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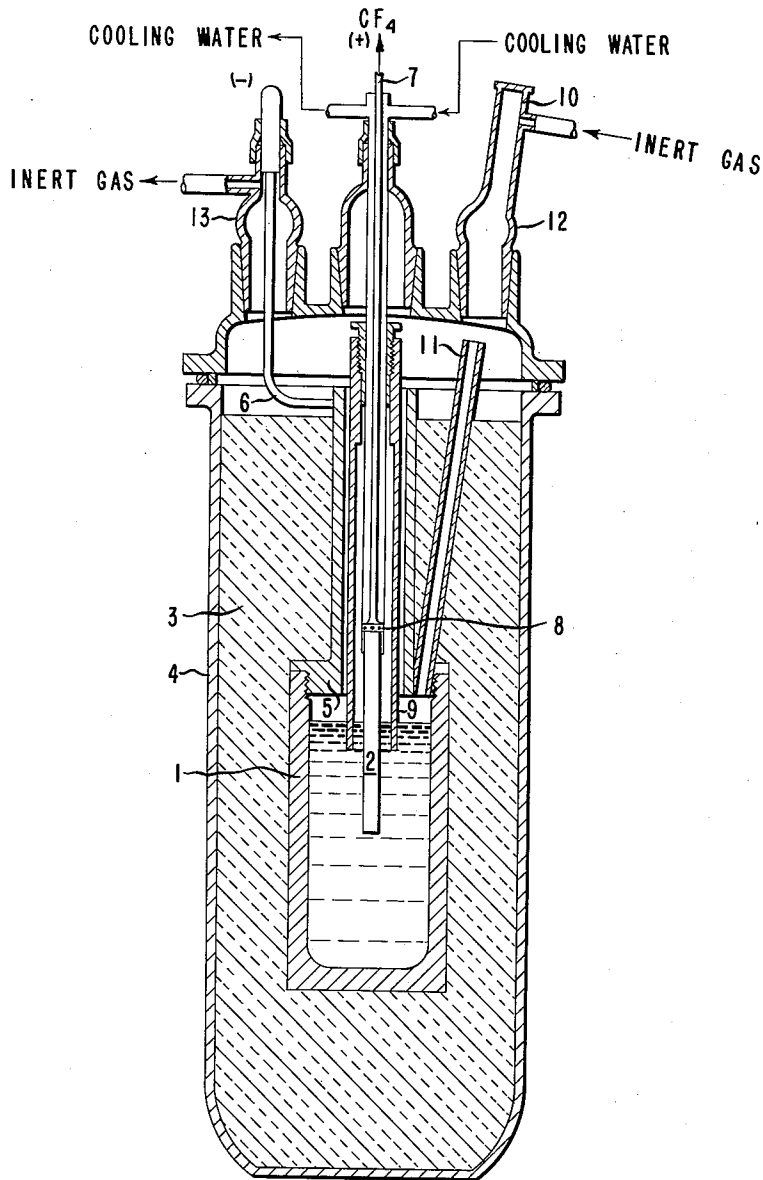
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PREPARATION OF CARBON TETRAFLUORIDE

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Fig. 1



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PREPARATION OF CARBON TETRAFLUORIDE
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This invention relates to a new process of preparing carbon tetrafluoride. More particularly, it relates to a process of preparing carbon tetrafluoride directly in a high state of purity. This application is a continuation-in-part of application Serial No. 522,101, filed July 14, 1955, now abandoned.

Carbon tetrafluoride is an important industrial chemical. Not only can it be used as such as refrigerant liquid, as dielectric material and as propellant in aerosols, but it is also the starting material in the synthesis of the highly valuable tetrafluoroethylene by the process described in U. S. Patent 2,709,192.

It was heretofore known that in the electrolysis of certain inorganic fluorides with a carbon anode, carbon tetrafluoride is one of the by-products formed at the anode. However, no electrolytic process has been described whereby carbon tetrafluoride of a very high degree of purity is prepared directly from the electrolysis, thus eliminating a costly purification operation.

It is the main object of the present invention to provide a process which will result in substantially pure carbon tetrafluoride.

The object of the present invention is accomplished by a process which comprises electrolyzing a molten electrolyte containing by weight at least 10% sodium fluoride, any other components being another alkali metal fluoride or alkaline earth fluoride or a mixture thereof, with a carbon-containing anode and a porous carbon crucible as cathode at a temperature of 1150-1650° C. and a cell voltage of 2 to 5 volts in the substantial absence of atmospheric oxygen. This process yields an anode gas which is substantially pure carbon tetrafluoride, i.e., above 95% and as high as 99% of the gas obtained from the anode is carbon tetrafluoride.

It is essential for the successful operation of this process that the temperature of the molten electrolyte be at least 1150° C. At lower temperatures, the carbon tetrafluoride is contaminated with other fluorocarbons. While the electrolysis temperature can be quite high, temperatures above 1650° C. are undesirable because of reduced current efficiency. The preferred temperature range is that from 1200 to 1400° C.

