Use can also be made of soluble organic and inorganic conductivity ad-

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ditives to permit of electrolyzing liquid hydrogen fluoride solutions thereof admixed with relatively insoluble organic starting compounds, such as alkanes, which do not provide adequate conductivity. Pure anhydrous liquid hydrogen fluoride, per se, is non-conductive. The electrolyte is free from water in more than a small proportion but need not be anhydrous in a strict sense.

Excellent results can be obtained with simple single compartment electrolytic cell arrangements. No diaphragm is needed between electrodes. Fluorination can be completed in one step to directly obtain fully fluorinated product compounds which are relatively insoluble and either evolve with the cell gases or settle to the bottom of the cell from which they can be drained, depending upon their boiling points. The process is suitable for continuous as well as batch operation. The cell can be operated at atmospheric pressure. The cell and the cathodes can be made of iron or steel, and the anodes of nickel, and such cells have been satisfactorily operated at 5 to 8 volts, D. C., in producing a wide variety of product compounds.

The reaction mechanism is not fully understood but the electrolyzing process apparently transforms the organic starting compounds at or adjacent to the anode and may be regarded as an anodic process. Hydrogen is evolved at the cathode, being derived from the hydrogen fluoride; and will also evolve in the cell by derivation from other hydrogen-containing compounds which may be present. Fluorine is not evolved, and the reaction mechanism does not involve the formation of molecular (free elemental) fluorine as an intermediate agent.

Product compounds are obtainable (both cyclic and non-cyclic) which have the same number of carbon atoms and same carbon skeletal structure as do the starting compounds, but with partial or total fluorine atom replacement of hydrogen atoms and other atoms and radicals bonded to the carbon skeleton of the molecule. Fluorine addition occurs in the case of unsaturated and aromatic types of starting compounds to produce fully saturated product compounds. Non-cyclic compounds (in addition to cyclic compounds) having the same number of carbon atoms are ob-

tainable from cyclic starting compounds as the result of bond cleavage and fluorine addition. Also, the use of polycarbon cyclic and non-cyclic starting compounds generally results in appreciable yields of product compounds having fewer carbon atoms in the molecule, due to fragmentation of the carbon skeleton and fluorine addition. Compounds having a greater number of carbon atoms than the starting compounds are obtainable as the result of coupling of carbon radicals formed in the solution. The kinds and relative proportions of product compounds obtainable in any given case will depend upon the starting compound and the operating conditions. By proper selection it is possible to obtain excellent yields of desired products, which can be readily separated by fractional distillation from each other and from low-yield by-product compounds. In commercial operations, use can be made of the production of multiple products in building up stocks of many useful compounds from a much more limited number of starting compounds.

In some cases resinous material is formed in the cell but is generally soluble in the electrolyte solution and does not interfere with the operation. Resinous products containing combined fluorine in proportions up to 60% have been obtained. In many cases no solid residual materials are found even after extended use of the cell. In general, there is little or no corrosion of the electrodes.

To briefly indicate at this point the versatility of the process in enabling the production of fluorocarbon derivatives, mention is made (for illustration and not limitation) of the following types designated by generic formulae wherein R represents saturated fluorocarbon radicals (cyclic or non-cyclic) consisting solely of carbon and fluorine atoms: R'OR'' (obtainable from ethers), R'R''R'''N (obtainable from tertiary amines), R'R''NF (obtainable from secondary amines), RNF₂ (obtainable from primary amines), RCOF (obtainable from monocarboxylic acids),

R'COOR''

(obtainable from esters), RCN (obtainable from nitriles) and RSF (obtainable from mercaptans). Fluorocarbon compounds which contain combined chlorine can be obtained from chlorine-containing starting compounds (e. g., chloroacetic acid). Heterocyclic compounds containing one or more oxygen or nitrogen atoms in the ring can be obtained by replacement of the hydrogen atoms by fluorine atoms in starting compounds of corresponding structure.

True fluorocarbons (carbon fluorides containing only carbon and fluorine atoms) can be directly obtained from hydrocarbon starting compounds, and also by electrolyzing solutions of various hydrocarbon derivatives, to obtain substantial yields of fluorocarbons having the same number of carbon atoms as the starting compounds. For example, alkanes, alcohols and monocarboxylic acids can be employed to yield fluorocarbons having the same number of carbon atoms. In addition, fluorocarbons having fewer and more carbon atoms are produced. Fluorocarbons having fewer carbon atoms than the starting compound can also be produced from hetero compounds wherein carbon atoms are linked by non-carbon atoms, as in the case of ethers and secondary and tertiary amines; the ——hy—— groups being released to form corresponding fluorocarbons. Fluorocarbons having

fewer or more carbon atoms than the parent hydrocarbon groups can also be obtained from such compounds. A feature of the present process is that it provides a simple and economical procedure for making normally liquid fluorocarbons, having five or more carbon atoms in the molecule.

The formation of fluorocarbons is accompanied by the formation of fluorocarbon hydrides and partially fluorinated hydrocarbons, due to incomplete hydrogen replacement in the case of some molecules. The proportions depend upon the conditions. The fluorocarbon monohydrides and dihydrides are of particular value because they have a high degree of thermal stability and chemical inertness and are non-combustible, and yet the hydrogen atoms offer points of attack for the synthesis of fluorocarbon derivatives. Thus these fluorocarbon hydrides can be thermally chlorinated and brominated to yield the corresponding fluorocarbon chlorides and bromides, as disclosed in a paper published in the Journal of the American Chemical Society, vol. 68, pp. 968-969 (June 1946) of which I was a co-author.

Saturated fluorocarbons and fluorocarbon derivatives are obtainable in good yields ranging from the simplest compound, CF_4, which is a low-boiling gas, up to high-boiling compounds having eight or more carbon atoms in the molecule and having boiling points above 100° C.

The fluorocarbon and related compounds obtainable by this process have utility for many purposes. The saturated fluorocarbons, fluorocarbon hydrides, fluorocarbon ethers, and trifluorocarbon amines, for example, have a high degree of thermal stability and chemical inertness, they do not burn, and they have uniquely low refractive indices and dielectric constants as compared with ordinary organic compounds. The liquid compounds (containing five or more carbon atoms) have exceptionally low surface tensions and viscosities, coupled with high densities. These and other compounds can be used for such purposes (depending upon boiling points) as refrigerants, fire extinguishers, inert solvents and diluents, heat exchange fluids, turbine impellents, dielectrics, hydraulic mechanism fluids, and lubricants. The products of this process can also be used as intermediates in the synthesis of other chemical compounds. In particular, the fluorocarbon acid fluorides (RCOF) provide the reactive starting compounds for making a vast number of derivative compounds containing a fluorocarbon radical and having unique properties on that account.

All organic compounds potentially capable of reacting with fluorine can be employed to produce fluorine-containing carbon compound products by the present process. Fluorine is the most chemically active substance. No organic material is completely resistant to fluorine except carbon tetrafluoride (CF_4). Even the polycarbon saturated fluorocarbons can react by carbon-carbon bond cleavage and fluorine addition, the stable end product being CF_4.

As a practical matter in respect to the commercial utilization of the process, the hydrogen-containing organic compounds which contain at least one hydrogen atom bonded to a carbon atom in the molecule are of main interest. These can all be used for making fluorocarbons, and other fluorine-containing carbon compounds which contain at least one fluorine atom bonded to a carbon atom in the molecule. The sub-classes of these organic starting compounds of particu-

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lar value for making fluorocarbons, and fluorocarbon derivatives of chief commercial interest, are the hydrocarbons (which contain only carbon and hydrogen), and the compounds which are oxygen-containing or nitrogen-containing in addition to being hydrogen-containing. Exemplary of the latter are the cyclic and non-cyclic organic acids, alcohols, ethers, esters, ketones, aldehydes, nitriles, amines, amides, etc. These oxygen-containing and nitrogen-containing organic starting compounds are soluble in anhydrous liquid hydrogen fluoride and provide adequate conductivity, no conductivity additive being needed. The hydrocarbons (which are relatively insoluble) can be employed when use is made of a conductivity additive, as explained in some detail later on. These sub-classes embrace the readily available and relatively inexpensive alkanes, alcohols, ethers, carboxylic acids (including the anhydride forms), and amines, both cyclic and non-cyclic, which can all be efficiently employed in the preparation of fluorocarbons and of other fluorine-containing carbon compounds.

Conjoint use can be made of two or more organic starting compounds and in some cases this will result in improving the operating efficiency. For example, the efficiency of the electrolysis of a solution of hexyl ether can be improved by including propionic acid as a second organic starting compound.

The proportion of the organic starting material relative to the hydrogen fluoride can vary over a wide range and it can be either a minor component or a major component of the solution.

