THE PREPARATION OF DISULPHUR DECAFLUORIDE

THE DENSITY AND VISCOSITY OF DISULPHUR DECAFLUORIDE

and

THE PREPARATION AND HYDROLYSIS OF ALUMINIUM AND ZINC ARSENIDES

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THE PREPARATION OF DISULPHUR DECAFLUORIDE

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Ph.D.

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The preparation of S_2F_{10} by the fluorination of sulphur using solid and gaseous diluents gives yields of S_2F_{10} (based on sulphur) as high as 28%. The variation of the yields of the reaction products S_2F_{10} , SF_6 and lower fluorides, with changes in the ratios of solid and gaseous diluents has been studied at different temperatures.

The fluorination of sulphur smoke gives a yield of S_2F_{10} of 9% of the gaseous mixture of S_2F_{10} and SF_6 .

The density of liquid S_2F_{10} has been measured, and ranges from 2.06 gm./c.c. at 0°C. to 1.91 gm./c.c. at 45°C.

The coefficient of viscosity of liquid S_2F_{10} at 20°C. has been measured and was found to be 0.0089 $\stackrel{+}{-}$ 0.0003 C.G.S. units.

The yields of arsine from arsenic, by the production and hydrolysis of Al₃As₂ and Zn₃As₂ have been measured.

HISTORICAL

I The Electrolytic Production of Fluorine

The first successful production of fluorine electrolytically was carried out by H. Moissan (1). He electrolysed anhydrous hydrogen fluoride, to which potassium hydrogen fluoride had been added to render it conducting. A platinum U-tube was used as a container, the openings being closed with fluorite stoppers in which platinum-iridium electrodes were set. Later he found a copper container to be satisfactory, but platinum electrodes were necessary, copper electrodes being unsuitable due to the formation of a non-conducting film of copper fluoride. He cooled the container with chloromethane to prevent excessive loss of hydrogen fluoride due to the heat generated by the passage of the electrolytic current.

Argo, Mathers, Humiston, and Anderson (2) found the Moissan type of cell using platinum electrodes to be unsatisfactory, the platinum anodes being attacked even though the temperature of the cell was kept at -30 to -60°. They tried an Acheson graphite anode (98% graphite) in this electrolyte, but it swelled and disintegrated due to the action of the hydrofluoric acid. They found molten potassium acid fluoride (KHF₂) to be a satisfactory electrolyte, using a cylindrical copper container which served as cathode, and an Acheson graphite anode surrounded by a perforated copper diaphragm. The anode was insulated from the diaphragm by a gland packed with powdered fluorspar. They attempted to use a Dixon graphite crucible instead of a copper container, but it was rapidly attacked. One difficulty was the frothing of the electrolyte when it was nearly exhausted, the froth entering the fluorine outlet tube and freezing there, blocking the exit. They passed a current of 10 amperes through the cell and obtained a current efficiency of 70%. They recharged the electrolyte by dissolving it in commercial hydrofluoric acid, followed by reheating gradually to 225° and electrolysing for several hours at 2 to 3 amperes.

Meyer and Sandow (3) made a more complicated generator of the same type, using potassium acid fluoride mixed with sodium fluoride, or sodium acid fluoride, or lead fluoride, which lowered the melting point of the electrolyte to 220 - 225°. They removed hydrogen fluoride from the fluorine stream by U-tubes filled with sodium fluoride.

J. Simons (4) used a cell of the Argo and Mathers type, but found three difficulties: foaming of the electrolyte, the method of regenerating the electrolyte was laborious, and shorting of the anode to the diaphragm through the insulating gland. A long vertical delivery tube of large size was flamed occasionally to prevent the foam from freezing. He recharged the electrolyte by allowing it to cool in a copper container, breaking it up and pouring aqueous hydrofluoric acid over it, and heating until all was

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It was then electrolysed at 200 to 220°, until molten. all the water was removed. His generator would run continuously for 20 to 30 hours at a current of 10 to 15 amperes, producing fluorine at about 4 liters per hour. He found Portland cement to be a good insulating material. The fluorine stream was passed through dry sodium fluoride to remove hydrogen fluoride. Lebeau and Damiens (5) found iron and nickel to be suitable container and anode materials when the electrolyte had a concentration of hydrogen fluoride corresponding to KF.3HF, melting at 56°. A magnesium container was found to be quite satisfactory by Bancroft and Jones (6). They used the Portland cement seal recommended by Simons (4), and their generator could be used for 30 to 40 hours at 5 to 6 amperes before recharging of the electrolyte was necessary. It delivered 250 c.c. of fluorine per ampere hour, and the current efficiency was 30%. Schumb and Gamble (7) found a "Monel" metal container to be very satisfactory.

Dennis, Veeder and Rochow (8) constructed a Vtype generator without a diaphragm, made of heavy copper tubing. They used Acheson graphite rods, twice baked to remove impurities, set in bakelite cement insulation. Their electrolyte was silicon-free potassium acid fluoride, and they purified the fluorine by passing it through copper U-tubes filled with granular sodium fluoride, which completely removed the hydrogen fluoride. They found the current efficiency to increase with current, reaching 76% at 9.3 amperes.

Denbigh and Whytlaw-Gray (9), using a cell of the Argo and Mathers type, tried various cements for supporting the anode, and found Portland cement, bakelite, and plaster of paris unsatisfactory. They finally used a paste of calcium fluoride and waterglass, which sets to a hard mass. They used sodium fluoride in U-tubes to remove hydrogen fluoride, and a series of copper liquid air traps to remove carbon fluorides (except CF_4 which boils at -186.8°.). At 15 amperes current, the current efficiency was 80%.

The Argo-Mathers type of cell, which forms the basis for most of the above generators, seemed to be the most satisfactory type. However several important difficulties were found.

(1) Solution of the cathode or container material.
 Copper is slowly dissolved, but magnesium (6) and "Monel" metal (7) appear to be satisfactory.

(2) Foaming of the electrolyte, and consequent
plugging of the delivery tube has been noted (2,3,4,9).
Simons (4) and Denbigh and Whytlaw-Gray (9) found a large
delivery tube (1 inch diameter) to obviate this difficulty.

(3) <u>Failure of the insulation</u> to withstand fluorine and hydrogen fluoride. Portland cement (4), bakelite
(8) and a paste of fluorspar and waterglass (9) appear to be the most successful, although none of these is really satisfactory.

(4) A long preliminary electrolysis to remove

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water was necessary. Dennis et al. (8) and Denbigh and Whytlaw-Gray (9) found that drying the electrolyte at 120° for 48 hours removed most of the water without undue loss of hydrogen fluoride.

(5) <u>Regeneration of the electrolyte</u>. Argo et al. (2) attempted to bubble in anhydrous hydrogen fluoride under pressure, but found the reaction slow and wasteful. Fredenhagen and Cadenbach (10) found that the reaction went easily with little loss. The method of Argo et al. (2) and Simons (4) is rather unwieldy. Dennis et al. (8) considered it cheaper to use fresh electrolyte than to recharge the old.

(6) <u>Removal of hydrogen fluoride</u> from the fluorine stream. The method of sodium fluoride granules recommended by Meyer and Sandow (3) and Dennis et al. (8) seems to be the best.

(7) Formation of a non-conducting coat of silica on the anode. This layer can be removed by sandpaper. Dennis et al. (8) found commercial potassium acid fluoride to contain about 1% silicon; and silica is present in the graphite anode. They used silicon-free potassium acid fluoride and had no further trouble.

Nearly all of the successful methods for producing fluorine electrolytically used one of the potassium acid fluorides as the electrolyte. The freezing points of potassium fluoride and hydrogen fluoride mixtures with an acid mole fraction of 0.4646 to 1.000 were determined by G. H. Cady (11). He also measured the vapour pressure of hydrogen fluoride over the molten solution at different temperatures. This curve is shown in Figure 1.



Figure 1

The dotted lines show the vapour pressure of hydrogen fluoride, the lowest line corresponds to 5 cm. of mercury, the middle one 10 cm., and the upper one 25 cm. He recommended three regions above the curve where electrolysis can be carried out satisfactorily. These are the regions above the eutectics corresponding to KF.4HF, KF.2HF, and KF.HF. In these regions, the vapour pressure lies below 5 cm. over a wide range of concentration. This is necessary to keep the loss of hydrogen fluoride to a minimum, and to allow the maximum amount of hydrogen fluoride to be electrolysed before the electrolyte needs to be recharged.

These three regions are:

(1) At an acid mole fraction greater than 0.925, corresponding to KF.4HF. The temperature should be about -80°.

(2) At an acid mole fraction between 0.647 and 0.697, corresponding to KF.2HF. The temperature should be about 72° .

(3) At an acid mole fraction between 0.485 and 0.508, corresponding to KF.HF. The temperature should be about 240°.

Moissan's electrolyte (1) in reality belonged to the first region, being cooled by evaporating chloromethane whose boiling point is -23.7°. The second region was used

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by Lebeau and Damiens (5), but is not satisfactory because KF.2HF is very deliquescent (11). The third region is quite satisfactory except for the increased solution of the container at elevated temperatures.

Sodium acid fluoride decomposes below the melting point, so is not useful as an electrolyte. According to Ruff (12), when ammonium acid fluoride was used, the fluorine produced reacted with the fluoride to form nitrogen and hydrogen fluoride, so that no fluorine was evolved. Mathers and Stroup (13) attempted to find a low melting double fluoride which would make a satisfactory electrolyte either alone, or mixed with potassium acid fluoride. Thev prepared K2SnF6, K2TiF6, K2PbF6, K2TeF6, K2MF6 and K2SeF6 by fusing the corresponding dioxide with excess potassium acid fluoride, and reacting the melt with hydrofluoric acid. All these double fluorides had melting points higher than potassium bifluoride. They prepared KSbF6 and ammonium acid fluoride, both of which fumed and gave no fluorine when electrolysed. Lithium acid fluoride decomposed like sodium acid fluoride. A caesium acid fluoride was produced, either 2CsF. 3HF, or a mixture of CsF.HF and CsF. 2HF. Mixtures of these were prepared melting as low as 19°. Fluorine was obtained, using this as the electrolyte in a magnesium container with a graphite anode. In order to keep the electrolyte molten, as the electrolysis proceeded, it was

-8-

necessary to keep raising the temperature. When 100° was reached, the electrolyte was regenerated. They found that copper fluoride dissolved in caesium or potassium fluoride imparted a blue colouration to it when water was present, the normal colour being yellow.

A more complete discussion of fluorine production will be found in "A Literature Survey on the Preparation of Fluorine" by J. C. Arnell (McGill C.E.3).

II The Fluorides of Sulphur

H. Moissan and P. Lebeau (14) first prepared sulphur hexafluoride by burning sulphur in fluorine vapour. They found it to be a colourless, odourless, tasteless, incombustible gas, solidifying at -55° to a white crystalline mass. They also reported (15) that sulphur hexafluoride did not react with potassium hydroxide solution, and was decomposed by sodium only at the boiling point. Prideaux (16) gave -56° for the melting point, -62° for the boiling point (at 760 mm.) and 54° for the critical temperature. He also reported (17) that as the vapour pressure of the solid reached one atmosphere at 62°, the solid sublimed, showing no melting point.

Ruff (18) found evidence of the formation of another fluoride of sulphur when metallic fluorides were heated with sulphur. Disulphur difluoride (S_2F_2) was obtained by Centnerszwer and Strenck (19,20) by heating in

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vacuo a mixture of 1 gm. of silver fluoride and 4 gm. of sulphur. About 100 c.c. of gas was evolved, part of which decomposed. It was also obtained by heating mercurous fluoride and sulphur. Its melting point was reported as -105.5°, boiling point -99°, and the specific gravity at -100° as 1.5. Disulphur difluoride decomposed with heat, was absorbed by potassium hydroxide solution, and deposited sulphur in the presence of air or moisture.

Sulphur tetrafluoride (SF₄) was prepared by Fischer and Jaenckner (21) by heating to 120° in quartz, a mixture of cobaltic fluoride, fluorspar, and sulphur. Sulphur tetrafluoride was absorbed by potassium hydroxide solution.

Schumb and Gamble (7) measured the vapour pressure of solid and liquid sulphur hexafluoride up to three atmospheres, covering a temperature interval from -72° to -45° . The vapour pressure was found to be 760 mm. at -63.8° , and the density of the gas to be 6.093 gm./l. at 753.5 mm. and 20°. They reported the melting point of pure SF₆ as $-50.8 \stackrel{+}{=} 0.2^{\circ}$. Yost and Clausen (22) obtained various thermodynamic constants for sulphur hexafluoride: the heat of formation 262,000 cal., the heat of fusion 1,390 cal., the melting point -50.8° , and sublimation point -63.8° . Pearson and Robinson (23) measured the parachor of sulphur hexafluoride and suggested that two fluorine atoms are attached to the sulphur atom by covalent linkages, and the

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remaining four by semipolar singlet links. Pauling and Brockway (24) found from electron diffraction experiments that the fluorine atoms in sulphur hexafluoride are at the corners of a regular octahedron, and they suggest that the gas has an ionic structure. Watson, Ras, and Ramaswamy measured the dielectric constant and found the molecule to have no moment.

