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PURIFICATION OF FLUORINE BY DISTILLATION

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ABSTRACT

A vacuum-jacketed metal still for purifying half-pound quantities of commercial fluorine is described. Operating characteristics of a prototype still and of the present still are reported. The distillate is analyzed by an improved mercury-titration method, and a middle fraction of 99.9 per cent or higher purity is collected. The impurities found in several cylinders of commercial fluorine by infrared and mass spectrographic analyses include nitrogen, oxygen, carbon dioxide, nitrogen trifluoride, hydrogen fluoride, carbon tetrafluoride, perfluoroethane, perfluoropropane, oxygendifluoride and argon.

INTRODUCTION

Recently, a high-precision rotating bomb calorimeter has been used in this laboratory for studying the heats of combustion of various metals in fluorine.^(1,2) Initial experiments with commercial fluorine of 98.5 to 99.5 per cent purity showed the measured heats to be significantly dependent upon the amounts of impurities present. Since the side products formed were mostly unknown, accurate thermal corrections could not be applied. A purer grade of fluorine was therefore considered essential for further calorimetric studies.

An attempt was made to prepare pure fluorine by thermal dissociation of chlorine trifluoride, a method described by Franck and Wicke.⁽³⁾ It was found that chlorine trifluoride could be readily dissociated into chlorine monofluoride and fluorine by passage through a nickel coil at 550°C and into a cold trap at liquid nitrogen temperature. The fluorine was passed through a second heated tube at 150 to 200°C to remove small amounts of the volatile chlorine monofluoride by recombination, and then was passed through another cold trap. However, the fluorine produced in several experiments contained 0.5 to 1.5 per cent impurities, which were probably chlorine monofluoride and oxygen from traces of chloryl fluoride.⁽⁴⁾ The method was not investigated further, since fractional distillation then appeared to be more promising.

A low-temperature still was built and tested with charges of commercial fluorine containing 0.5 to 2.5 per cent impurities. The least volatile components were easily removed, but careful fractionation was required to remove nitrogen and oxygen efficiently. Center fractions of 99.9 per cent fluorine were collected for the calorimetric experiments, and a second still, incorporating several improvements in design, was then built for permanent service. The mercury-titration method of analysis was adopted, since this has been greatly improved recently⁽⁵⁾ and is probably more sensitive than the cryoscopic method, which was used by Hu, White, and Johnston⁽⁶⁻⁸⁾ in earlier work with purified fluorine. In the following sections, the design of the stills, the operating characteristics, and the analytical procedures are described in detail.

PROTOTYPE STILL

The original fluorine still and its associated apparatus are shown in Figure 1. The fractionating column consisted of a $\frac{3}{8}$ -in. ID Monel tube, 46 in. long, filled to a height of 34 in. with $\frac{1}{8}$ -in. nickel Helipak. The welded Monel pot of 210-cc volume was heated by a 35-ohm resistance winding, and the space around the column and pot was evacuated by means of a diffusion pump. Copper-constantan thermocouples were attached to the still head, the top, middle, and bottom of the column, and the still pot.

A 10-in. length of the column above the packed section, serving as a reflux condenser, was cooled with liquid nitrogen. Originally, the entire chamber of the jacket was filled with liquid nitrogen to the bottom of valve V_1 in order to cool the inner wall, but this was found to be unnecessary. A partition was added to restrict the liquid nitrogen to the condenser region as shown. The condenser was kept full of liquid nitrogen by gravity feed from an external tank. Heat losses were reduced by a 2-in. layer of Styrofoam (not shown), which covered the entire still.

In charging the still, the pot was cooled initially by adding liquid nitrogen to the vacuum jacket through the standard-taper joint. The pot was evacuated, fluorine was condensed in slowly from a half-pound cylinder, and the residual fluorine in the cylinder and receiver (approx 300 mm Hg pressure) was pumped out. Liquid nitrogen was added to the condenser, the liquid nitrogen remaining in the jacket was blown out, and the jacket was evacuated with a forepump and diffusion pump.