As previously mentioned, this process does not involve the use or generation of free (molecular) fluorine at any stage. It is fundamentally different from processes wherein free fluorine is reacted with organic compounds which are dissolved in or mixed with liquid hydrogen fluoride, as by introducing gaseous fluoride into the reaction zone. For any given cell arrangement and charging stock there is a minimum cell voltage at and above which molecular fluorine (free elementary fluorine) is formed from the hydrogen fluoride, but the resultant effects are quite different from those obtained in the present process and can be easily recognized. When the cell voltage is raised to this critical value or higher, the onset of free fluorine formation manifests itself unmistakably by a marked change in product formation due to the rapid and powerful decomposition and fragmentation effects on the organic compounds in the cell; extensive corrosion of the electrodes occurs; some gaseous fluorine escapes and can be detected in the exit gas mixture even when present in trace amounts; and minor and even major explosions occur. Satisfactory yields of fluorinated compounds having a substantial number of carbon atoms in the molecule cannot be obtained.

The present process is based upon my discovery that liquid hydrogen fluoride solutions containing organic compounds can be efficiently electrolyzed to produce fluorocarbons and other fluorine-containing carbon compounds, by using a cell voltage which in any given case is below the minimum voltage required for free fluorine generation. For example, when using nickel-anode types of cells for which operating voltages in the range of 5 to 8 are quite satisfactory, it has been found that the voltage must be increased to at least 10 to 12 before evidence of free fluorine generation occurs.

The minimum theoretical cell voltage required

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for the generation of free fluorine (F_2) is approximately 3 volts. The reason why total cell voltages higher than this can be used in actual practice of the process without causing free fluorine formation is because a substantial part of the total cell voltage (measured across external anode and cathode connections) is utilized under the existing conditions in overcoming the resistances of the electrodes, the resistance of the electrolyte between the electrodes, and the blocking resistances of electrode polarization films.

In an experiment using a carbon-anode cell it was found that electrolysis of a hydrogen fluoride solution of acetic acid resulted in the formation of fluoromethane (CH_3F) at a cell voltage as low as about 0.5 volt. In another experiment using a nickel-anode cell, a hydrogen fluoride solution of acetonitrile (CH_3CN) was electrolyzed for five days at a cell voltage of 1.7 volts and the products included CF_3CN, CF_3H, CF_4, C_2F_5H and C_2F_6. These cell voltage values were very substantially lower than the minimum cell voltage (approximately 3 volts) required for generation of molecular fluorine even under ideal conditions. Hence these experiments conclusively demonstrate the utility of electrolyzing potentials which are insufficient to generate free fluorine and yet are sufficient to cause the production of fluorine-containing carbon compounds.

In a review paper written by me and published in 1931 (Chemical Reviews, vol. 8), long prior to the discovery of the present process, I referred to and summarized previously published experimental data of Fredenhagen and Cadenbach on the solubilities and equivalent conductivities of various inorganic and organic compounds dissolved in anhydrous liquid hydrogen fluoride (p. 223, et seq.). The well-known laboratory procedure for measuring conductivities of solutions employs a small cell provided with platinum electrodes and utilizes a rapidly reversing current (A. C.) of 1,000 cycles or more per second to substantially eliminate electrode polarization effects and to cause momentarily formed electrode products to revert with each alternation of electrode polarity rather than to escape from the electrodes as free products. In such experiments the current is passed, for each measurement of voltage versus current flow, during a very short time interval (a few minutes at most and often a few seconds or less), for otherwise accurate values for a desired temperature cannot be obtained due to heating of the electrolyte and for other reasons.

Fredenhagen and Cadenbach stated in their paper (Z. physikal. Chem., Abt. A., vol. 146, pp. 245–80) that they employed a conductivity cell vessel made of a gold-platinum alloy, which served as one electrode, and the other electrode was a platinum capillary tube extending through the stopper down into the vessel. The cell was a small one and contained 20.7 cc. of solution (approximately 1.3 cubic inches) when making a measurement. That they employed alternating current is made clear by the absence of any description of an unconventional procedure and by their use of a telephone receiver in balancing the bridge. Nothing was said to suggest that the total time of current flow for any given solution amounted to more than a few minutes at most, even when several measurements were made at intervals. Each solution had served its purpose and was discarded when the measurement work had been completed. There was no suggestion that detectable trace amounts of free

molecular hydrogen or other electrolysis products were produced. That none were formed is to be expected since precision conductivity measurement procedures are deliberately designed to avoid the irreversible production of free electrolysis products, as indicated above, which would consume energy and thus render the voltage-current relation inaccurate as a measure of the electrolyte resistance, as well as altering the composition of the solution being tested. These authors speculated as to the manner of ionic dissociation of the organic compounds when dissolved in the anhydrous liquid hydrogen fluoride, and on the possible formation of reaction products resulting therefrom, in commenting upon the various conductivity values, since the magnitudes of the latter would depend upon what it was whose conductivity was actually being measured. This had reference only to substances formed as the result of dissolving the original organic compounds in the anhydrous liquid hydrogen fluoride and not to the formation of free electrolysis products.

A mere scientific conductivity determination is not a useful process for making electrolysis products from a solution of a starting compound whose conductivity is being measured, and the objectives are antithetical. It will be understood that no attempt is being made herein to claim mere conductivity measurements.

When laboratory size cells are used in performing batch experiments on the present process, the runs continue for periods of hours (generally for a day or more). Likewise the commercial operation of the process using large cells requires electrolyzing the cell charge for a period of many hours in order to obtain a commercially desirable yield ratio of product compounds from the starting material, and a cell will normally be continuously operated for days before being shut down, the hydrogen fluoride and starting material being replenished during operation.

Alternating currents can be usefully employed in practicing the present process when polarizable electrodes (e. g., nickel electrodes) and a relatively low frequency (e. g., 60 cycles) are used. In this case each electrode alternately functions as an anode and as a cathode, but the operating conditions permit the release of free electrolysis products at the electrodes. The use of direct currents is greatly preferred. The efficiency of alternating currents is much inferior and greater heating of the electrolyte is produced. In the case of normal direct current operation each cathode and anode electrode continuously functions as such at a uniform voltage (which may be varied during the run for optimal operation), and the cathodes and anodes can be made of different materials adapted to produce the most efficient results. Pulsating unidirectional currents, unfiltered rectified A. C., and superimposed A. C. on D. C., can also be used and are to be regarded as types of direct currents.

As previously mentioned, pure anhydrous liquid hydrogen fluoride is non-conductive but a wide variety of organic starting compounds are soluble therein and provide adequate electrolytic conductivity to permit the passage of effective electrolyzing currents. The starting compounds of chief commercial interest in this respect are the oxygen-containing and nitrogen-containing organic compounds which have at least one hydrogen atom attached to a carbon atom in the molecule, of which various examples have already been given, and from these there can be obtained

not only fluorocarbons and fluorocarbon but also fluorine-containing carbon which contain oxygen or nitrogen atoms in the molecule.

Commercial anhydrous liquid hydrogen fluoride normally contains a trace of dissolved water, and traces of water are readily absorbed when there is contact with a moist atmosphere. Such water can be readily removed or reduced to a very low value by passing current through the liquid hydrogen fluoride prior to adding the starting compound, the water being consumed by the formation of hydrogen, oxygen fluoride (OF_2) and oxygen which evolve as gases. In actual practice, the first few hours of electrolysis of the hydrogen fluoride solution containing the soluble organic starting compound will generally cause the proportion of water to diminish to 0.1% or less and it is not necessary to subject commercial anhydrous hydrogen fluoride to a preliminary water-removal treatment. The "anhydrous liquid hydrogen fluoride" as used herein is employed, except when otherwise stated, to include liquid hydrogen fluoride which contains traces of water not exceeding 1% by weight. Liquid hydrogen fluoride containing 1% water has a low conductivity, being about 0.06 mho (reciprocal ohm) per centimeter cube at 0° C. The conductivity when there is a 0.1% water content is about 0.006 mho.

When the proportion of dissolved water in the liquid hydrogen fluoride is increased substantially above 1% there is a material decrease in the operating efficiency of the process in various respects. While a small proportion of water can be used to advantage as a means of the conductivity, a point shortly to be in connection with the use of conductivity additives, the presence of water in proportions exceeding 10% by weight of the total of water and hydrogen fluoride results in such marked inefficiency that it should be avoided for operation of the process and the obtaining of desirable yields of fluorocarbon compounds. Water in amount substantially exceeding 10% also gives rise to serious explosion hazards due to the evolution of readily explosive gas mixtures containing substantial proportions of oxygen fluoride and oxygen mixed with hydrogen. Some organic starting compounds may contain dissolved water in the commercial forms employed (as in the case of ethyl alcohol), and in such cases the starting compounds should be employed in proportions which will not result in there being more than 10% by weight of water relative to the total weight of water and hydrogen fluoride. It will be understood that the generic term "liquid hydrogen fluoride," when not restricted by the "anhydrous" adjective, includes not only anhydrous liquid hydrogen fluoride but also solutions thereof which contain small proportions of water in excess of 1% as above indicated.