Disulphur decafluoride was first reported by Denbigh and Whytlaw-Gray (26). During the fractional sublimation of impure sulphur hexafluoride samples they found a liquid residue which did not react with potassium hydroxide solution. In a later paper (27) they gave the products of the reaction of fluorine and sulphur as:

(1) Sulphur hexafluoride,

(2) A volatile lower fluoride, possibly S_2F_2 ,

(3) A volatile liquid which could be vapourized by warming with the hand, and which was not absorbed by potassium hydroxide solution,

(4) A residual oil which was not vapourized by warming with the hand.

They identified the third material as disulphur decafluoride (S_2F_{10}) by the molecular weight (254) and found it to be a colourless, very volatile liquid at room temperature, whose vapour had an odour suggesting sulphur chloride or sulphur dioxide. The vapour was insoluble in and unattacked by water and by potassium hydroxide solution. They gave the boiling point as $29^{\circ} \stackrel{+}{=} 1^{\circ}$, the melting point $-92^{\circ} \stackrel{+}{=} 1^{\circ}$, the liquid density at 0° as 2.08 $\stackrel{\pm}{=}$ 0.03 gm./c.c., the surface tension as 13.9 dynes /cm. $\stackrel{+}{=} 3\%$, the Trouton constant as 23.0, and the parachor as 236. They found disulphur decafluoride did not react with metals at ordinary temperatures, but did react at high temperatures, and with silica and glass at red heat. It was decomposed by molten alkali giving potassium compounds of sulphur and fluorine.

EXPERIMENTAL

I The Fluorine Generators

(a) The first fluorine generator used by the writer was one designed by J. T. Hugill, R. Mungen and R. Harvey, based on the design of Denbigh and Whytlaw-Gray (9). This generator is shown in Figure 2. It consisted of two cylindrical compartments separated by a perforated copper diaphragm. The outer container was a cylinder $8\frac{1}{2}$ inches outside diameter and 15 inches deep made from $\frac{1}{4}$ " sheet copper rolled and welded. Into this was welded a bottom of the same material, "low-melt" welding rod being found perfectly satisfactory. An inlet tube was supplied in the side of this container, through which hydrogen fluoride was to be added, a perforated false bottom serving to diffuse the gas over the area of the bottom. This method of adding hydrogen fluoride to the electrolyte was found to be impractical, due to freezing of the electrolyte in the tube.

Figure 2

The First Fluorine Generator

A -	copper	container	and	cathode
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- B calcium fluoride-waterglass insulation
- D copper diaphragm
- G graphite anode
- H primary and secondary heaters
- I hydrogen fluoride inlet tube
- K asbestos insulation
- M perforated copper false bottom
- 0 fluorine outlet tube
- P stirrer and hydrogen outlet
- T thermocouple



The diaphragm was made from $\frac{1}{4}$ " copper tubing $4\frac{1}{2}$ inches outside diameter and 14 inches long, and had a welded bottom of the same material. Three rows of $\frac{1}{4}$ " holes were drilled around the bottom of the diaphragm to allow mixing of the electrolyte. The fluorine outlet was a $1\frac{1}{4}$ " diameter copper pipe welded at a 45° angle into a hole in the diaphragm near the top. On the top of the diaphragm was threaded a $\frac{1}{2}$ inch thick copper plate, with a corresponding bushing which screwed down tightly on the plate, and made gas-tight with a lead washer.

The graphite anode was l_{\pm}^{1} inches in diameter and 18 inches long, and was supplied by the Canadian National Carbon Co. This anode was wrapped with sheet mica for a short distance on each side of the bushing, and cemented in place with a calcium fluoride and waterglass cement as recommended by Denbigh and Whytlaw-Gray (9). To make this seal gas tight, a space was left at the top of the collar into which a ring of molten lead was poured, which was insulated from the anode by the mica sheet.

The top of the outer container was fitted with a lid, spun from 1/16 inch thick copper sheet which had a flanged hole in the center 5 inches in diameter, in which the diaphragm was supported, by "Insolute" cement. Two holes were made in this lid, one to allow the escape of hydrogen from the cathode chamber, the other to carry a length of 3/8 inch diameter copper tubing closed off at the

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bottom, which served as a thermocouple well. The stirrer shown in the figure was not used.

The thermocouple used at first was a single copper-constantan junction, the leads being connected directly to a milliammeter. Since the temperature of the room was fairly constant, no cold junction was used. A calibration curve was made and checked against a thermometer. Later, a copper-constantan thermocouple having four hot junctions and three cold junctions connected in series, was used, which gave greater scale deflection and increased accuracy. The three cold junctions were left exposed to the air, since the few degrees of variation in the temperature of the room caused only a negligible error. This thermocouple was calibrated against four standard points - boiling water, naphthalene, diphenylamine and sulphur.

Thermocouple Calibration Table

Material	Temperature	Millivolts
Vapour over boiling water	99 . 0°	3,5
Vapour over boiling naph- thalene	218.0°	9.0
Vapour over boiling diphenyl amine	302.0°	14.2
Vapour over boiling sulphur	444.5°	22.0

The generator was heated by two heaters of 16gauge Nichrome wire, each drawing about 10 amperes. The

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primary heater covered the bottom of the container and two-thirds of the way up the side, and the secondary heater extended from near the bottom to within three inches of the top. These windings were insulated from the container and from each other by two layers of asbestos paper, and were then covered to a depth of l_{Σ}^{1} inches with a paste of asbestos and water and thoroughly dried. In addition, as much as possible of the exposed metal part of the generator was insulated in this way. The primary or continuous heater circuit included an external resistance which could be switched in or out. Current for both heaters was supplied from the 110 volt A.C. lines.

For the D.C. electrolytic circuit, contact was made to the container through the side tube, and to the graphite anode by a copper clamp. An external resistance, consisting of three 600 watt heating coils in parallel, was used in series with the generator, an ammeter and the 110 volt D.C. lines. A slide-wire resistance was placed in series with one of these coils to allow for adjustments in the electrolytic current. An A.C. voltmeter was connected between anode and cathode. A voltage drop of about 10 volts was observed when a current of 10 amperes was passed. A diagram of the electric circuit is shown in Figure 3.



Figure 3

In operation, this generator had several bad faults. The "Insolute" cement insulation between the diaphragm and the container cover was attacked by hydrogen fluoride from the electrolyte, and fragments of it dropped into the electrolyte after a short time, contaminating the electrolyte with silica. Similarly the calcium fluoride and waterglass insulation between the anode and the diaphragm was attacked by hydrogen fluoride and fluorine. The simplest test for leakage of fluorine was obtained by directing a stream of gas from an unlighted hand torch at the suspected region, the gas being ignited when fluorine was present. The mica around the anode disintegrated after about 40 hours operation, allowing the lead ring to short circuit the anode and the diaphragm.

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(b) <u>The second generator</u>. With these considerations in mind, the writer redesigned the diaphragm and anode assembly. The most important modification was the removal of the zones of insulation to a situation where no contamination of the electrolyte could take place, and the removal from the insulating material of the mechanical strain involved in supporting the shield in one case, and the anode in the other.

This design is shown in Figure 4. The insulation was contained in two circular troughs, one resting on the top of the outer container, the other welded to the top of the diaphragm. An insulating washer made of transite board or of sheet mica was laid in the bottom of each trough, on which the flanges of the container cover and the diaphragm cover rested. The outer trough did not have to make a gas tight seal, and a layer of molten potassium acid fluoride poured over the washer formed a satisfactory protection. The trough at the top of the diaphragm had to be gas tight, so it was considerably deeper than the other (1 inch deep). The washer was placed in this trough, the trough filled with molten potassium acid fluoride, and the diaphragm cover quickly pressed into place. Thus an insulating seal was formed. The temperature of these troughs was not high enough to melt the fluoride, but was high enough to prevent any excess hydrogen fluoride absorbing and lowering the melting point. The troughs and covers were spun from 1/8 inch thick sheet copper.

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Figure 4

The Second Fluorine Generator

- A copper container and cathode
- B copper diaphrogm
- C graphite anode
- ${\tt D}$ threaded copper rod
- E primary heater
- F secondary heater
- G outer insulation trough
- H inner insulation trough

ł

- J fluorine outlet tube
- K diaphragm cover
- L container cover
- H hydrogen outlet
- \mathbb{N} molten $\mathbb{N}HF_2$ electrolyte
- 0 asbestos insulation
- P thermocouple well



The collar of the diaphragm cover was $2\frac{1}{2}$ inches in diameter and was threaded to take a copper rod which narrowed to 1 inch diameter below the threads. The anode, of 1 inch diameter silica-free graphite supplied by the Canadian National Carbon Co., was fastened to this rod by a copper clamp which was small enough so that the rod and anode could be unscrewed and removed without disturbing the insulating seal. This facilitated the changing of the anode. The anode projected to within $1\frac{1}{2}$ inches of the bottom of the diaphragm.

About 35 lb. of potassium acid fluoride was required for a charge, and when first melted contained waxy impurities which floated to the surface and were removed by skimming. The water in the electrolyte was removed by approximately one hour of electrolysis. Under normal conditions the level of the electrolyte was about two inches above the top row of holes in the diaphragm. The rate of production of the fluorine per hour was calculated, using the data from Run 77. The amount of fluorine reacted was calculated from the products.

Calculation:

Run required 2.5 hours at 10 amperes for complete reaction.

Weight of S_2F_{10} produced = 4.13 gm.

Weight of fluorine in this = $\frac{4.13 \times 190}{254}$ = 3.09 gm.

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Weight of SF_6 produced = 8.40 gm.

Weight of fluorine in this = $\frac{8.40 \times 114}{146}$ = 6.56 gm. Weight of SF₄ produced = $\frac{40.0 \times 5 \times 108}{32}$ = 6.60 gm. Weight of fluorine in this = $\frac{6.60 \times 76}{108}$ = 4.75 gm. Total weight of fluorine = 14.4 gm. Volume of this amount at S.T.P. = $\frac{14.4 \times 22.4}{19}$ = 17.0 l. Rate of production of fluorine per hour (at 10 amperes) =

$$\frac{17.0}{2.5} = 6.8 \text{ liters per hour}$$

Amount of electricity = 10 x 60 x 60 = 36,000 coulombs Theoretical volume of fluorine per hour = $\frac{36,000 \times 22.4}{96,500}$ =

8.4 liters per hour

Efficiency of generator = $\frac{6.8}{8.4} \times 100 = 81\%$

The fluorine which passed through the reaction tube without reacting was not included in this calculation, so the efficiency may be slightly higher. Several precautions were necessary if satisfactory operation of this generator was to be obtained.

(1) If too much back pressure was exerted on the fluorine, a leak occurred through the insulation at the top of the diaphragm. A leak of fluorine under these conditions was not undesirable, since if too much pressure was exerted, the electrolyte in the inner chamber was depressed below the level of the top row of holes in the diaphragm, permitting fluorine to escape into the hydrogenfilled cathode chamber, causing an explosion. This safetyvalve action almost eliminated the danger of explosions with this generator.

(2) If the temperature of the electrolyte was allowed to rise much above 250°, electrolysis stopped occasionally and the voltage across the cell rose from the usual 10 to 12 volts to 50 or 60 volts. This was due either to polarization or to lack of wetting of the graphite by the electrolyte. If the circuit was broken and closed again, electrolysis usually resumed normally. If the temperature was allowed to remain too high, the hydrogen fluoride vapour pressure over the electrolyte became too high, and there was a danger of hydrogen fluoride being absorbed by the insulation, rendering it more or less

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liquid with consequent shorting of the anode and the diaphragm. Under normal conditions, the insulation lasted for 200 hours of operation.

(3) As the hydrogen fluoride in the electrolyte became exhausted the solubility of copper salts was apparently reduced, since large spongy masses of what appeared to be cuprous oxide were observed in the electrolyte. These were removed, since they were a potential source of shorting in the cell.

Regeneration of the electrolyte was accomplished very simply by bubbling in anhydrous hydrogen fluoride from a cylinder fitted with a long copper delivery tube reaching nearly to the bottom of the electrolyte. It was found that almost complete absorption took place, if the electrolyte was stirred, and the temperature lowered progressively. This is in agreement with the observations of Fredenhagen and Cadenbach (10) and in disagreement with those of Argo et al. (2). Probably Argo did not lower the temperature of the electrolyte sufficiently. It was found necessary to add hydrogen fluoride to the electrolyte after about 150 hours of operation.

This generator was found to be quite satisfactory provided the precautions mentioned above were observed.

(c) The third generator.

A third generator, of larger size, was designed by Dr. R. L. McIntosh, J. Davis and the writer and is shown in Figure 5.