The still was operated with 3 to 10 watts input to the heater, although the input could be raised to 55 watts before flooding occurred. The reflux ratio was controlled by the take-off rate through valve V_2 and the boil-up rate from the pot. With a take-off rate of 0.01 mole/min and an input of 10 watts, the reflux ratio was approximately 8, based upon a heat of vaporization of fluorine of 1564 cal/mole.⁽⁶⁾

Figure 1

Prototype Fluorine Still and
Associated Apparatus

Vapor samples were periodically analyzed to determine where to make the "cuts," and after removal of the nitrogen-rich forerun, a large center fraction containing 70 to 95 per cent of the initial charge was collected by condensation in the receiver at liquid nitrogen temperature. At the end of the distillation, valve V_4 was closed, the coolant was removed from the receiver, and the collected fluorine was allowed to expand back into the cylinder on warming to room temperature. The residue in the still pot, containing oxygen and other less volatile impurities, was then discarded to the vacuum pump.

With this still, initial quantities of 99.9 per cent fluorine were obtained by triple distillation of commercial fluorine. However, the cooling system was found to be inefficient, requiring large amounts of liquid nitrogen, and the column diameter proved too small to distill one-half pound of fluorine within a 12-hr period at high reflux ratios. The second still was designed to eliminate these deficiencies, and its operating characteristics, in most respects, are greatly superior to those of the original still.

IMPROVED FLUORINE STILL

The new still, which was built from detailed machine drawings No. CE-4302, is shown in Figure 2. Figure 3 is a photograph taken during assembly. In this still, the fractionating column and pot are suspended from the top plate, which is sealed to a flange of the surrounding brass cylinder by a neoprene "O" ring, so that the inner assembly can be lifted out for inspection and repairs. Electrical leads and coolant tubes are brought in through the top plate. The precooler consists of a jacket on the still pot, which can be filled with liquid nitrogen and emptied again without breaking the vacuum in the cylinder during operation of the still. The condenser at the top of the column is a similar jacket of smaller diameter.

The column of type 304 stainless steel has an internal diameter of $\frac{5}{8}$ in. and a height of 79 in.; it is filled to a height of 58 in. with $\frac{1}{8}$ -in. nickel Helipak. The 400-cc pot, also of type 304 stainless steel, is welded to the column. A 4.7-ohm heater is wound around the bottom of the pot, and copper-constantan thermocouples are attached to the head, the middle and bottom of the column, and the pot. A thin radiation shield is attached to the condenser and extends almost to the pot; it is unattached at the bottom but is aligned by a perforated Lucite disk.

The take-off lines leading from the still are made of $\frac{3}{8}$ -in OD, $\frac{1}{8}$ -in. ID, type 304 stainless steel. All valves, tees, crosses, and elbows are type 316 stainless steel fittings of the 30 VM series manufactured by Autoclave Engineers, Inc. Nickel rupture disks of approximately 1000-psi bursting strength, which lead to a surge tank (not shown), are attached to the receiver and the distillate line near the still head. The still and associated apparatus are all contained in a large vacuum-frame hood.

Figure 2
Improved Fluorine
Still

Figure 3
Photograph of the New
Still during Assembly

In the present mode of operation, the still is evacuated, the reflux head is cooled with liquid nitrogen, and fluorine is condensed in slowly from a cylinder, with the pressure in the head not exceeding 700 mm Hg. As the liquid fluorine cools the column and pot by evaporation, liquid nitrogen is also added to the lower jacket, until thermal equilibrium is reached. The initial flooding of the column, which wets the packing, is a recommended startup procedure. The heat leak to the pot through electrical leads and coolant lines provides a low boil-up rate, so no additional input to the 4.7-ohm heater is used at present.

The larger diameter and greater height of the fractionating column in the new still permit sharper separation of nitrogen and oxygen impurities from fluorine than before, without requiring very low take-off rates. It is estimated that the 58-in. packed section provides 30 or more theoretical plates, allowing for lower efficiency of the packing with fluorine than with hydrocarbons, for which the HETP is 1 to 2 cm.⁽⁹⁾ Usually it is possible to obtain a center fraction with 0.10 per cent or less impurities in a single distillation lasting 12 to 16 hours. In Table I, analyses and recoveries are shown for ten distillations completed thus far with the new still, using charges of commercial fluorine taken from two 6-lb cylinders.