Some organic compounds, such as acetic acid, react with liquid hydrogen fluoride to form an equilibrium mixture containing water and the anhydride of the starting compound, such as acetic anhydride. In such cases the total amount of water capable of being formed from the starting compound may exceed the 10% value previously mentioned without causing an uneconomically low operating efficiency, since it is not the mere equivalent of free water added all at once to the liquid fluoride. Liquid hydrogen fluoride containing a small

proportion of dissolved water, as described above, is also entirely different in other respects from the aqueous solutions of hydrogen fluoride which are sold in bottles and are commonly referred to as hydrofluoric acid. These contain less than 50% by weight of hydrogen fluoride as normally sold. Such solutions cannot be kept in glass or metal containers and if introduced into electrolysis cells such as are used in the present process (for example, a steel cell having nickel anodes and iron cathodes) would cause rapid corrosion of the metals contacted even in the absence of current flow. Whereas the boiling points of hydrofluoric acid solutions containing 50% by weight of hydrogen fluoride or less are in the range of 100° to 114° C., the boiling point of pure anhydrous liquid hydrogen fluoride is 19.5° C. and the presence of 10% by weight of water results in a boiling point of about 32° C. The specific gravity of aqueous solutions increases with increase of hydrogen fluoride from 1.0 to a maximum value of about 1.26 at about 75% hydrogen fluoride and then rapidly decreases to a value of 1.0 for anhydrous liquid hydrogen fluoride (measured at 0° C.). The conductivity decreases as the hydrogen fluoride percentage increases above 75%, and rapidly so as the percentage increases above 90%. These data are of interest as showing that liquid hydrogen fluoride, both when anhydrous and when containing a small proportion of dissolved water, as employed in the present process, differs radically in physical as well as chemical properties from hydrofluoric acid solutions which contain a large proportion of water and which cannot be employed in the present process.

The present process is not limited to the use of organic starting compounds which are soluble in anhydrous liquid hydrogen fluoride and provide adequate electrolytic conductivity to permit of effective electrolysis. I have made the surprising discovery that the necessary electrolytic conductivity can be provided by a third component >lute which can be either organic or inorganic, so that organic starting compounds which are insoluble in the liquid hydrogen fluoride can be effectively employed in admixture with liquid hydrogen fluoride solutions containing a dissolved conductivity additive. This feature of the generic process greatly extends its versatility and usefulness. Thus it makes possible the use of very cheap organic compounds, such as the hydrocarbons, as starting materials for producing fluorocarbons and fluorocarbon hydrides.

Examples of hydrocarbon starting compounds which can be effectively utilized when a conductivity additive is employed, are the alkanes (both cyclic and non-cyclic). The aromatic compounds, such as benzene and toluene, can also be employed. Moreover, this procedure permits of good yields of fluorocarbon compounds having the same number of carbon atoms as the starting compound. Thus hexane can be used for making C_6F_{14} (tetradecafluorohexane), a normally liquid fluorocarbon. As in the procedures utilizing soluble organic starting compounds, the electrolyzing potential employed is insufficient to generate free fluorine. In contrast, if it were attempted to fluorinate hexane (as an admixture dispersed in liquid hydrogen fluoride) with free fluorine, the reaction would be a violent one and fragmentation would be so severe that there would be no substantial yield of polycarbon fluorocarbons and little if any C_6F_{14} could be obtained. This illustrates again that the present

process is not an equivalent of direct fluorination processes but is an entirely different kind of process which does not involve the use or evolution of free (molecular) fluorine and which produces product compounds that cannot be obtained in significant proportions by direct fluorination with free fluorine.

The exact mechanism of the electrolyzing process remains a mystery. The gases and heat evolved in the cell vigorously agitate the cell contents so that a mixture of the insoluble organic starting compound and the liquid hydrogen fluoride electrolyte solution is present at the anode, and it is a fact that the existing conditions cause the formation of fluorine-containing carbon compounds, including fluorocarbons, at the anode.

The conductivity additives fall into two general groups, organic and inorganic.

The organic conductivity additives are compounds which can themselves be employed as starting compounds, and numerous examples have already been indicated. The most important are the oxygen-containing and nitrogen-containing organic compounds which contain at least one hydrogen atom attached to a carbon atom of the molecule. Illustrative examples are: acetic anhydride, acetic acid, propionic acid, caproic acid, methyl alcohol, diethyl ether, triethyl amine, pyridine, and 2-fluoropyridine, which have all been employed in experiments wherein hydrocarbon starting compounds were converted into fluorocarbons and fluorocarbon hydrides. The proportion of the conductivity additive to the hydrogen fluoride can be relatively small, e. g., ½ to 5%, but much higher proportions can be used. These additives are themselves converted during operation of the process, and hence the fluorine-containing carbon compound reaction products are derived in part from the soluble conductivity additive and in part from the insoluble organic starting compound. Thus, in effect, there are two types of organic starting compounds utilized in this procedure, one being soluble and serving also as a conductivity additive and the other being insoluble. For example, when hexane is employed in admixture with liquid hydrogen fluoride which contains dissolved pyridine, both the hexane and the pyridine are converted to produce fluorine-containing carbon product compounds, including fluorocarbons. Another example of an organic conductivity additive is mercuric cyanide, which also illustrates organic starting compounds that do not contain hydrogen.

The inorganic conductivity additives are inorganic compounds which are soluble in liquid hydrogen fluoride and provide effective electrolytic conductivity. The soluble fluorides, such as sodium fluoride and potassium fluoride, can be used and have the advantage of not decomposing and not being consumed. Ammonia can be used but is gradually consumed, yielding nitrogen trifluoride (NF_3) which is a low-boiling relatively insoluble gas and is evolved. Water can be used in limited amount. The proportion of water in the liquid hydrogen fluoride solution should not exceed a small proportion because otherwise there will be poor efficiency and a poor yield of desired compounds. Effective results can be obtained using as little as 1 to 2% of added water. The water is gradually consumed, yielding oxygen fluoride (OF_2), carbon dioxide (CO_2), oxygen and hydrogen, and must be replenished during extended runs. Some organic conductivity additives also

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provide water so that their use actually involves both organic and inorganic additives. Thus acetic acid is dehydrated by hydrogen fluoride to produce acetic anhydride and water, and alcohols may contain a small amount of dissolved water. Further illustrative examples are sulfuric acid and phosphoric acid. The illustrative inorganic additives named above have all been employed in experiments wherein hydrocarbon starting compounds were converted into fluorocarbons and fluorocarbon hydrides, including significant yields of fully fluorinated product compounds having the same number of carbon atoms as the starting compound. Thus C_8F_{18} has been made from octane, and C_7F_{14} and C_7F_{16} from toluene, for example.

Various combinations of two or more conductivity additives can be employed. Thus an organic additive and an inorganic additive can be jointly employed.

In some cases the soluble conductivity additive (depending upon the kind and amount used) will function as a mutual solvent so as to cause an otherwise insoluble organic starting material to be appreciably soluble in the electrolyte solution. This action does not appear to be necessary to the operation of the process, since useful results are obtained notwithstanding the insolubility of the starting compound.

The principle of using a conductivity additive can also be employed to increase the efficiency even when the organic starting compound is sufficiently soluble so that it could be used without such expedient. This is helpful in the case of starting compounds of limited solubility in anhydrous liquid hydrogen fluoride and which do not provide an efficient conductivity.

Another expedient is to change the operating temperature or pressure or both to cause a more favorable solubility relation. Thus a starting compound which is poorly soluble or relatively insoluble in liquid hydrogen fluoride at 0° C. may be made much more soluble therein by substantially increasing the temperature, while the solubility of normally gaseous compounds can be increased by using lower temperatures.

The accompanying drawing is a diagrammatic sectional elevation of an illustrative apparatus for carrying out the process and also serves as a flowsheet. The drawing has been simplified in the interest of clarity by omitting heat-insulating jackets and coverings, couplings, etc., and by employing conventionalized representations as commonly used in schematic chemical drawings. The apparatus as shown is suitable for laboratory experiments and can also in larger form be employed for pilot plant or small-scale commercial use. A large commercial plant would necessarily be designed on more complex lines, as chemical engineers will understand, but would embody the basic principles of the invention as illustrated and described.