It is also essential that the cathode be porous to permit diffusion of the cathode products out of the electrolyte thereby preventing their accumulation and eventual shorting out of the cell. If allowed to remain in the electrolyte, the cathode products also react with the anode products thereby decreasing current efficiency.

The presence of more than small amounts of atmospheric oxygen is to be avoided, since this results in damage to the equipment and contamination of the product. Substantial absence of oxygen, e.g., air, can be insured by operating either at reduced pressure or in an atmosphere of inert, non-condensable gas, or by a combination of these methods. The inert gas, if employed, can be used as a carrier to facilitate the removal of the gaseous reaction product. By inert, non-condensable gas is meant a gas such as argon, helium or nitrogen which condenses appreciably below the boiling point (-128° C.) of carbon tetrafluoride and is therefore readily separable from it. It is also possible by suitable design of equipment to use the carbon tetrafluoride produced at the anode as a blanket to prevent access of air to the electrolyte, and this is a preferred method of operation.

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The voltage applied to the electrolyte melt must be in the range of 2 to 5 volts. At lower potentials, electrolysis does not proceed well. At potentials in excess of 5 volts, the carbon tetrafluoride is contaminated with undesirably large amounts of other products and current efficiency falls off sharply.

The electrolysis is normally carried out at atmospheric pressure. However, if desired, pressures lower than atmospheric, e.g., of the order of 300-600 mm. of mercury can be employed. Under certain circumstances, e.g., when temperatures in the maximum range are employed, superatmospheric pressures may be beneficial in preventing excessive loss of electrolyte by vaporization.

The metal fluorides suitable for use as components of the electrolyte are the alkali metal and alkaline earth metal fluorides, including for example lithium fluoride, sodium fluoride, potassium fluoride, magnesium fluoride and calcium fluoride. As stated above, it is necessary that the electrolytes contain at least 10% sodium fluoride. The preferred electrolytes are those whose vapor pressure at 1150° C. is less than about 100 mm. of mercury. Mixtures of calcium fluoride and sodium fluoride containing from 50 to 90% of calcium fluoride by weight are especially advantageous technically and economically. The electrolyte is, of course, used in a substantially anhydrous state.

FIGURE 1 shows in vertical cross section a suitable type of electrolytic cell. Briefly described, this apparatus consists of a cylindrical crucible 1, constructed of porous graphite which contains the electrolyte and functions as the cathode, and an axially-located graphite or amorphous carbon rod 2 which forms the anode. The sides of the carbon anode may be fluted to increase the current-carrying capacity. The cell is embedded in carbon black thermal insulation 3 inside a vacuum tight jacket 4 made of heat-resistant glass. The assembly is heated to the desired temperature by means of an induction furnace (not shown). Sifting of the carbon black insulation into the electrolyte is prevented by the graphite cover 5 threaded onto the crucible. Electrical contact with the crucible 1 (the cathode) is made by means of the copper conductor 6 clamped around the upper rim of the crucible cover. The other end of the conductor 6 leads to an external connection which is water-cooled to dissipate the heat. Electrical contact with the carbon anode is made through the double-walled copper tube 7, which has perforations 8 at the end holding the anode. This tube can be raised or lowered to position the anode, and it is water-cooled since it is exposed to high temperatures.

The gases which form at the carbon anode are collected within an amorphous carbon tube, or "skirt" 9, which surrounds the anode and dips for a short distance into the molten electrolyte to form a seal. Optionally, the skirt is perforated with fine holes to form a diaphragm between anode and cathode. This skirt is electrically insulated from the anode but sealed at its upper end to the copper electrode holder 7, the seal being a cement consisting of equal weights of calcium fluoride and Portland cement. Anode gases which collect inside the skirt enter the hollow electrode holder through the perforations 8 and are conducted into traps cooled in liquid nitrogen (not shown) where they condense.

The temperature of the melt is determined with an optical pyrometer (not shown), the surface of the melt being viewed through a window of heat-resistant glass 10 and a hollow graphite tube 11 which traverses the carbon black insulation. A slow stream of helium or argon is bled into the pyrometer sight tube 12 to maintain an oxygen-free atmosphere within the apparatus, the inert gas leaving through the cathode lead-bearing outlet 13, which can be attached to a vacuum pump (not shown).

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The pressure within the cell itself can be reduced to any desired degree by means of a vacuum pump (not shown) attached through the liquid nitrogen traps to the lead-bearing outlet 13.

As will be obvious to those skilled in the art, various modifications can be made in the design of the apparatus provided the essential features enumerated above are preserved.

The electrolysis is normally carried out with a direct current of about 3 to 12 amperes and, as already stated, a potential of 2 to 5 volts. The usual procedure is to evacuate the entire system to about 0.2 mm. of mercury, then to fill it with an inert gas, e.g., helium or argon. A steady flow of the inert gas is maintained through the cell during the electrolysis. The gas, i.e., carbon tetrafluoride discharged at the carbon anode is led into a liquid nitrogen cold trap, where it condenses. At the close of the run, the apparatus is swept with inert gas to flush the residual anodic gas into the cold trap. The cold trap is then evacuated to remove the non-condensable gases, and the remaining condensate is transferred into a stainless steel gas cylinder.