Table I

DISTILLATION OF COMMERCIAL FLUORINE

Charge, gm	Initial Purity, per cent	Collected Fraction, gm	Purity of Collected Fraction, per cent
200	99.60	138	99.98
158	99.60	122	99.92
290	99.60	204	99.94
267	99.60	183	99.94
312	99.60	263	99.94
300	99.60	160	99.93
327	99.60	170	99.83
340	99.60	238	99.94
295	98.83	119	99.86
334	98.83	227	99.95

ANALYTICAL METHODS

The mercury-titration method of fluorine analysis used is similar to that used by Armstrong and associates at The National Bureau of Standards.^(5,25) A 100-cc Pyrex sampling bulb, containing 50 g of mercury, is attached to a small bellows valve by a Kovar seal and metal coupling. The bulb is evacuated, fluorine is added to prefluorinate the walls and the surface of the mercury, the bulb is evacuated a second time to 0.01 mm Hg or less, the fluorine to be analyzed is admitted, and the pressure is measured before the valve is closed. The pressure is either read to ± 1 mm on a Bourdon gauge, or the bulb is filled to approximately 800 mm pressure and vented to the atmosphere through the manifold, the atmospheric pressure being measured with a barometer. The bulb is then swirled to expose a fresh mercury surface to the fluorine; in 5 to 10 min, the fluorine is depleted, as indicated by a marked change in the appearance of the mercury. The bulb is cooled to room temperature, and the residual gas is expanded into an evacuated oil manometer. The pressure before expansion is then computed from the measured pressure and the expansion ratio, which is determined by calibration with air at various known pressures. The mole fraction of impurity in the fluorine is given by the residual pressure in the bulb divided by the initial pressure fluorine, both expressed in the same units.

The titration method allows distillate samples to be analyzed as fast as they are collected. The precision is ± 0.05 per cent, but the accuracy is somewhat lower and depends upon the nature of the impurities. The assumption is made that the impurities do not react with mercury, which appears to be true for most of the contaminants in commercial fluorine. Oxygen difluoride is an exception but is present only in very small amounts. A number of cylinders of fluorine used by the Chemistry and Chemical Engineering Divisions have been analyzed by this method, with the results shown in Table II. Recently, the method has also been modified by increasing the volume of the sample bulb to 1 liter and the amount of mercury to 500 gm. With the bulb evacuated by a diffusion pump, the precision of the method is then raised to ± 0.02 per cent.

The composition of the impurities in the commercial fluorine is partly known from mass spectrographic and infrared analyses. Residual gases in the analysis bulbs were examined with a Consolidated Electrodynamics Model 21-620 mass spectrometer and strong peaks were found for nitrogen, oxygen, and carbon dioxide, which together accounted for 80 to 95 per cent of the total pressure. Many low- and medium-intensity peaks were also found, which were attributed to singly- and multiply-charged ions of nitrogen trifluoride, hydrogen fluoride, argon, silicon tetrafluoride, water, and mercury. The silicon tetrafluoride and water were formed, at least in part, by the reaction of hydrogen fluoride with the Pyrex bulb. Although silicon tetrafluoride may have been present in the

fluorine initially, the water vapor was almost certainly introduced after the reaction with mercury. The residual gases from several large samples of distilled fluorine showed peaks for nitrogen, oxygen, and argon, but zero or trace amounts of the other impurities.

Table II
ANALYSES OF COMMERCIAL FLUORINE BY
TITRATION WITH MERCURY

$$I = \frac{100 \text{ ECP}_2}{P_1}$$

Cylinder Sampled	P ₁ , Initial Pressure (mm Hg)	P ₂ , Residual Pressure after Expansion (mm oil*)	E, Expansion Ratio	I, Per cent Impurity
A	742.8	156.1	1.255	1.77
A	742.8	160.5	1.255	1.82
A	746.0	161.6	1.255	1.83
B	740.5	89.7	1.240	1.01
B	739.4	95.5	1.240	1.07
C	745.4	159.0	1.250	1.79
C	745.4	162.8	1.250	1.83
D	749	58.7	1.260	0.67
E	739.9	131.8	1.240	1.48
F	430	26.9	1.245	0.52
F	406	25.7	1.245	0.53
F	743.7	44.9	1.390	0.56
F	743.7	40.8	1.390	0.51
G	748.4	22.0	1.370	0.27
H	747.0	89.0	1.420	1.14
I	400	19.4	1.235	0.40
J	300	49.8	1.051	1.17