Referring to the drawing, the heart of the apparatus is the electrolysis cell 1, which is provided with a cooling jacket 2 having an inlet 3 and outlet 4 for flow of a coolant liquid (such as an aqueous solution of ethylene glycol or methanol) which is pumped through the jacket and recycled through a refrigerator (not shown), so as to maintain a desired cell operating temperature. An operating temperature in the neighborhood of 0° C. is convenient and permits of simple operation at substantially atmospheric pressure. The cell has a removable cover 5 which can be bolted to an outward top flange of the cell body

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Suspended from the cover, so as to be located within the cell when the cover is in position, is the electrode pack consisting of a series of anode plates and an alternating series of intermeshed cathode plates. An extreme outward anode plate 6 and cathode plate 7 are shown, the other plates being to the rear and not visible in the drawing. The anode plates are connected and held in spaced relation by a cross bar connector 8 to which the tabs of the plates are welded; and similarly the cathode plates are joined by connector 9. The connectors are suspended from anode conductor rod 10 and cathode conductor rod 11, respectively. These rods pass through the cell cover, being insulated therefrom and sealed by concentric insulating material, and external connection is made to them from the power source.

The cell body can be conveniently made of steel. Iron cathode plates and nickel anode plates are suitable, and the cross bars and conductor rods can be made of the same metals as the electrode plates served by them. The plates can be closely spaced, a spacing distance between adjacent anode and cathode surfaces of the order of ⅛ to ¼ inch being quite satisfactory. "Teflon" (polytetrafluoroethylene) is a very satisfactory non-corroding material for insulating and sealing the conductor rods from the cover and for providing a gasket between the cover and body flange of the cell.

The bottom of the cell is provided with an outlet pipe 12 having a valve 13, used for draining the cell. This can be used during operation for draining liquid products which settle to the bottom of the cell.

The cell cover is provided with a vertical inlet pipe 14 (which connects to the bottom of the hydrogen fluoride condenser shortly to be described) and a charging inlet pipe 15, having a valve 16, connects thereto to permit of introducing into the cell the liquid hydrogen fluoride, the organic starting compound, and any other substance (such as a conductivity additive) which is to be present. This inlet pipe extends down into the cell a sufficient distance so that its lower end will be well below the surface of the liquid solution during normal operation, thereby making a liquid seal. It is located in front of the electrode pack and is spaced therefrom.

The cell cover is also provided with a vertical outlet pipe 17, for gaseous products evolved in the cell, which connects to the hydrogen fluoride condenser 18 located above the cell. This condenser has a jacket 19 to permit of circulating a coolant liquid for maintaining a desired low temperature. The pipe 17 extends down into the condenser short of the bottom, and may be in the form of a spiral for better heat transfer. The bottom of the condenser vessel is connected, through valve 20, with the aforesaid vertical inlet pipe 14 of the cell. This permits the liquid condensate to drain back into the cell.

The top of this condenser is connected by tube 21 to the reactor vessel 22, the tube extending down into the vessel, which is filled with a 15% sodium hydroxide solution. The top of the reactor is in turn connected by tube 23 to the drier vessel 24, the tube extending down into the vessel. This vessel is filled with a drying medium, such as potassium hydroxide pellets, for removing water from the gaseous mixture passing therethrough.

The top of the drier is connected by tube 25, having valve 26, to the product condenser vessel 27, the tube extending down short of the bottom. The tube can be spiralled so as to improve heat

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transfer. This vessel is provided with a removable liquid-air cooling jacket 28, for maintaining in the condenser a very low temperature sufficient for condensing even such low-boiling product compounds as carbon tetrafluoride (CF_4) and fluoroform (CF_3H), but insufficient to condense the accompanying hydrogen.

The top of this condenser is provided with an outlet tube 29, having a valve 30, for conducting the hydrogen gas to the gas meter 31, the latter being used for measuring the hydrogen production. The outlet tube is provided with a branch tube 32, having a valve 33, which connects on the upstream side of valve 30. During normal operation valve 26 and 30 are open and valve 33 is closed. However, valves 26 and 30 can be closed and valve 33 opened to withdraw the condensate compounds, the latter being vaporized by warming in the absence of the liquid air; and during this period the gaseous products from the cell can be diverted to an alternate recovery system (not shown) if continuous cell operation is in progress. The withdrawn products can be led to a fractional distillation system (not shown) for separating the various product compounds which have been formed.

The gaseous mixture evolved from the cell will normally contain some hydrogen fluoride (evaporated in the cell) in addition to hydrogen and to volatile fluorine-containing carbon product compounds. If an oxygen-containing organic starting compound is employed this will also result in the formation of some CO_2. The hydrogen fluoride condenser 18 is maintained at a temperature of about minus 40° C. and serves to condense out most of the hydrogen fluoride, which is returned to the cell. The other constituents of the gas mixture are substantially insoluble in the liquid hydrogen fluoride condensate and are carried along in vapor phase in the hydrogen gas stream. Vapors from any higher-boiling fluorine-containing carbon product compounds formed in the cell will also condense and return to the cell; such compounds in the main settling to the bottom of the cell.

The sodium hydroxide reactor 22 serves to remove from the gas stream any residual HF and also any CO_2 which is present. The drier 24 serves to remove water vapor which has been picked up in the reactor. The fluorocarbons and other fluorine-containing carbon product compounds are separated from the hydrogen by being frozen out in the product condenser 27, from which they can be withdrawn in the manner already indicated.

Other means can be used for separating the hydrogen from the purified gaseous product compounds. A condenser cooled by a mixture of solid-CO_2 and acetone can be included ahead of the liquid-air condenser to preliminarily condense out the higher-boiling product compounds. Instead of using a liquid-air condenser, the gaseous mixture can be compressed and refrigerated so as to condense out the product compounds. This can be done in several stages so as to first condense out the bulk of the higher-boiling compounds and then, at a lower temperature or higher pressure (or both), condense out the remaining product compounds. The hydrogen can also be separated by chemical means, as by passing the gas stream through heated copper oxide.

The aforesaid purifying and recovery system has a wide application but can be readily modified as desired. For example, an aqueous calcium chloride bubbler can be inserted in series before

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the sodium hydroxide bubbler for removal of residual hydrogen fluoride from the gas stream. Oxygen fluoride (OF_2), formed when water is present in the electrolyte solution of the cell, can be removed from the gas stream by bubbling through an aqueous potassium-sulfite-iodide solution contained in a reactor vessel included in the train ahead of the drier. When nitrogen-containing organic starting compounds are being processed, the gas stream will contain some nitrogen trifluoride (NF_3). This is a stable low-boiling gas and can be separated from the product compounds by fractionation.

A further alternative is to remove the residual traces of hydrogen fluoride from the gas stream leaving the hydrogen fluoride condenser by passing through a vessel packed with sodium fluoride pellets. It is not necessary to remove CO_2, OF_2 and NF_3 from the gas stream, and the use of aqueous purifying solutions can be omitted. The gas stream from the sodium fluoride vessel can go directly to the product condenser in this case as no drying is needed. The CO_2 (and any OF_2 and NF_3 present) can be separated from the products by distillation. This procedure is especially useful when reactive fluorocarbon derivatives (such as fluorocarbon acid fluorides made from carboxylic acids) are contained in the gas stream.

The principal non-volatile products of interest are insoluble in the hydrogen fluoride electrolyte solution and settle to the bottom of the cell from which they can be drained. The immiscible liquid drained from the cell may include normally solid compounds dissolved therein. This liquid can be washed with potassium hydroxide solution to remove traces of hydrogen fluoride and then fractionally distilled. Soluble product materials which remain in the electrolyte solution can be recovered by distillation following the run. Some product compounds (of intermediate volatility) will be recovered in part from the gaseous mixture evolved from the cell and in part from the immiscible liquid which is drained from the bottom of the cell.

The body of the electrolysis cell can be used as a cathode, being connected to the cathodes in the cell, or, as is generally preferable, it can simply "float," not being electrically connected or grounded.

The cathode elements do not need to be made of iron or steel. Any metallic conducting material which resists the corrosive action of the hydrogen fluoride solution can be used, including copper, magnesium, aluminum, nickel, nickel alloys, etc. Anode elements can be made of nickel alloys as well as of nickel, or of Monel metal, silicon carbide, carbon, etc.

Using iron cathodes and nickel anodes, operating cell voltages in the range of 5 to 8 volts have been found generally suitable for most efficient results, with 5 to 6 volts usually being the optimum. Current densities as high as 20 amperes or higher per square foot of anode surface are obtainable. A 50-ampere cell, having about 350 sq. in. of anode surface, has proved quite satisfactory for general laboratory research use and permits of making substantial quantities of product compounds for study of properties and for preliminary use evaluation. The compactness of the cells per unit of power is an advantageous feature of the process. Operating temperatures in the range of about minus 20° C. to plus 80° C. have proved highly effective. Within this range, temperatures of about 0° C. to 20° C.

readily permit of convenient operation at about atmospheric pressure (the boiling point of hydrogen fluoride being 19.5° C. and being raised by dissolved compounds), and the necessary cooling can be readily effected.

