STUDIES ON THE COMPOUNDS OF SULFUR AND FLUORINE

THE PREPARATION OF S2F10

AND

WORK ON PROBLEMS IN CHEMICAL WARFARE

by

Richard Mungen, M.Sc.

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Richard Mungen

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A study of the fluorides of sulfur has revealed that disulfur decafluoride (S_2F_{10}) is a toxic material. It is more toxic than phosgene and has special merits as an agent of chemical warfare. The yield of S_2F_{10} is increased by the fluorination of sulfur (by fluorine diluted with nitrogen) in the presence of certain fluorides. At the same time the yield of other lower fluorides of sulfur was increased and the yield of SF_6 was decreased.

HS solutions thickened with polyvinyl acetate are "stabilized" by the addition of acetic anhydride provided iron is excluded from the solutions.

The method of packing the charcoal in the test-cell is an important factor in the determination of volume activity.

Nickel carbonyl in the presence of air deposits nickel on a carbon surface which does not improve the service-time against arsine.

PART I

STUDIES OF THE COMPOUNDS OF SULFUR AND FLUORINE

THE PREPARATION OF $s_2 F_{10}$

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INTRODUCTION

The history of chemical warfare in World War I reveals the use of many chemical agents, the effectiveness of which was proven or disproven under fighting conditions. Only the most effective agents survived the actual field test. The available literature suggests these compounds are still likely to be used as agents of chemical warfare. However, this does not preclude the possibility that more effective compounds will be introduced in World War II.

The original purpose of the present work was to study the physiological properties of less common chemical compounds and in particular the gaseous fluorides. The fluorides of the sulfur group were chosen as a starting point and have proved sufficiently interesting to warrant concentrated effort. The patentialities of disulfur decafluoride as a chemical warfare agent have been shown to be great. The study of the properties and commercial production of the above compound constitutes the major portion of this thesis. The work has two justifications; to test our defensive equipment to assure adequate protection against the use of the new agent; and second, to prepare for use of the compound in offensive action.

The Fluorides of Sulfur

Sulfur hexafluoride was first reported by Moissan and Lebeau (1) and found to be highly stable, being unattacked by potassium hydroxide and decomposed by sodium only at the boiling point. Prideaux (2) gave the melting point as -56° to -55° and the boiling point as -62°. Schumb and Gamble (3) made a careful preparation of sulfur hexafluoride and measured the vapour pressure of the solid and the liquid up to pressures of three atmospheres. The temperature interval covered was from -72° to -45°. At -63.8° the pressure was 760 mm. They found the relative density (air = 1) to be 5.10 - theoretical 5.04. The melting point of pure sulfur hexafluoride was -50.8 ± 0.2° (3). Kleum and Henckel (4) measured the physical properties of sulfur hexafluoride and found them to be in agreement with those reported by previous workers. Yost and Claussen (5) calculated the heat of formation of the gas to be 262,000. cals :the heat of sublimation to be 5.640 cals: - the heat of fusion to be 1,390 cals. From electron diffraction experiments Pauling and Brockway (6) found that the fluorine atoms of sulfur hexafluoride lie at the corners of a regular octahedron. Their results also suggest that the gas has an ionic structure. Watson, Ras and Ramaswany (7) measured its dielectric constant and found that it has no moment. Coppock and Whytlaw-Gray (8) measured the coefficient of gaseous expansion and Pearson and

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Robinson (9) measured the parachor.

Ruff (10) found evidence for formation of another fluoride of sulfur when metallic fluorideswere heated with sulfur. Centnerszwer and Strenck (11) examined the gas obtained by heating silver fluoride with sulfur and found it to be S₂ F₂. This fluoride was not nearly as stable as SF₆, reacting with potash solution and decomposing when stored in glass, leaving a deposit of sulfur. These workers determined the melting point of S₂F₂ as - 105.5° and the boiling point as - 99°. They also measured the vapour pressure over a limited range of temperature near the melting point. They briefly mention the effect S₂ F₂ had on mice when the animals breathed a one percent (by volume) mixture of the gas in air. The mice were exposed for fifteen minutes but no toxicity data is given. The mice were said to first appear uncomfortable and then to show signs of suffocation.