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Figure 5

The Third Fluorine Generator



This generator is in operation at the C. W. Laboratories, National Research Council, Ottawa. No data as to its performance are available yet. A considerably larger flow of fluorine, perhaps 30 liters an hour, should be available from this generator due to increased anode and cathode surface area. The container is 12 inches in diameter and $18\frac{1}{2}$ inches deep, of $\frac{1}{4}$ inch thick copper sheet, rolled and welded. The diaphragm is 8 inches in diameter of 1/8 inch copper pipe. The anode consists of six $\frac{1}{2}$ inch diameter graphite rods clamped about the circumference of a 2 inch diameter copper pipe, which itself does not project into the electrolyte. This pipe is welded to a circular copper plate $\frac{1}{4}$ inch thick which is bolted down on the diaphragm cover, thus permitting the removal of the anode assembly without disturbing the insulation. The insulation is of the same type as in the second generator, and all other constructional details are the same.

A similar generator, but made of iron, has been constructed. A copper lining is to be made, to fit inside the outer container, and the diaphragm is to be plated with copper. Thus all parts of the generator in contact with the electrolyte will be of copper, reducing materially the amount of copper required in the manufacture.

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II The Fluorine Purification Train

Due to a shortage of sodium fluoride, the hydrogen fluoride and carbon fluorides (except CF4) were removed by passing the fluorine stream through a series of ice and liquid air traps. The first trap was made of copper and was attached to the outlet of the generator with 3/8 inch copper tubing and couplings. This trap was kept immersed in cracked ice. The fluorine was then passed through four glass traps immersed in liquid air. The first liquid air trap had a large diameter side tube, into which projected a 3/8 inch copper tubing lead from the copper trap, for a distance of three inches or more. The opening was then sealed with picene. The glass of this first trap was gradually attacked by hydrogen fluoride, and required replacement about once a month. If the liquid air was too fresh, a little fluorine was condensed, but liquid oxygen gave no condensation, the boiling point of fluorine being -187°, that of liquid oxygen being -183°. Carbon tetrafluoride (b.p. -186.8°) remained in the fluorine stream.

III The Nitrogen Diluting System

When it became necessary to dilute the fluorine stream with nitrogen, a glass mixing chamber was added to the end of the series of traps. This chamber was a glass trap, with two inlets in the side and a central outlet.

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The nitrogen was passed from a cylinder through two calcium chloride towers, then through two sulphuric acid bubblers. A Venturi-type flowmeter calibrated from 0 to 1400 cc./min. was used to measure the rate of flow.

The calibration of this flowmeter is given below.

c.c. per minute	height (cm.)
0	0
100	1.8
210	3.5
500	8.7
720	14.1
865	18.2
1000	22.7
1150	28.3
1260	33.0
1425	39.4

IV The Reaction Tubes

The first reaction tube was made from $\frac{1}{4}$ inch thick copper tubing with copper plugs threaded in the ends. In the inlet plug were two 3/8 inch copper tubing leads, projecting $\frac{1}{2}$ inch into the tube, and in the outlet plug was one 3/8 inch copper tubing lead projecting $\frac{1}{2}$ inch inside and 5 inches outside the plug.
The two later reaction tubes are shown in Figure 6, and were of the same type as the first, but they were provided with a third smaller copper tube in the inlet plug, which projected to within an inch of the outlet plug, serving as a thermocouple well. One of these reaction tubes was 1 inch inside diameter and 24 inches long, the other 1 7/8 inches inside diameter and 36 inches long. Both these tubes were later provided with cooling jackets when the effect of temperature was studied. The cooling jacket contained ethylene glycol and water solution (approximately 50%) which was circulated through the jacket and a copper cooling coil by means of an automobile water pump. The cooling coil was immersed in dry-ice-acetone mixtures or in water, depending on the temperature required. A thermometer -100° to +50° was mounted in the cooling jacket.

Temperatures at different points in the reaction tube were taken by a copper-constantan thermocouple which could be slid along inside the thermocouple well. The other junction of the thermocouple was immersed in water in a small dewar flask, the room temperature being fairly constant.

Figure 6

The Reaction Tube

- A inlet tube
- B outlet tube
- C thermocouple well
- D cooling jacket thermometer
- E expansion bulb for cooling mixture
- F ethylene glycol and water mixture
- G rubber stoppers



·V The Trapping System

The products from the reaction tubes were collected in glass traps, cooled in liquid air. When no nitrogen dilution was used, one trap was sufficient to collect the products. When nitrogen dilution was used, more traps were required in order to prevent some of the products from being blown through without condensing. The traps were made of glass tubing, the body of the trap being 30 mm, in diameter, the arms 15 mm, in diameter. This large size was necessary to prevent the tubes from being plugged by solidified product. The number and arrangement of the traps depended upon the rate of flow of nitrogen; for low nitrogen rates (100 c.c./min. or less) four traps arranged in two parallel pairs were used. For higher rates (up to 900 c.c./min.) as many as four pairs in series were required in order to catch all the product. The traps were connected with double wall rubber tubing, which was found to be attacked only slowly by fluorine, provided that air and moisture were excluded. The efficiency of this trapping system was found to be quite good, as the sulphur mass balances were close to 100%.

VI The Analysing System and its Manipulation

The final form of the analysing system is shown in Figure 7. It consisted of a purification train of bubblers, a trap (F), and a manifold to which were connected

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a density bulb (G), a five liter volume (S), four small bulbs (H,J,K,L) and the mercury manometer (M). The volume of the density bulb was 520.75 c.c. and the other volumes of the system were calibrated by expansion of air from it. At first, there was no side tube on the large flask (S), and only three bubblers (B,C,E) were used. B contained sodium hydroxide solution, C water, and E concentrated sulphuric acid.

The method of analysis was as follows: The liquid air traps containing the products from the reaction were connected in series with heavy rubber tubing; one end of the series was connected to B, the other end provided with a short rubber tube and pinch clamp. The stopcock between E and F was closed, the trap F thoroughly pumped down, and a dewar flask of liquid air placed around it. Then the stopcock between E and F was opened, allowing air, dried by the sulphuric acid, to fill the trap F at atmospheric pressure. Then the stopcock between F and the manifold was opened to the atmosphere, the open end of the line of traps containing the product was closed, and several of the traps were drawn partway out of the dewar flasks.

In this way the products were forced slowly through the bubbler train by their own vapour pressure. Fairly good control of the speed was obtained by raising or lowering the traps in the dewars. The lower fluorides S_2F_2 and SF_4 , if present, reacted with the sodium hydroxide solution; the SF_6 and S_2F_{10} passed through unreacted and were dried by the

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Figure 7

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The Analysing System



sulphuric acid and condensed in the trap F. For complete absorption of the lower fluorides, it was necessary to keep the bubbling rate at about one bubble per second. The last traces of product were removed from the line of traps by drawing air slowly through them and the bubbler train by means of the pump.

The stopcock between E and F was then closed and trap F, the manifold and the small bulbs were thoroughly pumped free of air. The dewar flask was then removed from the trap F and placed on the small bulb L, the sample transferred to this bulb by condensation, and again pumped free of air. The sample bulb G and the large 5 liter bulb S were evacuated, the stopcock on G was closed, and the sample was expanded into the large bulb S. When the pressure had reached a maximum, the stopcock on G was opened, and left open until the manometer became steady. The temperature of the gas was read by a thermometer graduated to 0.1°. Pressures were read by a cathetometer mounted in front of the manometer.

The stopcock on G was then closed, and all the gas in the manometer was condensed back into the small bulb L. Then the tap between G and the manometer was closed, and the density bulb removed. The ground glass joint was carefully cleaned with acetone, dried, and the density bulb weighed. The weight of the evacuated density bulb was checked from time to time. All the gas was then condensed back into the small bulb to await fractionation.

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From the molecular weight of the gas, the relative proportions of SF_6 and S_2F_{10} were calculated, and since the pressure, temperature and volume of the gas were known, the weights of SF_6 and S_2F_{10} present were calculated. A typical calculation is given in the section on results.

It was found later, when a higher percentage of S_2F_{10} was obtained, that this method of filling the density bulb gave values of the molecular weight which were too The error increased with larger amounts of S2F10. large. Due to its lower boiling point, the SF6 vapourized first, and the last of the sample to vapourize was almost pure S₂F₁₀. Mixing was slow because of the large molecular weight of S_2F_{10} , so that when vapourization was complete, the small bulb L, the manifold, and the lower part of the large bulb were filled with a gas having too large a proportion of S_2F_{10} . Thus when the density bulb was opened, the gas which filled it was too rich in S_2F_{10} , giving too large molecular weights. In fact, with samples having a large percentage of S_2F_{10} , the gas which filled the density bulb was practically pure S₂F₁₀. This error was discovered by noticing the different molecular weights obtained from the same sample by different workers, who allowed varying lengths of time for "thorough" mixing to be attained, before filling the density bulb.

This error was eliminated by providing a small side tube on the large bulb S. The procedure for determining molecular weights was then as follows: When the sample had

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been condensed in the small bulb L, the bulb L, manifold, and large bulb S were carefully pumped out. The dewar was then removed from L and placed around the side tube on the bulb S and the sample was all condensed in it. When condensation was complete (sometimes taking two to three hours) the system was pumped again to remove impurities, the stopcock on S was closed, and the dewar removed, allowing the sample to expand and fill S. Two or three hours were allowed for mixing to take place before the density bulb was filled. This method gave consistent molecular weights.

About the same time it became desirable to obtain an overall mass balance on sulphur, and a modification in the bubbling train was made, resulting in what is shown in Figure 7. The first two bubblers (A and B) contained sodium hydroxide solution, the next one water (C). The fourth one (D) was empty and served as a trap to prevent sulphuric acid from sucking back into the water and causing an error in the sulphur balance. In the first bubbler A, an ordinary delivery tube was found to plug easily, due to the formation of slowly soluble material (sodium fluoride or sodium sulphite) in the end of the delivery tube. The first bubbler A was then modified to the form shown in Figure 8, and consisted of an enlarged delivery tube and a glass rod which was used to dislodge the solid whenever there was danger of plugging. The glass rod was held on the top of the delivery tube by a piece of rubber pressure tubing which made a gas tight seal, and still allowed flexibility of movement.

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Figure 8

VII The Sulphur Smoke Generator and Reaction Tube

The reaction of fluorine with a sulphur smoke was carried out. The smoke generator and reaction tube are shown in Figure 9. The generator consisted of a 500 c.c. florence flask (A) which acted as a boiler, a nitrogen inlet tube (B) and a smoke outlet tube (C) surrounded by a water condenser (D). The nitrogen inlet tube was curved to face upwards into a small flange on the end of the outlet tube. A stream of 300 c.c./min. of dried nitrogen was passed through and the sulphur was boiled. The vapour rose up to the top of the boiler and was blown into the outlet tube. The condenser served to prevent sulphur vapour from being carried through as such by the nitrogen stream. Most of the smoke formed at the point where the cold current of nitrogen struck the hot sulphur vapour between the inlet and outlet tubes. The smoke was led over into the reaction vessel (E), entering it through one of the side arms. Fluorine was admitted in the other side tube and reaction took place right at the end of the sulphur inlet tube. The products were carried out through the central tube and collected in two glass traps immersed in liquid air.





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PROCEDURES, RESULTS AND DISCUSSIONS

I Preliminary Work on the Fluorination of Sulphur

At the time the writer was assigned to this problem, considerable work had already been done at McGill University by R. Mungen and J. T. Hugill on the preparation of disulphur decafluoride. It had been established that disulphur decafluoride was very toxic and had many properties which made it interesting from a military viewpoint. Various method of preparation were studied by these workers, in order to find a satisfactory synthesis.

By reacting fluorine with sulphur in a copper tube, they obtained a yield of S_2F_{10} of about 1% by volume of the total S₂F₁₀ and SF₆ gaseous mixture. They found that carrying out the reaction at the temperature of dry-ice and acetone mixtures gave no increase in yield. They diluted fluorine with nitrogen, using flows of 165 c.c. of fluorine per minute and 100 c.c. of nitrogen per minute, and obtained no increase in yield. Various sulphur compounds were reacted with fluorine. Sulphur chloride gave SF_6 but no S_2F_{10} , and carbon disulphide produced an explosion. An attempt was made to react S_2F_2 with fluorine, but it proved to be too unstable. The pyrolysis of SF6 in a quartz tube, and the reaction of hydrogen and SF6 using platinized asbestos as a catalyst, were carried out, but the products were sulphur and hydrogen fluoride. With nickel pellets and with activated alumina as catalysts, the same results were obtained and no intermediate

compounds were formed. They found that sulphur and SF₆ would not react at 230°C. under pressures up to 100 atmospheres. Sulphur, diluted with CuO, CuS, and CuF₂ up to equal weights of sulphur and diluent, was fluorinated with no increase in yield.