It is to be understood, however, that the invention is not restricted to the operating conditions noted above. Under appropriate conditions cell voltages as low as about ½ volt can be used. While higher cell voltages than those mentioned can be used under some circumstances without causing free fluorine generation, arrangements utilizing cell voltages not exceeding 8 volts are much preferred since the use of a higher voltage means that much energy is being lost in overcoming current blocking conditions in the cell. A wide range of operating temperatures and pressures can be employed. Thus temperatures as low as minus 80° C. and higher than plus 75° C. have actually been used in experiments. The freezing point of pure hydrogen fluoride is minus 83° C. and a still lower freezing point results when it contains dissolved material. Thus the liquid state of liquid hydrogen fluoride solutions can be maintained at very low temperatures. Temperatures higher than about 20° C. generally require operation at superatmospheric vapor pressures in order to elevate the boiling point of the solution. However, the necessary pressure can be minimized and even atmospheric pressure can be utilized by employing solutes which markedly lower the hydrogen fluoride vapor pressure, as by dissolving potassium or sodium fluoride in relatively large proportion in the hydrogen fluoride. Superatmospheric cell pressures are needed in some cases to maintain the starting compound in liquid phase or to prevent rapid evaporation, even though a low operating temperature is employed. This is especially true in the case of low-boiling starting compounds which are not dissolved in the liquid hydrogen fluoride. To take an extreme illustration, ethane has a boiling point of minus 88° C. at atmospheric pressure and hence the cell must be operated at an elevated pressure in order to maintain ethane in a liquid state in the cell at temperatures above this value.

It will be evident from the foregoing description that this invention pertains to a basically new unit process in chemistry and is not a mere process for producing a particular type of compound from a particular type of starting material. Practically all organic materials can be utilized as starting compounds, whether or not soluble in liquid hydrogen fluoride, and the process provides a new general method by which they can be transformed into a great variety of fluorine-containing carbon product compounds, including many novel compounds not hitherto made by any other process.

In all cases the basic generic principle of the present invention is employed, namely, the useful electrochemical preparation of fluorine-containing carbon product compounds from fluorinatable organic starting compounds, by electrolyzing for a period of hours a current-conducting mixture of liquid hydrogen fluoride solution and the organic starting material (either dissolved or admixed), which is free from water in more than a small proportion, at a temperature and pressure at which a liquid state is maintained and at an electrolyzing potential which is insufficient to generate free fluorine under the existing conditions, but which is sufficient to cause the production of fluorine-containing carbon compound

products at a useful rate, and recovering one or more fluorine-containing carbon compound products of the process.

In order to further illustrate the invention by specific examples, the following table is presented as a convenient summarization of the results of a large number of experiments. This table is not intended to set forth all compounds that have been made or can be made, and serves for illustration rather than limitation. It lists a considerable number of different fluorine-containing carbon product compounds which have been made by this process from soluble organic starting compounds dissolved in anhydrous liquid hydrogen fluoride. Boiling point values for most of the compounds are given in the left-hand column. These are to be regarded as approximate values. Many of these values were determined at about 740 mm. pressure and have not been corrected to standard condition (760 mm.) values, and hence are somewhat lower (1 to 3°) than the latter. These compounds were separated and clearly identified by physical and chemical properties. In all necessary cases the content of fluorine and of other non-carbon elements present was determined by analysis. In some cases where compounds of the same series or of an analogous series had previously been obtained and identified, it was not considered necessary to chemically analyze the product compounds for unambiguous identification; the physical and chemical properties, together with knowledge of the starting compound employed, being quite sufficient to enable definite identification. In some cases derivatives were made and identified, further corroborating the identification of the cell product. Infrared absorption spectra determinations have been made on various series of these compounds to supply further identification corroboration. Several compounds were analyzed by the mass spectrograph method.

Under the listing of each product compound there is listed in the indented column one or more HF-soluble starting compounds from which it was made. No attempt has been made at completeness in the latter respect—thus carbon tetrafluoride (CF_4) and fluoroform (CF_3H) were presumably produced in substantially all experiments. The product compounds are those which were regarded as of particular significance in the experiments on the listed starting compounds. Some starting compounds have produced significant yields of two or more types of compounds, as for example, the ethers have yielded both fluorocarbons and fluorocarbon oxides, the amines have yielded fully fluorinated nitrogen-containing carbon compounds as well as fluorocarbons, the carboxylic acids have yielded fluorocarbon acid fluorides as well as fluorocarbons, etc. Most of these product compounds have been, and all of them could be, produced with the type of cell arrangement which has been described in connection with the drawing, utilizing iron cathodes and nickel anodes and cell voltages below 8 volts D. C., and operating temperatures in the neighborhood of 0° C. The solubilities of these starting compounds in anhydrous liquid hydrogen fluoride at 0° C. permitted use of starting solutions containing at least about a 1 to 10 ratio by weight of the starting compound to the hydrogen fluoride and in many cases a substantially higher ratio was actually used. Thus in some experiments using acetic acid, the initial amount thereof exceeded that of the hydrogen fluoride.

B. P., °C.	Flourine–Containing Carbon Product Compounds made from the under-listed organic compounds
−128	CF₄ (carbon tetrafluoride)
	CH₃OH (methyl alcohol)
	C₂H₅OH (ethyl alcohol)
	CH₃COOH (acetic acid)
	CH₃COONa (sodium acetate)
	CH₃COCH₃ (acetone)
	CH₃COCl (acetyl chloride)
	CH₃CN (acetonitrile)
	C₂H₅COOH (propionic acid)
	C₃H₇COOH (butyric acid)
	CH₃OCH₃ (dimethyl ether)
	(CH₃)₃N (trimethylamine)
	Hg(CN)₂ (mercuric cyanide)
−78	C₂F₆ (hexafluoroethane)
	CH₃CN (acetonitrile)
	C₂H₅OH (ethyl alcohol)
	C₂H₅COOH (propionic acid)
	C₃H₇OH (propyl alcohol)
	C₃H₇COOH (butyric acid)
	C₂H₅OC₂H₅ (diethyl ether)
	(C₂H₅)₃N (triethylamine)
−38	C₃F₈ (octafluoropropane)
	(CH₃)₂CHOH (isopropyl alcohol)
	(CH₃)₂CHOCH(CH₃)₂ (di-isopropyl ether)
	C₂H₅COOH (propionic acid)
	C₃H₇COOH (butyric acid)
	C₃H₇CHO (butyraldehyde)
	(CH₃)₃CCOOH (pivalic acid)
	(C₃H₇)₃N (tripropylamine)
−2.5	C₄F₁₀ (decafluorobutane)
	C₄H₉OH (butyl alcohol)
	C₃H₇COOH (butyric acid)
	CH₃COOC₄H₉ (butyl acetate)
	C₄H₉NCO (butyl isocyanate)
	C₄H₉SH (butyl mercaptan)
	(CH₂)₄(COOH)₂ (adipic acid)
	C₅H₁₁OH (amyl alcohol)
	C₄H₉OC₄H₉ (diabutyl ether)
	(C₄H₉)₂NH (dibutylamine)
	(C₄H₉)₃N (tributylamine)
	(C₅H₁₁)₃N (triamylamine)
28	C₅F₁₂ (dodecafluoropentane)
	C₅H₁₁OH (amyl alcohol)
	C₅H₁₁OC₅H₁₁ (diamyl ether)
	C₅H₁₁COOH (caproic acid)
	C₆H₅OH (phenol)
	(CH₂)₈(COOH)₂ (sebasic acid)
	(C₅H₁₁)₃N (triamylamine)
	C₅H₅N (pyridine)
52	C₆F₁₂ (dodecafluorocyclohexane)
	C₆H₅OH (phenol)
	C₆H₅NH₂ (aniline)
56	C₆F₁₄ (tetradecafluorohexane)
	C₆H₁₃OH (hexyl alcohol)
	C₆H₁₃OC₆H₁₃ (hexyl ether)
	C₅H₁₁COOH (caproic acid)
	C₆H₅COOH (benzoic acid)
82	C₇F₁₆ (hexadecafluoroheptane)
	C₆H₅COOH (benzoic acid)
	C₇H₁₅COOH (caprylic acid)
104	C₈F₁₈ (octadecafluorooctane)
	C₈H₁₀COOH (capric acid)
	(CH₂)₈(COOH)₂ (sebasic acid)
	C₈H₁₇NH₂ (octylamine)
	C₇H₁₅CN (caprylonitrile)
	C₇H₁₇SH (octyl mercaptan)
127	C₉F₁₈ (octadecafluoropropylcyclohexane)
	C₉H₇N (quinoline)
128	C₉F₂₀ (eicosafluorononane)
	(CH₂)₈(COOH)₂ (sebacic acid)
	C₉H₁₉COOH (capric acid)
143	C₁₀F₂₂ (docosafluorodecane)
	C₉H₁₉COOH (capric acid)
	C₁₀H₂₁NH₂ (decylamine)
−78	CH₃F (fluoromethane)
	CH₃COOH (acetic acid)
−52	CF₂H₂ (difluoromethane)
	CH₃COOH (acetic acid)
−83	CF₃H (fluoroform)
	CH₃OH (methyl alcohol)
	CH₃COOH (acetic acid)
	CH₃COONa (sodium acetate)
	CH₃COCl (acetyl chloride)
	CH₃COCH₃ (acetone)
	CH₃OCH₃ (dimethyl ether)
	C₃H₇COOH (butyric acid)
	CH₃CN (acetonitrile)
	(CH₃)₃N (trimethylamine)
−48	C₂F₄H₂ (tetrafluoroethane)
	C₂H₅COOH (propionic acid)
	CH₃COC₂H₅ (methyl ethyl ketone)
−49	C₂F₅H (pentafluoroethane)
	C₂H₅COOH (propionic acid)
	C₃H₇COOH (butyric acid)
	CH₃COC₂H₅ (methyl ethyl ketone)
	CH₃CN (acetonitrile)
−1.5	C₃F₆H₂ (hexafluoropropane)
	C₃H₇COOH (butyric acid)
−16.5	C₃F₇H (heptafluoropropane)
	C₃H₇COOH (butyric acid)
	(CH₃)₂CHOCH(CH₃)₂ (diisopropyl ether)
−59	CF₃OCF₃ (di-trifluoromethyl ether)
	CH₃OCH₃ (dimethyl ether)
1	C₂F₅OC₂F₅ (di-pentafluoroethyl ether)
	C₂H₅OC₂H₅ (diethyl ether)
101	C₄F₉OC₄F₉ (di-nonafluorobutyl ether)
	C₄H₉OC₄H₉ (dibutyl ether)