The invention is illustrated in greater detail in the following examples.

Example I

Using the electrolytic cell with the porous cathode crucible described above (in this case, a perforated skirt 9 was employed), a mixture of calcium fluoride (67 parts by weight) and sodium fluoride (33 parts by weight) was electrolyzed at 1275–1340° C. at atmospheric pressure in an atmosphere of helium. A direct current of 8 amperes at 3.4–4.0 volts was used. The electrolysis was continued for 100 minutes. The anodic gas was found by mass spectrographic analysis to contain, on a molar basis, 98% carbon tetrafluoride, 0.2% carbon dioxide and 1.8% air. The current efficiency was calculated to be 44%.

In comparison, a substantial duplication of the same run, except that a current of 8 volts at 1 to 2.4 amperes was used, gave an anodic gas containing only 88.5% of carbon tetrafluoride. This gas also contained 0.4% of tetrafluoroethylene and 11.1% of various impurities, chiefly carbon disulfide, carbon dioxide, carbon oxysulfide and air. Moreover, the current efficiency was only 16%.

In further comparison, the electrolysis of a melt of the same composition but at a temperature of 935–1000° C., using a current of 3.5 volts and 1.3–3 amperes, gave an anodic gas containing only 85% carbon tetrafluoride, the remainder being chiefly hexafluoroethane.

Example II

Using the same apparatus, with an unperforated carbon skirt around the anode, pure sodium fluoride was electrolyzed at a melt temperature of 1280–1310° C. in an atmosphere of helium at ordinary pressure. A direct current of 3.5 volts at 10 amperes was passed through the electrolyte for 60 minutes. The anodic gas was found by mass spectrographic analysis to contain, on a molar basis, 98.8% carbon tetrafluoride, 0.1% carbon dioxide and 1.1% air.

Example III

The electrolytic cell used in Example I was modified by employing a perforated skirt closed at its lower end

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to form a diaphragm between the anode and porous carbon cathode. A mixture of calcium fluoride (67 parts by weight) and sodium fluoride (33 parts by weight) was electrolyzed at a melt temperature of 1290–1320° C., using a 3.3–3.9 volt direct current at 5 amperes, in an atmosphere of helium at ordinary pressure. The electrolysis was continued for 130 minutes. The anodic gas was found by infrared analysis to contain, on a molar basis, 99% carbon tetrafluoride and 1% silicon tetrafluoride. The current efficiency was calculated to be 42%.

Example IV

Using the same apparatus as in Example III, a mixture of calcium fluoride (90 parts by weight) and sodium fluoride (10 parts by weight) was electrolyzed with a 3.6–4.2 volt direct current at 10 amperes and at a temperature of 1600–1650° C. In this case, a reduced pressure of 400 mm. of mercury was maintained in the cell throughout the run, which lasted 60 minutes. The anodic gas was found by mass spectrographic analysis to contain 95.1% carbon tetrafluoride, 2.4% silicon tetrafluoride, 1.4% of various impurities (carbon disulfide, carbon dioxide, sulfur dioxide, carbon oxysulfide) and about 1% air.

This invention provides a method of producing directly from cheap and abundant materials, a product containing at least 95% of carbon tetrafluoride and in which the carbon tetrafluoride constitutes at least 99% of the fluorocarbons present. A product of this purity can be employed as such in practically any use involving carbon tetrafluoride, thus saving time-consuming and expensive fractionations.

I claim:

1. A process for the preparation of carbon tetrafluoride comprising electrolyzing a metal fluoride from the class consisting of alkali metal fluorides, alkaline earth metal fluorides and mixtures thereof, said metal fluoride containing at least 10% by weight of sodium fluoride, with a carbon containing anode, in the substantial absence of oxygen, in a porous carbon crucible cathode, at a temperature of 1150° C. to 1650° C., with a cell voltage of 2 to 5 volts, and recovering from said anode essentially pure carbon tetrafluoride.

2. The process of claim 1 wherein the fluoride electrolyzed is sodium fluoride.

3. The process of claim 1 wherein the fluoride electrolyzed is a mixture of calcium fluoride and sodium fluoride.

4. A process for the preparation of carbon tetrafluoride comprising electrolyzing sodium fluoride with a carbon-containing anode in a porous carbon crucible, said crucible being the cathode, in the substantial absence of oxygen, at a temperature of 1200° C. to 1400° C., with a cell voltage of 2 to 5 volts, and recovering essentially pure carbon tetrafluoride.

References Cited in the file of this patent

UNITED STATES PATENTS

785,961 Lyons et al. _____ Mar. 28, 1905
2,841,544 Radimer _____ July 1, 1958

FOREIGN PATENTS

896,641 Germany _____ Mar. 15, 1954

OTHER REFERENCES

Rimbach et al.: "Beryllium," published in 1932, pp. 58–64.