At first the writer worked in collaboration with Mr. R. Mungen and an attempt was made to repeat the preparation of S_2F_{10} from pure sulphur and fluorine. The procedure was as follows: The reaction tube (of the first type) was filled about three-quarters full with sulphur and connected directly to the generator without any fluorine purification train. The outlet of the reaction tube was connected with rubber tubing to a glass trap immersed in liquid air. The generator was then turned on and fluorine was passed into the reaction tube until a sample sufficiently large for analysis had collected in the glass trap. The sample was then analyzed by the first method (page 33) and the molecular weight obtained. Many runs were made in this way, and the molecular weights varied from 87 to 135, showing the presence of a product with low molecular weight, probably CF4 or SiF4 mixed with the SF6. At this point Mr. Mungen was assigned to another problem and the writer continued alone.

During these runs the generator gave much trouble, and the second design (Figure 4) was developed. It operated very well, but the same low molecular weights were obtained. A suggestion was made by Mr. Mungen that the sulphur might have absorbed water due to the humid weather prevailing at

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that time. A run was made using sulphur which had been dried at $105^{\circ}C$. and a sample having a molecular weight of 146, and containing about 1.8% S₂F₁₀ (by weight of the gaseous mixture) was obtained. The S₂F₁₀and SF₆ were separated by distillation, S₂F₁₀ having a vapour pressure of 1.4 mm. in a dry-ice-acetone mixture.

At this time it was communicated to the writer that Alexander, working at the C.W. Laboratories of the National Research Council in Ottawa, had found that the fluorination of sulphur which had been mixed with sodium acid fluoride gave a higher yield of S_2F_{10} than did pure sulphur. Schneider, working at the same place, used NaF, NaHF₂, KHF₂, KF.3HF, CuF₂, and cryolite as solid diluents in various proportions. The results were not consistent, but he found the yield of S_2F_{10} to be increased by NaHF₂, KHF₂, KF.3HF, and cryolite, but not by NaF or CuF₂. The average high yields reported were 12% by volume or 20% by weight of the gaseous mixtures of S_2F_{10} and SF_6 .

At about the same time, Burg, at the University of Southern California, found that using fluorine which was diluted with ten times its volume of nitrogen, gave 10%yields of S_2F_{10} based on sulphur. He used 5 liters of fluorine per hour, 50 liters of nitrogen per hour, and a reaction tube of copper one inch in diameter and 30 inches long, cooled by an air blast.

A yield of 4.0% of S_2F_{10} by weight (of the gaseous mixture of S_2F_{10} and SF_6) was obtained by Mr. L. Siminovitch

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and the writer, using a mixture of 75 gm. of potassium acid fluoride and 5 gm. of sulphur, both previously dried. A mixture of the same proportions of potassium fluoride and sulphur gave a yield of 10% of S_2F_{10} , as did sodium fluoride and sulphur.

The fluorine purification train was then built and the hydrogen fluoride was removed from the fluorine during all succeeding runs. A run was made diluting both the fluorine and the sulphur. The reaction charge was an intimate mixture of 75 gm. of dry potassium fluoride and 5 gm. of dry sulphur. A flow of about 130 c.c. per minute of fluorine was diluted with 300 c.c. per minute of nitrogen, and a yield of 24% of S_2F_{10} by weight of the gaseous mixture was obtained.

II Fluorination of Sulphur Smoke

Since higher yields of S_2F_{10} were obtained by diluting the fluorine and the sulphur, and since the decomposition temperature of S_2F_{10} was known to be low (200°), it appeared that the effect of these dilutions was to lower the temperature at the point of reaction. The role of the solid diluent was considered to be that of a heat-conducting medium, although other workers considered the effect might be catalytic. It was thought that if the fluorination of a sulphur smoke gave a higher yield of S_2F_{10} , the catalysis theory would be disproven.

The apparatus described on page 36 and shown in

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Figure 9 was set up, and the following results obtained: Current through generator = 10 amps. Nitrogen flow rate = 300 c.c./min. Pressure of $SF_6-S_2F_{10}$ = 70.0 mm. Temperature = 296.4° K. Weight of gaseous mixture = 0.3073 gm. Molecular weight = $\frac{R}{V}$. $\frac{WT}{P}$ = 119.8* x $\frac{0.3073 \text{ x } 296.4}{70.0}$ = 156.

This is about 9% S₂F₁₀ by weight.

The reaction went very quietly and without the evolution of a great amount of heat, although when the concentration of sulphur smoke in the reaction tube became high, a faint blue luminescence was observed.

III The Fluorination of Sulphur with Solid and Gaseous Diluents

A series of runs was made by six men, J.C.Arnell, J. Davis, R. Mungen, L. Siminovitch, A. P. Stuart, and the writer, working in three groups of two in eight-hour shifts. This was done in order to supply the National Research Council with 60 gm. of pure S_2F_{10} for canister testing. It was decided that during this series the fluorination of sulphur would be carried out under conditions varying the nature and amount of the solid diluent, the amount of nitrogen dilution, and the temperature of the reaction tube. In order to obtain

* For convenience, the volume of the density bulb, the gas constant R=0.08207, and the atmosphere denominator 760 were compressed into the "bulb constant" 119.8.

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were mixed, and diluted to 1 liter with distilled water. A 50 c.c. aliquot portion of this was taken, neutralized with hydrochloric acid using phenolphthalein as an indicator, and 1 c.c. in excess added. Then 5 c.c. of concentrated (30%) hydrogen peroxide was added, the solution diluted to 300 c.c. and boiled for half an hour. Then 4 gm. of boric acid was added, and the sulphate precipitated by adding, dropwise, barium chloride solution (40 mg./c.c.). The sample was then allowed to digest over night and the barium sulphate was filtered out in a sintered glass crucible, washed with 10 c.c. of water and 10 c.c. of acetone, dried, and weighed.

In order to make sure that all the lower fluorides were absorbed by the potassium hydroxide, two hydroxide bubblers were used as shown in Figure 7. After a few runs had been made, the mass balance accounted for practically 100% of the sulphur. Average values were from 95% to 105%. This confirmed the observation that no colloidal sulphur was present and that the method of analysis would be satisfactory.

2. The first series of runs

(a) Procedure.

This series of runs was performed by the six men mentioned above. The four variables: amount of solid diluent, amount of gaseous diluent, temperature, and diameter of the reaction tube, were varied in an attempt to find the best conditions for the production of S_2F_{10} . For some of these runs, the reaction tube was cooled, at first using an ice and water

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container around the reaction tube, later using the cooling system shown in Figure 6. The nitrogen rate was varied from 0 to 500 in units of 100 c.c./min. It was decided to use sodium fluoride as the solid diluent since it gave as good yields as any other diluent used up to that time, and was much easier to dry and more finely divided than potassium fluoride, permitting more intimate mixing with the sulphur.

The charge was made by weighing out exactly 5 gm. of dry sulphur and placing it in a mortar with the desired amount of dry sodium fluoride. This mixture was thoroughly ground in the mortar and transferred to the reaction tube, being distributed as evenly as possible along the length of the tube. The charged tube was then weighed, the ends screwed on, and one of the inlet tubes attached to the end of the fluorine purification train by means of a short piece of rubber tubing. The other inlet tube was closed off, and was not used in this work. The outlet tube was closed off and was not in this work. The outlet tube was blown through for a few minutes to remove the air. A schematic diagram of the apparatus is shown in Figure 10.

The generator was then turned on, the current set at 10 amperes, and the nitrogen rate adjusted to the desired value. The time was recorded. The temperature at four positions evenly spaced along the length of the reaction tube was taken every half-hour by means of the thermocouple in order to follow the progress of the reaction. Fluorine was

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passed into the reaction tube until the temperature at the outlet end of the tube had fallen to room temperature or to the temperature of the cooling jacket. Occasionally the trapping system plugged due to solidification of the product in the upper part of the trap. This was removed by withdrawing the plugged trap partially from the dewar flask to allow the product to melt.



Figure 10

A - copper trap

B - picene seal

C - four glass liquid air traps

D - mixing chamber

E - reaction tube

F - cooling coil

G - water pump

H - expansion chamber

J - glass liquid air traps

When the reaction was complete, the generator was turned off, and nitrogen was blown through the system for one hour, while the reaction tube was heated to 50°. This temperature was well above the boiling points of the products, and well below their decomposition points, so that the nitrogen removed any product which had condensed in the reaction tube. This flow also removed the fluorine from the traps. The reaction tube was then weighed to obtain the weight of sulphur which had reacted. The products were passed through the bubbler train and the contents of the bubblers analyzed as described on page 43ff. and the volume and molecular weight of the S_2F_{10} - SF_6 mixture found as described on page 34.

(b) Results of the First Series.

The first 27 runs were rejected because of the incorrect molecular weights obtained by the first method (page 33). From Run 28 on, the new method (page 34) was used, and all the runs are listed in Table I except those which were unreliable due to generator trouble or to low mass balances. Some runs with low mass balances are listed because they contain other information of interest. The temperatures listed in the "Temperature of Run" column are those at which the cooling liquid was maintained during the run. Where no temperature is given, the reaction tube was not cooled, but left exposed to the air.

TAB]	Ε	Ι

Generator current = 10 amperes

Run No.	N2 c.c./min.	Size	Used gm.	Diluent NaF gm. Cu	Te gm. of	mp. Run	% S as S ₂ F10	% S S]	5 as ⁷ 6	% S as Lower Fluorides	Total <u>% S</u>
28	300	1	4.65	50		-	18.2	34	1.2	51.6	94.0
29	300	l	4.27	40		-	26.2	32	8.8	55.0	114.0
30	300	1	4.51	75		-	21.5	30	0.0	45.8	97.3
31	400	1	4.81	75		-	20.0	20	0.8	59.5	100.3
38	300	1	4.69	75		-	15.2	23	3.7	61.1	100.0
39	200	l	4.72	75		-	12.3	28	3.0	50.7	91.0
40	100	1	4.95	75		-	12.6	35	5.8	44.3	92.7
41	0	l	4.84	75		-	5.03	58	3.2	29.3	92.5
42	0	1	5.00	75		0°	3.50	33	3.2	25.3	6 2.0
43	100	l	5.00	75		0 °	15.7	18	3.3	61.8	95.8
44	200	l	4.90	75		0 °.	9.65	1:	3.4	70.0	93.1
45	300	, 1	4.95	75		0 °	17.5	11	1.1	63.1	91.7
48	400	l	4.68	75			15.5	2	5 .5	57.5	98.5
49	400	1	4.83	75		0°	17.2	10	6.0	67 .3	100.5
50	300	l	4.97	75		0 °	24.1	18	3.2	55 . 3	97.6
51	500	l	4.90	75		0 °.	14.5	1:	5.1	67.8	97 .4
52	500	1	4.34	75		_ /	16.7	2	5.0	53.3	95.0
54	200	1	4.81	75		0°	20.3	24	1.9	50.4	95.6
55	400	1	4.99	75		0 °.	18.8	18	3.1	64.7	101.6
56	200	1	5.00	75		-	19.9	38	5.1	49.5	104.4
57	200+10SF6	1	4.86	75		-	10.7	29	9.2	55,9	95.8
58	100	l	4.80	20	1	2°	9.38	67	7.7	23.0	100.1
61	100	l	4.60	20	-2	0 °	22.7	3.	1.5	34.5	88.7
62	100	l	5.00	20	-3	0 °.	18.2	3'	7.3	49.4	104.9
63	100	1	5.00	20	-2	0°	21.7	20	5.6	47.9	96.2
64	100	l	5.21	20	-1	0°	18.9	2'	7.0	51.2	97.1
65	100	l	5.05	20		0 °.	18.9	48	3.9	29.0	96.8
66	100	1	5.02	20	-2	5°	22.6	ç	9.45	63.4	95.5
67	100	1,	4.37	70	-1	0°	26.8	20	3.4	50 .0	103.2
68	100	1-7/8	5.05	70	-1	0°	22.5	2	5.7	53.5	101.7
69	100	1-7/8	4.88	20	-1	0°.	22.6	20	0.1	53,5	96.2
70	100	1-7/8	4.90	20	-1	5°	25.1	10	6.0	42.3	83.4
71	100	1-7/8	5.00	70	-1	٥°	28.6	2	3.9	48.5	101.0
72	100	1-7/8	4.81	20	-1	0°	25.2	2	2.0	53 1	100 3

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A typical set of data of this series is given below.

<u>Run 50</u> Charge - 75 gm. NaF and 5 gm. sulphur Nitrogen rate - 300 c.c./min. Reaction tube used - 1 inch diameter Temperature of run - 0° Weight of sulphur used (by difference) - 4.97 gm. Time started - 1:15 am.

			Position	L
Time	1.	2.	3.	4.
1:30	·ll°	8°	6°	2°
2:00	8°	10°	6°	З°
2:30	7°	9°	13°	7°
3:00	4°	8°	20°	15°
3:30	3°	3°	17°	18°
4:00	0 °	0°	4°	10°
4:30	0 °	0°	0°	0 °

Time stopped - 4:45 a.m.