B. P., °C.	Flourine–Containing Carbon Product Compounds made from the under-listed organic compounds
138	C₅F₁₁OC₅F₁₁ (di-undecafluoroamyl ether)
	C₅H₁₁OC₅H₁₁ (diamyl ether)
172	C₆F₁₃OC₆F₁₃ (di-tridecafluorohexyl ether)
	C₆H₁₃OC₆H₁₃ (dihexyl ether)
35	C₄F₉OCF₃ (nonafluorobutyl-trifluoromethyl ether)
	C₄H₉OCH₂CH₂OH (ethylene glycol monobutyl ether)
	O(C₂H₄OC₄H₉)₂ (diethylene glycol dibutyl ether)
14	CF₃OCF₂CF₂OCF₃ (decafluoro-glycol dimethyl ether)
	CH₂OCH₂CH₂OCH₂ (1,4-dioxane)
97	C₂F₅OCF₂CF₂OCF₂CF₂OC₂F₅ (octafluorodiethylene glycol di-pentafluoroethyl ether)
	C₂H₅OCH₂CH₂OCH₂CH₂OC₂H₅ (diethylene glycol diethyl ether)
81	C₆F₁₁OCF₃ (undecafluorocyclohexyl trifluoromethyl ether)
	C₆H₅OCH₃ (anisole)
1	C₄F₈O (octafluorotetramethylene oxide)
	C₄H₈O (tetramethylene oxide)
32	C₅F₁₀O (decafluoropentamethylene oxide)
	C₅H₁₀O (pentamethylene oxide)
−42	OCF₂CFCF₃ (hexafluoropropylene oxide-1,2)
	OCH₂CHCH₂Cl (epichlorohydrin)
−60	CF₃COF (trifluoroacetyl fluoride)
	CH₃COOH (acetic acid)
−28	C₂F₅COF (pentafluoropropionyl fluoride)
	C₂H₅COOH (propionic acid)
-------	C₃F₇COF (heptafluorobutyryl fluoride)
	C₃H₇COOH (butyric acid)
-------	C₅F₁₁COF (undecafluorocaproyl fluoride)
	C₅H₁₁COOH (caproic acid)
-------	C₇F₁₅COF (pentadecafluorocaprylyl flyoride)
	C₇H₁₅COOH (caprylic acid)
-------	C₉F₁₉COF (nonadecafluorocapryl fluoride)
	C₉H₁₉COOH (capric acid)
-------	C₆F₁₁COF (undecafluorocyclohexanecarboxylic acid fluoride)
	C₆H₅COOH (benzoic acid)
-------	C₆F₁₁CF₂COF (tridecafluorocyclohexylacetyl fluoride)
	C₆H₅CH₂COOH (phenylacetic acid)
	C₆H₁₁CH₂COOH (cyclohexylacetic acid)
−61	CF₃CN (trifluoroacetonitrile)
	CH₃CN (acetonitrile)
124	FC₅H₄N (2-fluoropyridine)
	C₅H₅N (pyridine)
77	C₆F₁₁NF₂ (tridecafluorocyclohexylamine)
	C₆H₅NH₂ (aniline)
48	C₅F₁₀NF (undecafluoropiperidine)
	C₅H₅N (pyridine)
−11	(CF₃)₃N (tri-trifluoromethylamine)
	(CH₃)₃N (trimethylamine)
69	(C₂F₅)₃N (tri-pentafluoroethylamine)
	(C₂H₅)₃N (triethylamine)
129	(C₃F₇)₃N (tri-heptafluoropropylamine)
	(C₃H₇)₃N (tripropylamine)
177	(C₄F₉)₃N (tri-nonafluorobutylamine)
	(C₄H₉)₃N (tributylamine)
216	(C₅F₁₁)₃N (tri-undecafluoroamylamine)
	(C₅H₁₁)₃N (triamylamine)
115	(CF₃)₂NC₆F₁₁ (N,N-di-trifluoromethyl-undecafluorocyclohexylamine)
	(CH₃)₂NC₆H₅ (dimethylaniline)
165	(C₂F₅)₂NCF₂C₆F₁₁ (N,N-di-pentafluoroethyltridecafluorocyclohexylmethylamine)
	(C₂H₅)₂NCH₂C₆H₅ (diethylbenzylamine)
93	(C₂F₅)₂NC₃F₇ (N,N-di-pentafluoroethyl-heptafluoropropylamine)
	(C₂H₅)₂NC₃H₇ (diethylpropylamine)
113	(C₂F₅)₂NC₄F₉ (N,N-di-pentafluoroethyl-nonafluorobutylamine)
	(C₂H₅)₂NC₄F₉ (diethylbutylamine)
111	(C₃F₇)₂NC₂F₅ (N,N-di-heptafluoropropyl-pentafluoroethylamine)
	(C₃H₇)₂NC₂H₅ (dipropylethylamine)
108	(i-C₃F₇)₂NC₂F₅ (N,N-di-heptafluoroisopropyl-pentafluoroethylamine)
	(i-C₃H₇)₂NC₂H₅ (diisopropylethylamine)
159	CF₃(CF₂)₇SF (octadecafluorooctyl mercaptan)
	CH₃(CH₂)₇SH (octyl mercaptan)

Many of the product compounds listed in the foregoing table have not been disclosed in prior publications or patents and are believed to be novel. Some of them are claimed as new compositions of matter in the following applications of which I am in each case the sole or a joint applicant, and which describe their preparation by the present process and give further information on their physical and chemical properties, viz.: Ser. Nos. 29,955 (filed May 28, 1948), now abandoned, 38,751 and 38,752 (both filed July 14, 1948), 39,999 (filed July 21, 1948), 48,777 (filed

September 10, 1948) and 70,154 (filed January 10, 1949). Ser. Nos. 38,751 and 38,752 have since issued as Patents Nos. 2,490,098 and 2,490,099, dated December 6, 1949, and Ser. No. 39,999 as Patent No. 2,500,388, dated March 14, 1950.

The following examples are based on actual experiments and further serve to illustrate the invention. Additional detailed examples have been set forth in my aforesaid parent applications, Ser. Nos. 384,729, 569,265, 626,434, and 677,407, to which reference may be made, but in the interest of brevity have not been set forth in the present specification.

Example I

In this experiment use was made of a 100-ampere cell. The casing was a rectangular steel box having a removable steel cover plate bolted to the flanged top of the casing. The conductor rods were insulated and sealed from the cover plate by means of "Saran" (polyvinylidene chloride) tubing, which was also employed in sheet form as a gasket between the cover and the casing flange. Eight anode plates of nickel and seven interleaving cathode plates of iron were used, spaced so that the distance between adjacent electrode surfaces was 0.29". The dimensions of each plate were 18" x 11½" x $\frac{1}{8}$". The distance between the outer anode plate surfaces and the cell walls was 0.40". The cell casing served as a cathode element and was connected to the cathode plates. The anode plates had a total operating area of 23 sq. ft. (21,400 sq. cm.). The cell was maintained at a temperature during operation of from minus 5° C. to plus 10° C. by means of a chilled brine bath.