Fischer and Jaenckner (13) heated cobaltic fluoride with sulfur and found the gas formed was SF_4 . It is less stable than SF_6 and had to be prepared in a quartz apparatus since it attacks glass. It is decomposed by potash solution, attacks mercury but not rubber or paraffin oils. These workers measured the vapour pressure of SF_4 over a limited range of temperature between the melting point (-124°)

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and the boiling point (- 40°).

Disulfur Decafluoride was first reported by Denbigh and Whytlaw-Gray (14) (15). This new fluoride was fractionated from a sample of impure SF_6 . On a very small sample these workers performed a molecular weight determination and an analysis to prove the identity of the compound. The compound was found to be colorless, very volatile and to have an odor resembling sulfur chloride or sulfur dioxide. The vapour was insoluble in and unattacked by water as well as being unaffected by concentrated sulfuric acid and concentrated potassium, hydroxide solutions. Metals were reported attacked at high temperatures but unattacked when cold. Glass and silica were attacked by the gas at red heat. The vapour pressure was measured from - 56.1° to 22.4°. The melting point was reported as - 92°±1° and the boiling point as 29°± 1°. The liquid density was given as 2.08 ± 0.03 . These workers also measured the surface tension and then calculated the parachor.

Two oxyfluorides of sulfur S 0 F₂ and S 0₂ F₂ have been described by Moissan and Lebeau (16).

Preparations of sulfur fluorides involving the use of fluorine as a fluorinating agent efter contain traces of CF4 due to reaction with the carbon anode. Ruff and Keim describe the properties of this fluoride. All that need be said at this point is, that CF_4 is very inert and has a melting point of - 186.8 \pm 0.5°

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EXPERIMENTAL

Materials

(a) Fluorine

Fluorine was prepared by the electrolysis of molten potassium bifluoride. G.H. Gady (18) has determined the freezing points and vapour pressures of the system potassium fluoride - hydrogen fluoride from an acid mole fraction of 0.4646 to 1.000 (Fig. 1.).



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The highest vapour pressure curve is for a pressure of 25 cm. the middle for 10 cm. and the lowest for 5 cm. of mercury. The areas on the diagram bounded by the freezing point curve and the line representing a vapour pressure of 5 cm. of mercury are the ones most suitable for use as the electrolyte for the preparation of fluorine. If the temperature is kept at 240° the mole fraction should lie between 0.485 and 0.508. Molten potassium bifluoride has an acid mole fraction in this range and was chosen as the most suitable electrolyte since it is readily available.

The first type of cell used for the electrolysis is described by Dennis, Veeder and Rochow (19). This cell was used only temporarily during the period of construction of a larger cell of different design. The cell was in the shape of a V, constructed of heavy copper tubing which may be obtained commercially in the required size. The copper tubing used was $2\frac{1}{2}$ inch pipe, with wall thickness of about 5 mm. Two pieces of this heavy tubing, each 10 inches long were cut so their lower ends could be joined in a V at an angle of about 70° (Figure 2). They were brazed together at the junction using welder's "low-melt".

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The upper end of the anode side A was built in and fitted with a collar E which was threaded to receive the electrode bushing B. The electrode bushing was insulated from the electrode by a thin sheet of mica and made gas-tight by a paste of sodium silicate solution and calcium fluoride. This paste was made with as little sodium silicate as possible. An exit tube D was brazed to the upper end and lower side of A. The upper end of the cathode side C did not need to be gas-tight and was merely fitted with a flanged disc and collar that supported the cathode as shown. The collar was insulated from the electrode with mica.

The two arms of the cell were covered with asbestos paper to within one or two inches of the upper ends and then wound with chromel wire of length and resistance calculated to give the desired temperature. The wire was then covered with a layer of asbestos cement. The winding was connected to a 110 volt a.g. circuit through a rheestat.