Analysis of products:

Pressure of gaseous mixture	144.9 mm.
Temperature of gaseous mixture	297.6° K.
Weight of gaseous mixture	0.7693 gm.
Molecular weight of gaseous mixture	$e = \frac{119.8 \times 297.6 \times 0.7693}{144.9}$
	= 189.2

This corresponds to 40.0% of S_2F_{10} by weight

Weight of S_2F_{10} produced = $\frac{144.9 \times 40.0 \times 6.00 \times 254}{760 \times 100 \times 0.082 \times 297.6} = 4.76 \text{ gm}$. Yield of S_2F_{10} (on sulphur) = $\frac{4.76 \times 64 \times 100}{4.97 \times 254} = 24.1\%$ Weight of SF_6 produced = $\frac{144.9 \times 60.0 \times 6.00 \times 146}{760 \times 100 \times 0.082 \times 297.6} = 4.11 \text{ gm}$. Yield of SF_6 (on sulphur) = $\frac{4.11 \times 32 \times 100}{4.97 \times 146} = 18.2\%$ Weight of barium sulphate precipitate = 1.0025 gm. Yield of lower fluorides (on sulphur) = $\frac{1.0025 \times 20 \times 32}{4.97 \times 233} = 55.4\%$ Sulphur accounted for: 24.1% 18.2 55.497.7%

(c) Discussion of the first series

The results of this series are inconsistent in places, but they show several important facts:

(1) The need for more accurate control of the variables.

(2) An increase in the yield of S_2F_{10} is found with increased nitrogen dilution. At the same time the yield of SF_6 decreased and the lower fluorides increased. The results were not consistent enough to plot, but the trend was indicated. The largest change in the yields occurred between 0 and 100 c.c./min. of nitrogen, and the effect diminished with increased nitrogen flow, becoming slight at 500 c.c./min.

(3) The effect of cooling the reaction tube to 0° was mainly to increase the production of lower fluorides and

lower that of SF_6 . A slight increase in yield of S_2F_{10} was noticed. Lowering the temperature still further increased this effect slightly.

(4) The effect of using a larger diameter reaction tube was to increase the yield of S_2F_{10} at the expense of the SF₆. Not much change in the amount of lower fluorides was evident.

(5) Powdered copper was a better solid diluent, volume for volume, than sodium fluoride, and gave yields of S_2F_{10} 4 to 5% higher.

Occasionally during the first part of the run, when a little product had collected in the traps, a yellow ring which appeared to be sulphur was observed around the inside of the first trap or pair of traps just above the solidified product. This ring disappeared toward the end of the run. The possibility that this ring was caused by sulphur dust blown from the reaction tube was unlikely, because of its position on the side of the tube, and because no sulphur was observed in the connecting tubing. This ring formed evidence for the possible production of S_2F_2 in the reaction, as will be discussed later.

Run 57 was carried out in the usual way, except that 10 c.c. per minute of SF_6 were mixed with the 200 c.c. per minute of nitrogen to dilute the fluorine stream. The SF_6 was obtained from previous runs and was contained in a pressure bomb. The amount of SF_6 used was subtracted from the amount present in the products of reaction. An increased amount of lower fluorides and a decreased amount of S_2F_{10} and SF_6 were obtained.

3. The second series of runs

This series was carried out by L. Siminovitch and the writer, and the experimental error was reduced by several changes in procedure, as well as by more uniform technique.

(a) Procedure.

The method used in Series I of obtaining the amount of sulphur which reacted was inaccurate. It was decided to carry out the reaction until all of the sulphur had been fluorinated. To insure this, fluorine was allowed to flow for onehalf hour after it had reached sufficient concentration at the outlet of the last trap to ignite a gas burner. At the end of the half hour, the generator was turned off, and nitrogen blown through as before. A more satisfactory method of filling the reaction tube was developed. The charge was placed evenly in a metal trough which was inserted into the reaction tube, inverted, and removed. This insured an even distribution of charge throughout the tube, and prevented the development of "hot-spots" due to a local concentration of charge. When starting the run, the generator was turned on, and the reaction tube disconnected until the full flow of fluorine was reached, when the generator was disconnected temporarily, the reaction tube connected, and the generator turned on again. This procedure insured that the initial concentration of fluorine was

correct. To obtain the yields based on current, the time was taken when the reaction tube was connected, and when the fluorine reached full flow at the outlet.

(b) Results of the second series.

The results of this series are given in Table II. A typical set of data is given below:

Run 78

Charge - 75 gm. NaF and 5 gm. sulphur Nitrogen rate - 300 c.c./min. Reaction tube used - 1 inch diameter Temperature of run - 0° Generator current - 10 amperes Sulphur used - 5.00 gm. Time started - 3:45 p.m. Time fluorine detected - 5:45 p.m. Time fluorine shut off - 6:40 p.m. Time for run - 140 minutes Temperatures:

			Posi [.]	tion
Time	l.	2.	3.	<u> 4 </u>
4:00	10°	20 °	6°	0°
4:30	6°	12°	8°	6°
5:00	0°	6°	12°	6°
5:30	0 °	0 °	10°	16°
6:00	0 °	0°	2°	6°
6:30	0°	0 °	0°	0°

Pressure of gaseous mixture - 173.0 mm. Temperature of gaseous mixture - 295.4° K. Weight of gaseous mixture - 0.8947 gm.

Molecular weight of gaseous mixture =

= 183.1

This corresponds to 34.3% of S_2F_{10} by weight

Weight of S_2F_{10} produced (as before) = 4.93 gm. Yield of S_2F_{10} (on sulphur) = 24.8% Weight of SF_6 produced = 5.42 gm. Yield of SF_6 (on sulphur) = 23.8% Weight of barium sulphate precipitate = 0.9760 gm. Yield of lower fluorides (on sulphur) = 53.6% Sulphur accounted for: 24.8% 23.8

102.2%

Yield of S2F10 based on current:

Amount of electricity - 10 x 60 x 140 = 84,000 coulombs. If the generator were 100% efficient and all the fluorine reacted to form S_2F_{10} , the theoretical amount of S_2F_{10} produced would be: $\frac{84,000 \times 19 \times 254}{96,500 \times 190} = 22.1 \text{ gm.}$ Actual amount produced = 4.93 gm. Yield of S_2F_{10} (on current) = $\frac{4.93 \times 100}{22.1} = 22.3\%$

TABLE II

Generator current = 10 amperes Reaction tube = 1 inch diameter Sulphur used = 5.00 gm.

Run	N2 c.c./min	Diluent NaF gm Cu gm	Temp.	% S as	% S as SFc	% S as Lower Fluorides	Total %S	% S ₂ F ₁₀ on current
1.0.	0.0.7	Har Bur Oa Bur		-2-10	0			
76	100	75	0°	14.7	53.8	35.2	103.0	11.6
77	200	75	0 °.	20.8	36.8	40.0	97.6	16.9
78	300	75	0 °	24.8	23.8	53.6	102.2	22.2
79	400	75	0 ° .	23.4	22.7	51.8	97.9	21.0
80		Run spoil	.ed					
81	100	75	-10°	19.4	53.2	37.4	110.0	
82	100	75	-20 °	14.9	47.8	41.4	104.1	12.5
83	0	75	0 °.	5.65	67.9	27.4	101.0	4.4
84	500	75	0 °	18.1	12.7	68.5	99.3	12.6
85	100	75	-30 °	18.1	42.6	46.7	107.4	15.1
86		Run spoil	.ed ·		·			
87		Run spoil	ed					
88	100	240	0°	18.0	28.5	39.8	86.3	
8 9	100	75	-10°	20.1	46.5	39.8	106.4	15.8
90	100	75	+20 °	18.1	51.2	34.8	104.1	13.7
91	600	75	0 °	23.4	14.9	69.8	109.2	
92	100	75	-20°	17.5	39.8	43.9	101.2	
93	700	75	0 °.	18.8	10.7	69.4	98.9	
94	100	0	0 °.	4.47	61.6	33.7	99.8	
95	600	75	0 °,	17.5	12.1	70.5	100.1	
96	800	75	0 °.	20.8	10.4	73.5	104.7	
97	900	75	0 °.	10.4	12.8	72.0	95.2	
98		Run spoil	.ed			x		
99		Run spoil	ed					
100	100	75	-10°	10.7	29.3	58 .9	98 .9	
101	100	75	10°	8.92	45.2	52.7	106.8	
102	100	75	30 °	10.9	53.7	40.0	104.6	

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TABLE II (continued)

Run	N2	Diluent	Temp.	% S as	% S es	% S as Lower	Total	% S ₂ F ₁₀
No.	c.c./min.	NaF gm. Cu gm.	of Run	S ₂ F10	SF6	Fluorides	%S	on current
103	100	75	20°	11.6	36.7	57.2	105.5	
104	100	75	10°	13.2	40.2	51.8	105.2	
105	100	75	-20°	13.7	48.8	36.8	99.3	
106	100	75	-10°	10.9	40.1	55.0	106.0	

.

(1) The effect of gaseous diluent.

In the first part of this series, including the runs up to Run 97, the effect of increasing the nitrogen dilution was studied. The results confirmed the trends shown by Series I, but were much more consistent. The most consistent of these results (from Runs 76, 77, 78, 79, 83, 84, 93, 95 and 96) were plotted and are shown in Figure 11. With increasing flow rates of nitrogen, the yield of lower fluorides increased, that of SF_6 decreased, and that of S_2F_{10} increased up to a rate of 300 to 400 c.c. per minute and then decreased. The second increase of S₂F₁₀, at about 600 to 700 c.c. per minute, has not been confirmed. Runs 95, 93, and 96 showed this increase, and Run 97 did not. The dotted line in the graph indicates the possible trend of the yield of S_2F_{10} if the result of Run 97 is correct, and Runs 95,93 and 96 incorrect. Great difficulty was encountered in making runs with such a high flow of nitrogen on account of the large back pressure produced in the liquid air traps. A new type of trap with lower resistance is being used by L. Siminovitch and C. Bishinsky, and may eliminate this difficulty.

(2) The effect of temperature.

The effect of changing the temperature of the reaction tube was not as marked as that of the nitrogen dilution, and the deviations between individual runs were much greater. The most reliable data for the effect of temperature are collected in Table III.

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Figure 11

The Effect of Witrogen Dilution

on the Yield of S_2F_{10}

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TABLE III

	Gene Read Sulj Char Nitr	erator cur ction tube phur used rge rogen flow	rrent = 10 = 1 = 5 = 75 = 100	amperes inch diame .00 gm. gm. NaF ar c.c./min.	eter 1d 5 gm. sulphu	r
Run NO.	Temp.of Run	% S as S ₂ F10	% S as SF ₆	% S as SF4	Total S	
102	30°	10.9	53.7	40.0	104.6	
90 103	20 ° 20 °	18.1 11.6	51.2 36.7	34.8 57.2	104.1 105.5	
104	10°	13.2	40.2	51.8	105.2	
43 76	0 ° 0 °,	15.7 14.7	- 53.8	- 35 . 2	103.0	
81 89	-10° -10°	19.4 20.1	53.2 46.5	37.4 39.8	110.0 106.4	
92 82	-20° -20°	17.5 14.9	39.8 47.8	43.9 41.4	101.2 104.0	
85	-30°	18.1	42.6	46.7	107.4	

As can be seen from these data, a slightly greater yield of S_2F_{10} was obtained at lower temperatures, but any change in the amounts of SF_6 and lower fluorides (SF₄) was masked by the deviations between runs. These results show clearly the need for more accurate control of the variables. One possible source of error here was the difficulty of placing the charge evenly in the reaction tube, since any irregularities resulted in the local temperature of the reaction being too high or too low. Another source of error was the variation in the rate of production of fluorine by the generator at different times, which was indicated by the

unusually long time taken for the reaction to be completed on some occasions. The preponderance of mass balances exceeding 100% will be noticed in this table. This was found particularly in the last runs. Although the reason for this is not known, it is believed that the error lies in the analysis of the lower fluorides, and not in the estimation of the gaseous mixture. Thus the yields of S_2F_{10} given are not likely to be in error.

(3) The effect of solid diluents.

The effect of diluting the sulphur with sodium fluoride and with copper powder was quite marked.

The most reliable results are collected in Table IV.

TABLE IV

		Generator Reaction Sulphur us Nitrogen Temperatus reaction	current = tube = sed = flow = re of n tube =	= 10 ampe: = 1 inch = 5.00 gr =100 c.c., 0°	res diameter n. /min.	
Run <u>No .</u>	Dilu Naf gn	ient 1. Cu gm.	% S as S ₂ F ₁₀	% S as SF ₆	% S as SF4	Total S
94	0		4.47	61.6	33.7	99.8
65	20		18.9	48.9	29.0	96.8
76	75		14.7	53.8	35.2	103.0
67*		70	26.8	26.4	50.0	103.2
88		240	18.0	28.5	39.8	86.3

With increasing amount of diluent, the yield of S_2F_{10} increased rapidly, reached a maximum and decreased. The yields of SF_6 and lower fluorides (SF4) decreased with

the amount of diluent and then increased. The best mixture for the production of S_2F_{10} is apparently with an amount of sodium fluoride between 20 and 75 gm. to 5 gm. of sulphur. Although Run 67 was made at -10° instead of 0° it is included here, because of the small effect of 10° difference in temperature on the yield, as is seen above. The amounts of copper powder used were calculated from the relative densities of copper and sodium fluoride, in order to give the same volume of diluent. Volume for volume, copper powder was a better diluent for production of S_2F_{10} .