This cell was charged with 4.45 kg. (50.5 mols) of n-butyric acid (approximately 10 pounds) and with 27.5 kg. (1375 mols) of commercial anhydrous liquid hydrogen fluoride (approximately 61 pounds). The applied cell voltage was 5.3 volts, which produced an average current of 100 amperes, the average current density being about 4.4 amps./sq. ft.

The exit gas mixture from the cell was conducted through a tube (connected to the cover plate) to a condenser where the bulk of the HF was condenser and drained back to the cell, then through a sodium fluoride tube for further removal of HF, then through a potassium hydroxide bubbler to remove CO₂ and any residual HF, a potassium iodide and sodium thiosulfate bubbler to remove OF₂, a liquid air trap to condense the fluorocarbon compounds, and lastly a wet test meter for measuring the quantity of hydrogen.

The materials collected in the liquid air trap during a portion of the run were transferred to a gas holder over water. The weight of this purified condensate was 745 grams, produced during an operating period of 54.4 hours, with 232 faradays being passed. This material was fractionated into nine portions with yields as shown in the following table. Molecular weights of the fractions were obtained by using a gas density balance and applying the ideal gas law; they represent approximate weighted averages in the case of fractions boiling over an appreciable range. The weight amount of each fraction was obtained from the pressure of the gas when the fraction was allowed to vaporize into a receptacle of known volume, applying the ideal gas law. The first cut was a mixture of CF₄, CF₃H and C₂F₆. Other cuts consisted of relatively pure single compounds, as shown.

Cut	Boiling range, °C.	Quantity, grams	Mol. wt.	Identity	Formula wt. of pure comp.
#1	−133 to −48	60	90	CF₃H.... / CF₄.... / C₂F₆....	70 / 88 / 138
#2	−48 to −42	20	168	Intercut...	---------
#3	−42 to −41	80	186	C₃F₈......	188
#4	−41 to −38	280	186	...do......	188
#5	−39 to −23	60	185	...do......	188
#6	−23 to −16	70	170	C₃F₇H....	170
#7	−16 to −4	50	165	Intercut....	---------
#8	−4 to −2	30	152	C₃F₆H₂....	152
#9	−2 to +13	30	150	Residue....	---------

It will be evident from the above table that the gaseous mixture contained a large proportion of fluorocarbon compounds having three carbon atoms in the molecule, i. e. C₃F₈ (octafluoropropane), C₃F₇H (heptafluoropropane) and C₃F₆H₂ (hexafluoropropane).

After several runs using this same charge (without replenishment of the butyric acid) the following materials were collected from the gas mixture: Boiling below −38° C., 1141 grams; at approximately −38° C., 1988 grams; between −38 and −17° C., 182 grams; between −17 and −4° C., 1183 grams; above −4° C., 972 grams. The residual solution in the cell, after an extended period of electrolysis, was found to contain 2.27 kg. (5 pounds) of organic material which contained about 40% by weight of combined fluorine. Thus non-gaseous fluorine-containing carbon compounds were also produced by the process and remained in the cell.

Other experiments have demonstrated the formation from butyric acid of a substantial yield of C₄F₁₀ (decafluorobutane), having a boiling point close to 0° C., as well as other compounds, including the fluorocarbon acid fluoride compound C₃F₇COF.

Example II

A small laboratory cell was used. The cell body was constructed of a one-foot length of iron pipe (3" diameter) having an iron plate brazed to one end to form the bottom. An iron rod (½" dia.) was brazed to the center of the bottom and extended upwardly to near the top. The pipe and this center rod constituted the cathodes. An iron cover plate was secured to a flange at the upper end of the pipe. Through the center of the cover passed an anode conductor support rod sealed and insulated therefrom, to which was fastened a cylinder of sheet nickel (1½" dia.) surrounding the iron center rod and forming the anode. "Saran" was used for sealing and gasketing. An outlet tube was connected to the upper end of the pipe for withdrawing gaseous products. The cell was cooled in an ice bath to maintain an operating temperature in the neighborhood of 0° C.

The cell was charged with 400 grams (20 mols) of commercial anhydrous liquid hydrogen fluoride, 93 grams (1 mol) of toluene, and 5 grams (0.3 mol) of added water, serving as a conductivity additive. The toluene was substantially insoluble in the hydrogen fluoride solution but became admixed therewith during operation.

Electroylsis proceeded at 5 volts and 1.1 amperes for a period of 12 days, during which 88 liters of gas were evolved which yielded 11 grams of condensate in a liquid air trap. The condensate was distilled to yield a 0.5 gram portion boiling below −80° C., a 0.5 gram portion boiling at about 0° C., and a principal fraction of 10 grams

boiling above room temperature. The latter was redistilled in a fractionating column and the following fractions were separated:

Boiling range (° C.):	Weight (grams)
57–60	1.6
60–63	1.6
63–64	3.2
Residue	0.7

The 63–64° C. fraction had a molecular weight of 383, corresponding to a 7-carbon fluorocarbon.

Using the same cell arrangement, the formation of fluorocarbons from n-octane, using water as a conductivity additive, was demonstrated. The cell was charged with 550 grams (27.5 mols) of commercial anhydrous liquid hydrogen fluoride, 160 grams (1.4 mols) of n-octane, and 10 grams (0.6 mol) of added water. An electrolysis proceeded during the 600 hour run period, a total of 440 additional grams of hydrogen fluoride and 60 grams of water were added from time to time to replenish the hydrogen fluoride and to maintain the conductivity. The cell voltage varied from 6.5 to 7.7 volts and the cell current varied in the range of 1.5 to 3.0 amperes. A total of 47.3 faradays passed. Fractionation of the product mixture demonstrated that the original octane had been (to a large extent) converted to fluorocarbon compounds, of which more than one-third was C_8F_{18}. Substantial yields of C_7F_{16} and C_6F_{14} were also obtained.

The production of fluorocarbons from n-octane was also demonstrated in experiments using ammonia, mercuric cyanide, and pyridine, as conductivity additives. In the absence of the n-octane, a solution of mercuric cyanide in anhydrous liquid hydrogen fluoride yielded CF_4 and NF_3 when subjected to a cell potential of about 7.5 volts, and with the liberation of free mercury.

Example III

A cell of the type described in the preceding example was charged with 205 grams (5 mols) of acetonitrile (CH_3CN) and 785 grams (39.3 mols) of anhydrous liquid hydrogen fluoride (which initially contained a substantial trace of water). Current was passed for five days at an average of 5.5 amperes. The cell voltage averaged 1.7 volts and remained close to this value during this five day period. Fluorocarbon compounds were formed during the entire run. The identified products included OF_2, CF_3H, CF_4, C_2F_5H, C_2F_6 and CF_3CN.

The C_2F_5H and CF_3CN appeared to form an azeotropic mixture and separation by distillation was not accomplished. This mixture fraction (boiling in the range of −73 to −48° C.) was chemically treated to identify the CF_3CN in the following way: The gaseous mixture was passed through 50% aqueous potassium hydroxide at 60–70° C., then into a standard HCl acid solution, through a drying tube, and recondensed in a liquid air trap. Titration of the acid indicated that 3.2 grams of CF_3CN had been hydrolyzed, equivalent to 5.1 g. of CF_3COOK. The basic solution was neutralized with HCl and evaporated to dryness. The residue was then dried and was subjected to an analytical procedure which demonstrated the presence of 5.1 g. of CF_3COOK. The gas from the liquid air trap was found to have a molecular weight range of 118 to 124 and was mainly C_2F_5H (formula wt. 120).

Example IV

A small copper cell having a nickel anode was charged with acetic acid and $KF \cdot 3HF$ in the ratio of 1 to 3.4 by weight. Current was passed through the cell at about 8 volts and 9 amperes until 6 faradays had passed. The operation was conducted at atmospheric pressure and a temperature averaging 75° C. This operating pressure was possible, despite the elevated temperature, due to the low vapor pressure of the complex of potassium fluoride and hydrogen fluoride, which remained in a non-boiling liquid state. The products included CF_4 and CF_3H.

A similar experiment, using a cell charge of sodium acetate and $KF \cdot 3HF$ in the ratio of 1 to 6.8 by weight, was conducted under similar conditions and with similar results.

Example V

Use was made of an iron laboratory cell containing nickel anodes and iron cathodes, operating at atmospheric pressure and a temperature of 0° C. The initial cell charge consisted of 7,500 grams of highly anhydrous liquid hydrogen fluoride and 700 grams of dried pyridine. Additional pyridine was added during the run to make a total of about 2,000 grams. The pyridine employed was dried over solid sodium hydroxide and then distilled. Current was passed for a period of four days, at an average cell voltage of approximately 6.0. A total of 447 faradays was passed.