*Octoil S; C = conversion factor to mm Hg at 25° = 0.0672

Infrared analyses were made with a Beckman IR-4 spectrophotometer, using a sodium chloride prism. Gas samples were contained in a nickel cell, 80 mm long, with windows of either silver chloride, barium fluoride, or fluorinated polyethylene.^(4,10) With impure fluorine in the cell at pressures of 420 to 770 mm Hg, prominent bands of carbon tetrafluoride (1283 cm⁻¹) and hydrogen fluoride (3960 cm⁻¹) were seen.

Higher partial pressures of impurities were obtained by condensing 0.1 to 0.2 mole of fluorine in a metal trap cooled with liquid nitrogen, pumping off the fluorine, warming the trap to room temperature, and expanding the collected vapors into the cell. At total pressures of 40 to 300 mm Hg, a number of additional bands were then observed, which were attributed to perfluoroethane, perfluoropropane, nitrogen trifluoride, carbon dioxide, and oxygen difluoride. Table III lists the observed frequencies and those reported in the literature for the strongest bands. Some of the expected bands were obscured by bands of other compounds in the mixtures. The spectra were examined for evidence of silicon tetrafluoride⁽¹¹⁾ and carbonyl fluoride,⁽¹²⁾ but peaks of these compounds, if present, were masked by peaks of carbon tetrafluoride and nitrogen trifluoride. In fluorine from one cylinder, bands at 818, 826, 887, 947, and 993 cm^{-1} were attributed to a mixture of sulfur hexafluoride⁽¹³⁾ and disulfur decafluoride,⁽¹⁴⁾ although the 826- cm^{-1} band overlapped a band of oxygen difluoride.

Table III

IDENTIFICATION OF IMPURITIES BY INFRARED ABSORPTION

Compound	Literature Reference	Strongest Bands (cm^{-1})	Observed Bands (cm^{-1})	Compound	Literature Reference	Strongest Bands (cm^{-1})	Observed Bands (cm^{-1})
HF	(15)	3961.64	3960	C_3F_8	(19)	726.2	-
OF_2	(16)	826	826			731.0	-
		929	930			735.3	-
CF_4	(17)	632	633			1006	1008
		1283	1283			1155	1155
		1538	1540			1210	1212
		2187	2185			1264	-
		2556	2560			1350	1345
C_2F_6	(18)	707.3	706	NF_3	(20)	907	910
		714.03	714			1031	1030
		720.2	-			1809	-
		1110	1110			1929	1925
		1116.9	1117	CO_2	(21)	667	665
		1125	1124			2349	2355
		1250.5	-				

RELATIVE VOLATILITIES OF IMPURITIES

The boiling points of fluorine and the major impurities are given in Table IV. The boiling points indicate that nitrogen should appear in the forerun during distillation, and that oxygen, argon, and all other impurities should remain behind in the pot. Since the reflux condenser of the still is maintained at -196°C by the coolant, the pressure in the head varies as the composition changes. From published vapor pressure equations of fluorine,⁽²²⁾ nitrogen,⁽²³⁾ oxygen,⁽²³⁾ and argon,⁽²⁴⁾ the vapor pressures at -196° are computed to be 297, 760, 160, and 198 mm Hg, respectively. If it is assumed that the solution of liquid fluorine and impurities obeys Raoult's Law, the relative volatilities of nitrogen-to-fluorine, fluorine-to-oxygen, and fluorine-to-argon are 2.56, 1.86, and 1.50, respectively. Argon is seen to be the most difficult component to separate, but fortunately it is present in much smaller amounts than oxygen or nitrogen, so its removal is relatively unimportant.

Table IV

BOILING POINTS OF FLUORINE AND IMPURITIES

Substance	Boiling Point ($^{\circ}\text{C}$)
HF	19.7
C_3F_8	- 38
C_2F_6	- 78
CO_2	- 78.2 (sublimes)
CF_4	-127.7
NF_3	-129.0
OF_2	-144.8
O_2	-183.0
Ar	-185.6
F_2	-188.2
N_2	-195.8

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