IV General Discussion

The best conditions for the production of S_2F_{10} found in this work were those of Run 71, where the $l_2^{\frac{1}{2}}$ inch diameter reaction tube at a temperature of -10° was used. Copper powder was the diluent, and a nitrogen flow of 100 c.c. per minute was employed. This gave a yield of 28% of S_2F_{10} based on sulphur. The highest yield, based on current, obtained was that of Run 78, a yield of S_2F_{10} of 22.2% being obtained. The yields based on current are lower than those based on sulphur due to the fact that the generator was only about 80% efficient, and also to the fact that a considerable amount of fluorine was blown through the reaction tube without reacting, particularly near the end of the run. The yields of S_2F_{10} based on reacted fluorine were much higher. This calculation was made on Run 71:
Weight of S_2F_{10} produced = 5.69 gm. Weight of F₂ in this = $\frac{5.69 \times 190}{254}$ = 4.25 gm. Weight of SF₆ produced = 5.44 gm. Weight of F₂ in this = $\frac{5.44 \times 114}{146}$ = 4.25 gm. % SF₄ = 48.5 so weight of SF₄ = $\frac{48.5 \times 5}{100}$ = 2.42 gm. Weight of F₂ in this = $\frac{2.42 \times 76}{108}$ = 1.70 gm. Total weight of fluorine which reacted = 10.20 gm. Then yield of S₂F₁₀ = $\frac{4.25 \times 100}{10.20}$ = 41.6%

Calculations on other runs showed values of from 30% to 40% of S_2F_{10} based on reacted fluorine. Obviously, if the ratio of products formed for similar time intervals during a run is the same, yields approaching this could be obtained by using a much longer reaction tube, or by stopping the reaction and recharging before the sulphur was used up.

Since it was found by Laidler (National Research Council, Ottawa) that S_2F_{10} decomposes at temperatures as low as 160°, it is quite possible that an S_2F_{10} molecule may be broken down by the heat of reaction shortly after it is formed. The sulphur fluorides in order of increasing stability are S_2F_2 , SF_4 , S_2F_{10} and SF_6 . This is also the order of increasing fluorine content per sulphur atom. The effect of a high temperature of reaction would be to favour the decomposition of S_2F_2 , SF_4 and S_2F_{10} , thus increasing the production of SF_6 . This condition exists when undiluted fluorine is

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reacted with undiluted sulphur, as in the preliminary work described. In these reactions the heat generated was enough to melt the sulphur and to render the outside of the reaction tube quite hot to the hand (60° or 70°). This meant a high local temperature at the point of reaction, with consequent decomposition of S_2F_2 , SF_4 , and S_2F_{10} to form SF_6 . The experimental results confirmed this, only about 1% of S_2F_{10} being obtained, along with little lower fluorides, and a large amount of SF_6 .

With undiluted sulphur the effect on the local reaction temperature of cooling the reaction tube would be slight, since the heat generated by the reaction is large, and the conduction of sulphur poor. On the other hand, when the sulphur is distributed throughout an inert mass with fairly good heat-conducting properties, cooling the reaction tube might materially lower the local reaction temperature. This was borne out by the experimental results. With no diluent and no cooling of the reaction tube, the yield of S_2F_{10} was about 1%. Cooling the tube to 0° raised the yield to 4.47% and adding sodium fluoride diluent and cooling to 0° raised it further to 5.65% (Runs 83 and 94). The effect of copper powder as a diluent should be correspondingly greater, due to the better heat conduction of copper. This was confirmed by the high yields obtained when copper powder was used.

It was suggested by various workers that the effect of the solid diluent was mainly catalytic, since the diluents

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used by Schneider and others were mainly crystalline fluorides which all had the same type of ionic lattice. They found other diluents which did not have this structure did not give good yields of S_2F_{10} . These discrepancies in the effect on the yield of various diluents were found to disappear more or less completely on closer examination. In effect, there are too many substances which increase the yield, with as widely differing physical and chemical properties as sodium fluoride and copper powder, for the catalytic theory to be retained.

The effect of temperature on the production of $S_{2}F_{10}$ is in general confirmed by the effect of nitrogen dilu-The local reaction temperature may be lowered by the tion. presence of nitrogen, and certainly the temperatures measured in the reaction tube were lower with high rates of nitrogen flow. The same amount of heat is generated per minute in the reaction tube whether or not the nitrogen is passing through with the fluorine, since the rate of fluorine is the same. The cooling effect must then be due to the absorption of the heat by the nitrogen. This suggests the use of a gas with higher specific heat and more degrees of freedom than nitrogen as a gaseous diluent. The main effect of the nitrogen stream is probably that of removing the lower fluorides and S_2F_{10} from the point of reaction to cooler regions before they have time to decompose. This is borne out by the increase in the yield of lower fluorides and S_2F_{10} , and the decrease in the yield of SF₆ found with increasing nitrogen flow up to 300 or 400 c.c. per minute.

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The consequent decrease in the amount of S_2F_{10} produced with nitrogen flow rates between 400 and 600 c.c. per minute can be explained if the possibility of the fluorination of the lower fluorides S_2F_2 and SF_4 to S_2F_{10} is admitted. The higher the flow rate, the shorter is the time that the lower fluorides would be in contact with the fluorine before they are condensed in the traps, and the shorter the time for the equilibrium to be displaced toward S_2F_{10} .

If all the S_2F_{10} were formed directly from sulphur, the yield of S_2F_{10} would increase with increasing nitrogen dilution and become constant, without decreasing. Thus the existence of two sets of equilibria can be postulated. The first set could exist at the point of reaction and involve the production of S_2F_2 , SF_4 , and S_2F_{10} and their pyrolysis to form SF_6 . The second equilibrium could exist in the cooler part of the reaction tube and involve the fluorination of S_2F_2 and SF_4 to S_2F_{10} and finally to SF_6 .

The higher yields of S_2F_{10} with the larger diameter reaction tube also confirm the possibility of the second equilibrium. With the same flow rate of nitrogen, a lower space velocity existed in the larger tube, and a longer time was required to remove the lower fluorides from the action of the fluorine. A longer time was also required to remove the lower fluorides and S_2F_{10} from the point of reaction. Since the yield was higher, the first effect must predominate. With the larger tube, greater volume dilution could exist, before

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the fluorination equilibrium was affected.

In the fluorination of the sulphur smoke, the products would be blown away from the point of reaction in the same way as above, and this is probably the reason for the 9% yield of S_2F_{10} (by weight of the gaseous mixture of S_2F_{10} and SF_6) obtained. If this reaction were cooled, a higher yield would no doubt be obtained.

Of the sulphur fluorides produced in all these reactions, SF_4 , S_2F_{10} and SF_6 were present in relatively large quantities. The formation of S_2F_2 is suggested by the presence of the sulphur ring in the first liquid air trap as mentioned before. If this ring was due to the decomposition of S_2F_2 to fluorine and sulphur, it is hard to imagine why the decomposition would take place at the temperatures of liquid air, rather than in the reaction tube or the connecting tube; unless S_2F_2 is more unstable in the liquid form than in the gaseous form, and the decomposition took place during condensation.

The existence of an S-S link in S_2F_{10} has been proven by several workers, and the suggestion has been put forward by some that S_2F_{10} cannot be prepared by fluorination of any substance not having an S-S link. The conclusion is that S_2F_{10} can be prepared by fluorinating sulphur or S_2F_2 but not SF4. This also precludes the possibility of forming S_2F_{10} by removing fluorine from SF6. This belief should not stand in the way of attempting to fluorinate to S_2F_{10} materials

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not possessing an S-S link. Since S_2F_{10} contains this link, at some point in the formation of S_2F_{10} an S-S link must be set up, unless the formation of S_2F_{10} involves a complicated collision. It is possible that temporary configurations or free radicals having this link may be formed under the conditions of the reaction; for instance, two SF4 molecules could unite even temporarily to form S_2F_8 and be fluorinated to S_2F_{10} .

V Suggestions for Future Work

(1) The lower fluorides (SF₄ mainly) should be separated from the rest of the reaction products and a study made of their fluorination. If they could be fluorinated to S_2F_{10} , the over-all yield of S_2F_{10} of the process would be materially increased. As it is rather difficult to separate the lower fluorides from SF₆, the next best thing is to remove the S_2F_{10} from the reaction products and fluorinate the residue. This is being done at this laboratory by L. Siminovitch and C. Bishinsky.

(2) The reaction of sulphur smoke with fluorine should be more carefully studied, as it is the easiest method of production to handle on a large scale. The reaction should be carried out at low temperatures with more dilute smoke than was employed.

(3) The possibility exists that SF_6 can be broken down by pyrolysis or reaction to form some S_2F_{10} . The reaction of SF_6 with atomic hydrogen has been carried out by LeRoy at the National Research Council in Ottawa, and the

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production of some S_2F_{10} has been reported.

(4) More work should be done using copper powder as a diluent for the sulphur with higher flow rates of nitrogen. The only data obtained using copper powder were with a nitrogen flow of 100 c.c. per minute, and higher yields might be obtained with greater flow rates. The maximum with NaF was reached at 300-400 c.c./min., but the position of this maximum might be lower due to the greater heat conductivity of copper.

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PART II

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THE DENSITY AND VISCOSITY OF DISULPHUR DECAFLUORIDE

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TAB	LE	OF	CONT	TENTS

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Density			
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	tions		5
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Since liquid disulphur decafluoride could be used for filling gas shells, a knowledge of its temperature coefficient of density and its viscosity is valuable. The density at the boiling point can also be used to calculate the molecular volume according to the equation:

> Molecular volume = Molecular weight Density x Avogadro's No.

This value for the molecular volume can be compared with values obtained from a consideration of the length of the S-S link. The density of liquid disulphur decafluoride was measured from 0° to 45°C., using a dilatometer, and the viscosity at 20°C. determined using a modified Ostwald viscometer.

EXPERIMENTAL

Density

Apparatus and Procedure

A small dilatometer, shown in Figure 1, was made from heavy wall pyrex tubing and a piece of pyrex capillary etched in centimeter divisions. A male ground-glass joint which fitted the female on the analysing system (described in Part I) was sealed to the top end of the etched capillary. The dilatometer was then calibrated by filling to various levels with clean mercury and weighing. The levels were read in a water bath at 10°C. A plot of volume against scale reading was made giving an excellent straight line. A thick-walled constriction was then made at the top of the capillary just below the ground-glass joint, and the dilatometer was weighed and connected to the analysing system.



Figure 1

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E - side tube

Viscometer and Dilatometer

A - upper constriction
B - upper bulb
C - capillary
D - lower bulb
F - dilatometer bulb
G - etched capillary
H - constriction
J - ground-glass joint

A sample of ${\rm S}_2{\rm F}_{10}$ was purified in the analysing system by fractional distillation at 0°C. until a pressure of 235 mm. was obtained. A dewar of dry-ice and acetone mixture was then placed around the dilatometer, and S_2F_{10} was condensed in until the liquid level was just below the opening of the capillary. The stopcock between the dilatometer and the analysing system was then closed, and a dewar flask containing liquid air was placed around the dilatometer. After solidification of the S_2F_{10} was complete, the constriction of the dilatometer was sealed off. The dilatometer was allowed to come to room temperature and then weighed together with the sealed-off joint. It was then placed in a water bath, and the height of the liquid meniscus was read at temperatures from 0° to 45°C.

Results

The results are listed in Table I and were plotted as in Figure 2, giving a straight line, which was extrapolated to 60°.

$\frac{\text{Table I}}{\text{Weight of } S_2F_{10} = 1.6512 \text{ gm}.}$

Temp.(°C.)	Volume (c.c.)	Density (gm./c.c.)
0°	0.799	2.06
10°	0.813	2.03
15°	0.823	2.01
20°	0.827	2.00
30°	0.843	1.96
45°	0.864	1.91

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Figure 2

The error in reading the mercury level in the calibration of the volume of the dilatometer was estimated to be 0.1 of a division, representing about 0.001 c.c. The same error was involved in reading the S_2F_{10} meniscus, or a total of 0.002 c.c. This is an error of about 2 parts in 800 or 0.25%. The errors in weighing are negligible compared with this. The approximate error in the density is then 0.25%, and the above values of density may be considered to be in error by $\stackrel{+}{=}$ 0.005 gm./c.c.

The value of the density at 60° obtained by extrapolation is 1.86 gm./c.c. The temperature coefficient of density is then .00333 gm./c.c./°C.

Laidler (1) using a value of 2.08 Å for the length of the S-S link, calculated the molecular volume of S_2F_{10} to be 198.0 Å³. He obtained an experimental value of the

(1) K.J.Laidler - "Theoretical Considerations Regarding the Fluorides of Sulphur, la - Further Remarks on Structure," National Research Council, Ottawa, report.