The liquid cell product mixture was drained from the bottom of the cell, treated with lime to remove residual HF, and was fractionally distilled. There was obtained about 250 grams of a liquid fraction which was identified as relatively pure $C_5F_{10}NF$ (undecafluoropiperidine), a cyclic compound having the following measured properties:

Boiling point (at about 740 mm.) ____°C__	48
Refractive index (at 20° C.)	1.281
Density (grams/cc. at 20° C.)	1.744
Surface tension (dynes/cm. at 20° C.)	13.6
Molecular weight (from vapor density)	285
Per cent F	73.4
Per cent N	4.87

The values for the pure compound as calculated from the formula are: molecular weight, 283; Per cent F, 73.1; Per cent N, 4.95.

Other products included 2-fluoropyridine, C_5F_{12} and NF_3.

The C_5F_{12} (dodecafluoropentane) is formed by cleavage of the ring (eliminating N) and fluorine replacement and addition to produce the saturated open chain. Substantially all of the C_5F_{12} formed from pyridine is of the normal, straight-chain type. A highly purified sample (obtained from another experiment in which pyridine was used) having a molecular weight value (determined from vapor density) of 288, in agreement with the formula weight of 288, and which was estimated from the freezing point range to be at least 99.5 mol per cent pure, was found to have the following physical properties:

Boiling point (at 760 mm.) _____°C__	27.9
Freezing point _____°C__	−125.65
Dielectric constant (at 20° C.) _____	1.68

Example VI

Use was made of an iron-cathode nickel-anode cell of the type shown in the drawing, operating at atmospheric pressure and a temperature of

about 0° C. The initial cell charge consisted of 1800 grams of anhydrous liquid hydrogen fluoride and 400 grams of di-n-butyl ether. Additional ether was added during the run to replenish that consumed. The cell voltage was in the range of 4 to 6 volts and produced a current density of about 20 amperes per square foot of anode surface.

At the end of 60 hours, 1355 grams of immiscible liquid was recovered from the bottom of the cell, and this was washed with potassium hydroxide solution to remove traces of HF, and was then fractionally distilled to yield a liquid fraction which was identified as relatively pure normal C_4F_9—O—C_4F_9 (di-n-nonafluorobutyl ether). This fraction had the following measured properties:

Boiling point (at 741 mm.) _____ °C__ 100.7
Refractive index (at 25° C.) _____ 1.261
Density (grams/cc. at 34° C.) _____ 1.689
Dielectric constant (at 20° C.) _____ 1.82
Molecular weight (from vapor density) __ 459

The formula weight of the pure compound is 454.

This compound has boiling point, refractive index, and density values which are slightly but appreciably lower than those of the normal C_8F_{18} fluorocarbon (mol. wt. 438) which have been found to be 104° C., 1.267, and 1.765, respectively, and may be compared with the values given above.

This butyl ether starting compound also produces a substantial yield of the C_4F_{10} fluorocarbon, and lesser yields of lower fluorocarbon compounds. Minor yields of fluorocarbon ethers having fewer than eight carbon atoms are also produced. Some material is also produced which is higher boiling than the C_4F_9—O—C_4F_9 product. There is some evidence for the formation C_8F_{18}, presumably formed by the combination of C_4F_9 radicals in the solution.

The fluorocarbon ethers are so stable that direct analytical determination of the oxygen content is extremely difficult. The formation of such compounds from hydrocarbon ether starting compounds has been further substantiated by homologous series runs down to and including the production of CF_3—O—CF_3 and

$$C_2F_5—O—C_2F_5$$
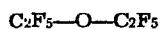
from dimethyl ether and diethyl ether, respectively. These products were found to have boiling points of minus 59° C. and plus 1° C., respectively, and the measured molecular weights (vapor density method) were the same as the formula weights. Their identification was further confirmed by mass spectrograph analyses which admit of no doubt since the mass numbers of the ionic fragments were measured with ample precision.

Having described various embodiments and examples of my novel process for purposes of illustration rather than limitation, what I claim is as follows:

1. A new and useful electrochemical process of making fluorine-containing carbon compounds from fluorinatable organic starting compounds, which comprises electrolyzing for a period of hours a current-conducting mixture of the organic starting material in liquid hydrogen fluoride free from water in more than a small proportion as herein described, at a temperature and pressure at which a liquid state is maintained and at a cell voltage which is insufficient to generate free fluorine under the existing conditions but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate, and recovering at least one fluorine-containing carbon compound product of the process.

2. A new and useful electrochemical process of making carbon compounds which have at least one fluorine atom bonded to a carbon atom in the molecule, which comprises electrolyzing for a period of hours a current-conducting mixture of liquid hydrogen fluoride free from water in more than a small proportion and an organic starting compound having at least one hydrogen atom bonded to a carbon atom in the molecule, at a temperature and pressure at which a liquid state is maintained and at a cell voltage which is insufficient to generate free fluorine under the existing conditions but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate, and recovering a carbon compound product of the process which has at least one fluorine atom bonded to a carbon atom in the molecule.

3. A new and useful electrochemical process of making carbon compounds which have at least one fluorine atom bonded to a carbon atom in the molecule, which comprises electrolyzing a current-conducting mixture of liquid hydrogen fluoride free from water in more than a small proportion and an organic starting compound having at least one hydrogen atom bonded to a carbon atom in the molecule, by passing direct current through the solution for a period of hours at an electrolyzing potential which is insufficient to generate free fluorine under the existing conditions but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate, the temperature and pressure being such as to maintain a liquid state, and recovering a carbon compound product of the process which has at least one fluorine atom bonded to a carbon atom in the molecule.

4. A process according to claim 3 wherein an oxygen-containing starting compound is employed which has at least one hydrogen atom attached to a carbon atom in the molecule.

5. A process according to claim 3 wherein a carboxylic acid starting compound is employed.

6. A process according to claim 3 wherein a nitrogen-containing starting compound is employed which has at least one hydrogen atom attached to a carbon atom in the molecule.

7. A process according to claim 3 wherein an amine starting compound is employed.

8. A process according to claim 3 wherein a hydrocarbon starting compound is employed.

9. A process according to claim 3 wherein an alkane starting compound is employed.

10. A new and useful electrochemical process of making fluorine-containing carbon compounds from fluorinatable hydrogen-containing organic starting compounds which are readily soluble in anhydrous liquid hydrogen fluoride to form electrolytically conducting solutions, which comprises electrolyzing in a nickel-anode cell a current-conducting solution of the organic starting material in anhydrous liquid hydrogen fluoride by passing direct current through the solution for a period of hours at an electrolyzing potential which is insufficient to generate free fluorine under the existing conditions but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate, the temperature and pressure being such

as to maintain a liquid state, and recovering at least one fluorine-containing carbon compound product of the process.

11. A process according to claim 10 wherein the temperature is maintained in the range of about minus 20° to plus 80° C., and the total cell potential does not exceed 8 volts.

12. A new and useful electrochemical process of making fluorine-containing carbon compounds from fluorinatable organic starting compounds, which comprises electrolyzing for a period of hours a current-conducting solution essentially consisting of liquid hydrogen fluoride containing a dissolved conductivity additive and also containing an admixed undissolved organic starting compound and which is free from water in more than a small proportion as herein described, at a temperature and pressure at which a liquid state is maintained and at an electrolyzing potential which is insufficient to generate free fluorine under the existing conditions but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate, and recovering at least one fluorine-containing carbon compound product of the process.

13. A process according to claim 12 wherein a soluble organic compound is employed as a conductivity additive.

14. A process according to claim 12 wherein a soluble oxygen-containing organic compound which contains at least one hydrogen atom bonded to a carbon atom in the molecule is employed as a conductivity additive.

15. A process according to claim 12 wherein a soluble monocarboxylic acid is employed as a conductivity additive.

16. A process according to claim 12 wherein a soluble nitrogen-containing organic compound which contains at least one hydrogen atom bonded to a carbon atom in the molecule is employed as a conductivity additive.

17. A process according to claim 12 wherein a soluble inorganic compound is employed as a conductivity additive.

18. A process according to claim 12 wherein a soluble fluoride salt is employed as a conductivity additive.

19. A new and useful electrochemical process for making fluorine-containing carbon compounds, which comprises electrolyzing in a nickel-anode cell a current-conducting solution essentially consisting of liquid hydrogen fluoride containing a dissolved conductivity additive and also containing an admixed and undissolved fluorinatable hydrogen-containing organic starting compound and which is free from water in more than a small proportion as herein described, by passing direct current through the solution for a period of hours at an electrolyzing potential which is insufficient to generate free fluorine under the existing conditions but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate, the temperature and pressure being such as to maintain a liquid state, and recovering at least one fluorine-containing carbon compound product of the process.

20. A process according to claim 19 wherein anhydrous liquid hydrogen fluoride, and a hydrocarbon starting compound, are employed.

JOSEPH H. SIMONS.

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