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molecular volume of 203.7 \AA^3 from a density value of S_2F_{10} of 2.07 gm./c.c. at the boiling point. This value of the density is not in agreement with the value found above. Laidler reported Yost's value of the S-S distance obtained from electron diffraction to be 2.38 Å and from this calculated the molecular volume to be 212 Å³. Using the value of the density at the boiling point of 1.96 gm./ c.c. obtained above, the molecular volume of S_2F_{10} at the boiling point was calculated as follows:

Molecular volume = $\frac{254}{1.96 \times 6.06 \times 10^{23}}$ = 2.14 x 10⁻²² c.c. = 214 Å³

This is in good agreement with the value calculated from Yost's value of the S-S distance. This bears out Laidler's conclusion that S_2F_{10} does not possess an S-F-S bridge.

Viscosity

The Viscometer and Theoretical Considerations

A viscometer of the Ostwald type, but capable of being evacuated and sealed off was constructed of pyrex glass tubing, and is shown in Figure 1. This viscometer differed from the Ostwald type in that both sides were projected upward and joined, and a side tube was provided for introducing liquids. The same theoretical considerations of viscosities which apply to the Ostwald viscometer were considered to apply to this design. The following theoretical considerations are discussed in Bingham "Fluidity and Plasticity," pages 16, 18, 75.

The Poiseuille formula is $V = \frac{\pi g p R^4 t}{8 l q}$ where V = volume of efflux in time t $p = pressure in gm./cm.^2$ g = acceleration due to gravity R = radius of capillaryl = length of capillary

Applying the correction for loss of kinetic energy as heat, the formula becomes:

$$\gamma = \frac{\pi g p R^4 t}{8 V 1} - \frac{m \rho V}{8 \pi 1 t}$$

where m = a constant here equal to unity,

 ρ = density of the fluid.

For a civen viscometer $\frac{\pi g R^4}{8 V 1} = C$, a constant and $\frac{N V}{8 \pi 1} = C'$, a constant then $\gamma = C p t - C' \rho / t$

If we have a standard liquid with viscosity η_o , and a liquid to be measured with viscosity η , then:

$$\frac{\eta}{\eta_{o}} = \frac{C p t - C' \rho / t}{C p \cdot t_{o} - C' \rho / t_{o}} - - - - - - - - Ecn. (1)$$

 η = coefficient of viscosity of fluid

If η is very nearly equal to η_o , or if t and to are very large, this may be written

$$\frac{n}{n_o} = \frac{p t}{p \circ t_o} - - - - Eqn_o(2)$$

Since the pressure is proportional to the density of the liquid in an Ostwald viscometer, then,

$$\frac{\eta}{\eta_o} = \frac{\rho t}{\rho_o t_o} - - - - - - Eqn.(3)$$
or $\eta = K\rho t - - - - - Eqn.(4)$

In order to obtain this constant K, the times of flow of a known volume of two liquids, water and benzene, were measured.

Procedure for Viscosity

The time of flow of the same volume of water, benzene, and disulphur decafluoride, were measured. Due to the design of the viscometer, it was impossible to pour in a given volume of a liquid, and very inaccurate simply to add liquid until a given level on the lower bulb of the viscometer was reached. It was decided to condense a convenient amount of S_2F_{10} into the viscometer, obtain its volume from the weight, and calculate the weight of this volume of water and of benzene. This weight of water or of benzene was then added while the viscometer was supported on a balance.

The procedure for filling the viscometer with S_2F_{10} was as follows: The viscometer was carefully cleaned with dichromate solution, thoroughly rinsed with distilled water

and acetone, and dried. A constriction was made near the end of the side tube, and the viscometer was weighed and connected with pressure tubing to the analysing system (described in Part I) which contained pure S₂F₁₀. This S_2F_{10} had been purified by fractional distillation at 0° until the vapour pressure was 235 mm. A dewar flask containing dry-ice and acetone mixture was then placed around the viscometer, and S_2F_{10} was condensed in until a convenient amount had collected. The stopcock between the viscometer and the analysing system was then closed, and the viscometer was immersed in a dewar flask containing liquid air. When the S_2F_{10} had all solidified, the constriction was sealed with a hand torch, and the viscometer was allowed to reach room temperature. The filled viscometer was then weighed, together with the sealed-off portion of the side tube. The volume of S_2F_{10} was calculated from the density at 20° and the weight, and the weight of this volume of benzene and of water at 20° were calculated from their density at that temperature.

In order to take a reading, the small bulb of the viscometer and the capillary tubing were filled with liquid by inverting the viscometer and tapping to remove bubbles. The inverted viscometer was then supported in a water bath at 20° and allowed to reach temperature equilibrium. The viscometer was then turned upright, and the time noted for the liquid meniscus to pass from the upper constriction to

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the opening of the capillary. The average of five readings was taken.

The S_2F_{10} was then removed by placing the viscometer in a dewar flask of liquid air, breaking off the end of the side arm, and connecting the viscometer to the analysing system as before. The S_2F_{10} was condensed back into the analysing system with liquid air, and the viscometer was cleaned and dried as before and weighed. The viscometer was then tared on a balance, the calculated weight of water added, and the side arm sealed off. Five readings of the time of flow at 20° were taken. The viscometer was filled with the same volume of benzene and five readings taken at 20° in the same way.

Results

The values of K for water and benzene were calculated, and found to disagree. The viscometer was again filled and the time taken for both liquids, but the original values were confirmed within 1%. The values of time of flow and K for water and benzene are given in Table II. The values of time are the averages of five readings, the values of K are obtained from equation (4), and the values of for water and benzene are taken from the Chemical Rubber Handbook.

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Liquid	Trial	Time t	Avg. t	Density at 20°	η C.G.S.	K
					units	-
Water	1 2	33.9 33.6	33.8	0.998	0.0100	0.000296
Benzene	1 2	25.6 25.5	25.6	0.0879	0.00649	0.000288
					Average	0.000292

TABLE II

The average of five values of the time of flow of S_2F_{10} at 20° was 15.4 sec. The density of S_2F_{10} at this temperature is 1.99 gm./c.c., and the value of η for S_2F_{10} was calculated from equation (4) as follows:

 $\eta = K_{\rho} t = 0.000292 x 1.99 x 15.4 = 0.00895 C.G.S.$ units

PART III

THE PREPARATION AND HYDROLYSIS OF ALUMINIUM AND ZINC ARSENIDES

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DISCUSSION

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INTRODUCTION

The purpose of this work was to study the preparation and hydrolysis of various metallic arsenides, with a view to their use in chemical warfare. The generation of arsine from arsenides is a relatively easy matter, even moist air being sufficient to hydrolyse some arsenides, while water or dilute acids are required for others. Aluminium arsenide Al3As2 is hydrolysed by moist air or water, but zinc arsenide Zn3As2 requires dilute sulphuric acid. Arsenides could be useful in gas warfare for the production of arsine to fill shells, or spread over the ground as a powder, which would evolve arsine. In this work an attempt was made to find the efficiency of the preparation of arsenides from the elements, and of arsine from the arsenides. In order to find the most efficient mixture of the elements to use, various arsenides were prepared using proportions of the elements varying around the stoichiometric proportions. These arsenides were hydrolysed and the yields of arsine measured.

HISTORICAL

According to Mellor, F. Wöhler heated a mixture of powdered arsenic and aluminium, forming a dark grey powder with incandescence. The resulting aluminium arsenide was decomposed slowly by cold water and rapidly by hot water, with the evolution of arsine. Mellor also states that Q. A. Mansuri found the proportions in this compound to be those of Al₃As₂, and that the equilibrium diagram is probably like that of the system aluminium antimony. The alloy does not dissolve to any appreciable extent in molten aluminium, nor does it alloy with arsenic to form a eutectic mixture.

According to J. Newton Friend, the melting point of Al₃As₂ was found to be 1200°C. by Natta and Passerini (Gazetta <u>58</u>, 458 (1928). Al₃As₂ is less stable at ordinary than at high temperatures, a little arsenic being slowly liberated. X-ray analysis by the powder method suggests that the crystals belong to the cubic system, and resemble the blendes. The density calculated from crystallographic data is 3.81 gm./c.c. and the observed density 3.60 gm./c.c. It is unstable in moist air.

Two arsenides of zinc exist -- Zn_3As_2 and $ZnAs_2$ melting at 1015° C. and 771°C. respectively. Mellor indicates that Zn_3As_2 may be prepared by melting zinc in arsenic vapour and hydrogen, by subjecting zinc and arsenic

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in appropriate proportions to a pressure of 6500 atmospheres, or by heating a mixture of the elements at 800° out of contact with air (Natta and Passerini, ibid p.541). A compact but fragile crystalline mass of density 5.578 is obtained, having a cubic lattice. Arsine is evolved when the arsenide is reacted with sulphuric acid.

Zinc diarsenide ZnAs₂ is prepared, according to Mellor, by heating zinc and arsenic together in suitable proportions. It dissolves in acids with evolution of arsine. The system Zn-As is shown in Figure 1 (from Mellor: Inorganic and Theoretical Chemistry, Volume 4, Chapter 30, Figure 6).

The production of arsine by hydrolysis of calcium arsenide was carried out by Lebeau and Moissan by the action of water or dilute acid. According to Friend, the moisture was removed by cooling the gas to -20° and passing it through a series of tubes containing metaphosphoric acid. Pure arsine at ordinary temperatures is a colourless gas, with an obnoxious odour. It is extremely poisonous, causing lysis of the red corpuscles.



Figure 1

EXPERIMENTAL

Apparatus

The arsine generating system is shown in Figure 2. It consisted of a generator (A) in which the metallic arsenide was hydrolysed, a drying tube (G) for the arsine, and a manifold (I) to which were connected five storage volumes (J), a calibrating volume (S), a sample bulb (\mathcal{W}), a McLeod gauge (P), a manometer (M) and a trap (1).

The generator, A, consisted of a 300-c.c. roundbottomed flask with a long neck ending in a ground-glass joint, which fitted into a short chamber connected to a rough manometer B, and to the vacuum line C and the drying tube G. The rough manometer served as a safety valve in case the drying tube became plugged. A reservoir, D, led

Figure 2

The Arsine Generating System

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through a stopcock into the generating flask, ending in a capillary jet of 1 mm. bore about $l\frac{1}{2}$ inches from the bottom of the flask.

The drying tube G was about 1 meter long and 3 cm. in diameter, and was fitted at each end with glass wool plugs. It was filled with calcium chloride in sections separated by loose plugs of glass wool to prevent packing. For about six inches at the end remote from the generator, code line was used instead of calcium chloride. The drying tube opened into the manifold I. Connected to this manifold were the five one-liter storage bulbs J, which could be closed off with the stopcocks K. Also connected to the manifold was the McLeod gauge P, which could be isolated by the stopcock Q. The McLeod gauge was used to test for completeness and permanence of the evacuation of the system. Then arsine was present in the system, the stopcock Q was closed to prevent arsine from decomposing in the gauge and contaminating the mercury.

The large manometer N was connected to the manifold through the stopcocks L and N. The two sides of this manometer were of 2 cm. diameter tubing, and at the bottom there was a constriction to prevent large oscillations of the mercury. The levels could be altered using the three-way stopcock 0, which was connected to the vacuum line C and to the atmosphere.

The volume of the two-liter flask S had been calibrated with water before sealing on, and it was used to

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calibrate the volumes of the system by expansion of air. The small trap U was not used. The stopcock V was used to admit dry air into the system through a drying tube (not shown). The sample bulb was of 300 c.c. capacity, and its exact volume was calibrated with water. A groundglass joint Y permitted the removal of the sample bulb for weighing.

The trap 1 was connected through the stopcock 2 to the manifold, and through the stopcock 3 to the vacuum line. This trap was immersed in a dewar flask containing liquid air, and prevented arsine from being drawn into the pump. A ground-glass joint permitted removal of the trap and its contents.

This apparatus was found to be quite satisfactory for the measurements which were made. The weight of the sample bulb *N* was found to be reproducible within 0.0005 gm., if care were taken in greasing and cleaning the ground-glass joint. The largest error in measurement lay in reading the right-hand side of the manometer, which became coated with an arsenic mirror due to decomposition of the arsine. This caused considerable distortion of the mercury meniscus.

Due to the large volume of the right-hand side of the manometer, it was necessary to measure its change of volume with height, if an accurate measurement of the volume of arsine produced were to be obtained. To do this, the vol-

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ume of the manifold and the manometer was measured at different pressures and a graph was drawn giving the volume at any pressure.

Technique

(1) The Technique of the Production of the Arsenides.

Various proportions of the metal and the arsenic were employed in order to find what proportions gave the greatest yield of arsenide and of arsine. Proportions varying both ways from the stoichiometric were tried. The procedure followed for the production of the aluminium and the zinc arsenides is given below.

The stipulated amount of powdered arsenic was weighed out on a tared watch glass, and then brushed into a small mortar and thoroughly ground. The corresponding amount of aluminium powder or zinc powder was then weighed out and ground into the arsenic little by little, giving a fine silvery gray powder. This was placed in a small crucible, covered, and heated strongly with a lieker burner in a fune cupboard. After a few seconds, reaction occurred and the charge became red hot, cooling to a solid mass. This mass was then placed in a weighed can with a tightly fitting lid, and allowed to cool. The can and contents was then weighed, and the loss of weight during the reaction determined. From this the yield of impure arsenide was calculated. This loss was due to sublimation of the arsenic. The mass was

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broken up and ground carefully in a small mortar and stored in a small bottle in a desiccator. For the production of the aluminium arsenides, a charge of 10 gm. was used; for the zinc arsenides, a charge of 20 gm.

(2) The Technique of Hydrolysis of the Arsenides.

It was found by trial that about 7 gm. of the metallic arsenide would produce enough arsine on hydrolysis to fill the generator, drying tube, manifold, and sample bulb, at a pressure of about one atmosphere. For a run, a weighed amount of about 6 gm. of the arsenide was placed in the generating flask and tapped occasionally to release enclosed air, while the whole system was evacuated. The pressure was then checked with the McLeod gauge, and if sufficiently low, the left-hand side of the manometer and the sample bulb were closed off.

In the case of aluminium arsenide, 40 c.c. of distilled water was placed in the reservoir D and all but a few drops was allowed to run down into the generating flask. Evolution of arsine took place quite slowly at first, reached a maximum after one hour, decreased rapidly during the third hour, and was practically complete at the end of the third hour. The rest of the system was left open to the generator during the run, so that the rate of evolution of arsine could be followed with the manometer. Since zinc

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arsenide was not hydrolysed by water, it was necessary to use dilute sulphuric acid. It was found that 40 c.c. of 2 N sulphuric acid gave about the right rate of hydrolysis. The rate had to be slow enough for the arsine to be completely dried on passing through the drying tube.

When the evolution of arsine had stopped, the generating flask was closed off at the stopcock F, and the pressure was read on the large manometer. The temperature of the fume cupboard in which the apparatus was placed varied less than 0.5° per hour. This temperature was read by means of a thermometer graduated to 0.1°. The sample bulb was then closed off at the stopcock X, and the arsine in the system was allowed to expand into the storage volumes (J). The excess was condensed in the trap 1 with liquid air, and the manifold was filled with dry air. This was done to prevent the escape of arsine into the air from the space between stopcocks X and Z when the sample bulb was removed. The sample bulb was then removed, and the ground-glass joint was carefully cleaned with acetone and dried. The bulb was weighed, then evacuated and weighed again. The weight of the arsine produced was calculated using the formula given in the section on results.

RESULTS

Results of Arsenide Production

The yields of the impure arsenides from the elements are given in Table I and Table II. The percentages

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are by weight, and the yields are based on the weight of impure arsenide left after the reaction.

TABLE I

Al₃As₂ Stoichiometric Proportions - 35% Al, 65% As

Sample No.	% Al	% As	搅 Yield of Arsenide
4	30	70	83.0
5	35	65	88 .5
3	40	60	94.7

TABLE II

Zn As2

Stoichiometric Proportions - 57% Zn, 43% As

Sample No.	% Zn	% As	% Yield of Arsenide
4	50	50	61.5
3	55	45	93.0
6	60	40	96.3
5	65	35	99.0

The reaction of aluminium with arsenic was more violent than that of zinc, but both reactions went quite smoothly. The highest yields of impure arsenide naturally occurred when no excess arsenic was present originally, since the other metal (Al or Zn) was not volatilized at the temperature of the reaction. When an amount of arsenic in excess of the stoichiometric proportions was present, a large loss of arsenic occurred, although the resulting arsenide was purer than the former. When a large excess of arsenic was present, the heat of reaction was not sufficient to volatilize all of it.

An attempt was made to form iron arsenide Fe₃As₂ in this way, but no reaction took place. An attempt to make Zn.As₂ with 62% As and 38% Zn failed, because the arsenic was volatilized and the arsenide formed was Zn₃As₂ mixed with some arsenic. This reaction was also carried out in a bomb, in order to prevent the arsenic vapour from escaping. The bomb was filled and kept at 770° for one hour, then cooled and opened. There was evidence of compound formation, but no evolution of arsine took place on hydrolysis with water or dilute sulphuric acid. Hydrogen was evolved with nitric acid, showing the presence of unreacted zinc.

Results of Arsenide Hydrolysis

In order to express correctly the weight of arsine produced, two corrections were considered, the solubility of arsine in the water in the generating flask, and the amount of water vapour in the arsine which filled the generator.

(a) Correction for solubility of arsine.

The solubility of arsine in cold water is about 0.007 gm. per 100 gm. of water, or about 0.003 gm. in 40 c.c. of water. This correction was not applied, since it was

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negligible compared with the amount of arsine evolved, about 2.5 gm. on the average.

(b) Correction for volume of water vapour.

The arsine in the generating flask and tubing up to the drying tube was saturated with water vapour, and that in the rest of the system was dry. The pressure exerted by the arsine was thus too large by an amount depending on the partial pressure of water in the generating flask and tubing, and the volume of this system compared with that of the whole system. The formula expressing the weight of arsine only is derived below.

Let V = the volume of the system containing arsine V_g = the volume of the generator and tubing = the volume of arsine and water vapour mixture V_d = the volume of rest of system = the volume of dry arsine P = the total pressure in system P_w = the partial pressure of water in generator P_a = the partial pressure of arsine in generator W_1 = the weight of arsine in dry part of system W_2 = the weight of arsine in wet part of system W_2 = the total weight of arsine

Then
$$PV_d = \frac{W_1}{M} RT$$
 (1)
and $P_aV_g = \frac{W_2}{M} RT$ (2)

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and
$$P_w + P_a = P$$
 and so $P_a = P - P_w$ (3)
and $V_d + V_g = V$ (4)

Subst. (3) in (2)
$$V_g(P-P_w) = \frac{W2}{M} RT$$
 (5)

Add (1) and (5)
$$PV_d + V_g(P-P_w) = \frac{W_1 + W_2}{M} RT$$

Rearrange -
$$PV_d$$
 + PV_g - P_WV_g = $\frac{W}{M}$ RT (6)
Subst. (4) in (6) PV - P_WV_g = $\frac{W}{M}$ RT or $W = \frac{PVM}{RT} - \frac{P_WV_gM}{RT}$ (7)

 $= \frac{W}{RT}$

This equation was left in this form and not placed over one denominator in order to facilitate the use of logarithms by avoiding a subtraction in the numerator. P_W was the vapour pressure of water at the temperature T.

A typical calculation of the molecular weight of arsine, and the yield of arsine from the impure arsenide is given below.

Aluminium Arsenide Sample No.5

Weight of arsenide used = 6.7538 gm: Pressure of gas = 655.0 cm. Temperature = 295.6 °K.

At this pressure the volume of manometer and manifold = 276 c.c. volume of generator = 693 c.c. volume of density bulb = <u>320 c.c</u>. Total 1289 c.c. Volume of water added = 40 c.c.Net volume V = 1249 c.c. Volume of density bulb = 0.3199 liters Weight of arsine in density bulb = 0.8846 gm. Molecular weight of arsine (from the perfect gas law) = 77.83 Weight of arsine produced = $\frac{\text{PVM}}{\text{RT}} - \frac{\text{PwVgM}}{\text{RT}}$ = 3.45 - 0.06 = 3.39 gm. (Here P_w = 20.5 nm.) Theoretical yield = $\frac{6.75 \text{ x } 156}{231}$ = 4.56 gm. % Yield = $\frac{3.39 \text{ x } 100}{4.56}$ = 74.3 % Yield/gm. arsenide = $\frac{3.39}{6.75}$ = 0.502

The yields of arsine obtained from three samples of aluminium arsenide are listed below in Table III.

TABLE III

Sample No.	% Al	% As	% Yield of AsH ₃ from Al ₃ As ₂	Yield/gm.
4	30	70	78.7	0.532
5	35	65	74.3	0,502
3	40	60	64.0	0.432

The percentages of the metals given are those used originally to make the arsenide, and not those present in the arsenide. The yields of arsine obtained from four samples of zinc arsenide are listed in Table IV.

Sample No.	% Zn	% As	% Yield of Arsine	Yield per gm.arsenide
4	50	50	48.8	0.220
3	55	45	45.0	0.203
6	60	40	64.6	0.293
5	65	35	70.5	0.310

The arsine evolved from Al₃As₂ had a molecular weight in excess of 77.5 in most cases. The ideal molecular weight is 77.95. The arsine from Zn₃As₂ had a molecular weight of about 76.5 on the average. In order to express the yields of arsine on the original materials, the yield of arsine was multiplied by the yield of arsenide for each sample. These results are given in Tables V and VI.

TABLE V

 Al_3As_2

Sample No.	% Al	% As	% Yield of arsenide	% Yield of arsine	% over-all yield
4	30	70	83.0	78.7	65.3
5	35	65	88.5	74.3	65.8
3	40	60	94.7	64 . 0	60.6

TABLE IV

TABLE VI

Zn3As2

Sample No.	<u>% Zn</u>	% As	% Yield of arsenide	% Yield of _arsine	% over-all yield of arsine
4	50	50	61.5	48.8	30.0
3	55	45	93.0	45.0	41.9
6	60	40	96.3	64.6	ő2 . 2
5	65	35	99.0	70,5	69.8

Discussion

With aluminium arsenide, the highest yield of arsine from the arsenide occurred in sample No. 4, which had the largest amount of arsenic originally. This means that this arsenide was purer than the other two due to the fact that excess arsenic was volatilized, but excess aluminium was not volatile at the temperature of the reaction. The yield of arsenide from the elements was lowest in this sample for the same reason. The over-all yield of arsine reached a maximum in sample No.5, which was made with a ratio of Al to As of 35 to 65, corresponding to the stoichiometric proportions.

With zinc arsenide, the maximum yields of both arsenide and arsine were reached with an amount of zinc in excess of the stoichiometric proportions. In this case, the heat of reaction was not great enough to volatilize much of the excess arsenic. The yield of arsine per gram of arsenide was roughly twice as great from aluminian arsenide as from

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zinc arsenide, although the maximum over-all percentage yields were about the same. This is in accordance with the greater arsenic content of aluminium arsenide. If ZnAs₂ could have been satisfactorily prepared, it should have given a higher yield per gram than Zn_3As_2 , due to its greater content of arsenic. Due to the action of the dilute sulphuric acid on the unreacted zinc in the impure arsenide, the arsine contained a small amount of hydrogen. This accounts for the slightly lower molecular weight of arsine produced from zinc arsenide. The yields of both arsenide and arsine could undoubtedly be increased by using much larger charges of the elements, and proper temperature control in the preparation of the arsenide.

For preparation of arsine under field conditions, Al₃As₂ would be a much more useful material than Zn₃As₂, due to its higher yield per gram, and to the fact that it is readily hydrolysed by water or moist air.

CLAINS TO ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

Claims to original work

A modification of the Argo-Mathers type of fluorine electrolytic cell has been made, with a new type of insulation, and which permits the easy replacement of the anode. A further modification was made with increased anode area, and larger current capacity.

An apparatus was constructed for the production and fluorination of sulphur smoke.

A method of production of disulphur decafluoride (S_2F_{10}) from the fluorination of sulphur was developed, using both solid and gaseous diluents. The effect of varying both these diluents was studied.

The variation in density of liquid S_2F_{10} with temperature was measured from 0°C. to 45°C.

A modification of the Ostwald viscometer suitable for use with toxic liquids was made, and the coefficient of viscosity of liquid S_2F_{10} at 20°C. was measured.

The over-all yields of arsine from arsenic were measured in the production and hydrolysis of Al₃As₂ and Zn₃As₂.

Contributions to knowledge

(1) The fluorination of a sulphur smoke in a glass reaction tube at room temperature gives a yield of S_2F_{10} of about 9% of the gaseous mixture of S_2F_{10} and SF_6 .

(2) A yield of 28% (based on sulphur) of S_2F_{10} can be obtained by the fluorination of sulphur, using both solid and gaseous diluents.

(3) When sulphur is diluted with sodium fluoride, and reacted with fluorine diluted by a stream of nitrogen, the yield of S_2F_{10} and other lower fluorides is increased, and that of SF_6 is decreased. At higher flow rates of nitrogen, the yield of S_2F_{10} is decreased.

(4) Sulphur diluted with copper powder and reacted with diluted fluorine gives a higher yield of S_2F_{10} than sulphur diluted with sodium fluoride, when the reaction tube is cooled to -10°C.

(5) The density of liquid S₂F₁₀ ranges from 2.06 gm./c.c. at 0°C. to 1.86 gm./c.c. at 60°C.

(6) The coefficient of viscosity of liquid S_2F_{10} at 20°C. is 0.0089 \pm 0.0003 C.G.S. units.

(7) A yield of arsine of 66% (based on arsenic) can be obtained by the production and hydrolysis of Al₃As₂. The yield for Zn₃As₂ is 70%.

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