The electrodes were silicon free, graphite rods supplied by the Canadian Carbon Company, Montreal. They were $\frac{3}{3}$ of an inch in diameter and sufficiently long to reach within an inch of each other in the cell.

The cell was charged with KF. HF and the heating current turned on. Sufficient salt was added so that the fused material reached about half way up the arms of the cell. The electrodes were then fitted into place and their outer ends connected to a 110 volt d.c. circuit through a rheostat and ammeter. The current was usually adjusted to 6 amps. at 15 volts.

The difficulties encountered using this type of cell have been mentioned by other workers - Dennis et al (19).

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The cell did not produce a sufficiently large volume of fluorine for the present work. The greatest annoyance was the long, preliminary electrolysis required to remove traces of water from the electrolyte before any fluorine was evolved. Another source of trouble was cessation of evolution of fluorine. At this point the cathode would be covered with a reddish deposit of copper which prevented electrolysis. Removing this deposit only temporarily remedied the situation. Also, it was difficult to prevent fluorine from escaping through the insulating material about the anode.

The second generator used was similar to that described by Denbigh and Whytlaw-Gray (22), and was designed by J. T. Hugill, R.B. Harvey and the writer. It was of the diaphragm type first described by W.L. Arge (20). Bancroft and Jones (21) and Schumb and Gamble (3) describe generators which were modifications of that described by Argo (20).

The entire cell was constructed of copper with the exception of the graphite anode and the insulating material (Figure 3).

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The cell consisted of an outer vessel A, constructed of 1 inch copper sheet welded into an 8 inch inside diameter cylinder, fifteen inches in length, and fitted with a brazed-on bottom. This vessel also acted as the cathode. The diaphragm D was a 4 inch standard size copper pipe, closed in at the bottom by a circular plate. Three rows of $\frac{1}{2}$ inch holes were drilled through the diaphragm to provide circulation of the electrolyte around the graphite anode G. The outlet tube 0 at the top of the diaphragm was a one inch standard size copper pipe brazed onto the side of the diaphragm at a 45° angle. The free end of the outlet was threaded to fit a 45° standard brass coupling. The top of the diaphragm pipe was threaded to fit a 1 inch copper plate to which the electrode bushing was bolted. A lead gasket made a gas-tight joint. The graphite anode $(1\frac{1}{4})$ inches in diameter and 18 inches long - Canadian Carbon Company, Montreal) was cemented into the lower part of the collar of the bushing with one inch of an insulating cement, made of calcium fluoride powder and "water glass". A mica ring was placed around the upper portion of the anode within the bushing collar and molten lead was poured in to make a gas-tight seal. The electrical lead was fastened to the anode by a sheet copper clamp.

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The whole diaphragm assembly was cemented into a ring in the cover of the main vessel, using a cement of calcium fluoride and "Insalute." Two tubes were placed in this cover; one closed at the lower end held the thermocouple shown at T, the other open tube P, served as the hydrogen outlet and also as an opening for the stirring mechanism. The cover was made to fit over the outer vessel and the whole assembly could be removed with little trouble.

The thermocouple used was of the copper-constantan type. Since room temperature varied but a degree or two, the leads of the thermocouple were connected directly to a milliammeter without the use of a constant-temperature cold junction. The needle of the ammeter was adjusted so that the reading gave the temperature of the electrolyte directly (room temperature 20°). A calibration graph was drawn up and checked against an ordinary thermometer. The agreement was satisfactory for the intended purpose.

A circular perforated plate M, rested on three legs at the bottom of the main vessel and was intended to diffuse the anhydrous hydrofluoric acid introduced from a tank through a $\frac{1}{4}$ inch tube I. Actually the hydrofluoric acid was introduced by removing the diaphragm assembly and bubbling the gas directly into the electrolyte.

Two heating coils of 16 gauge nichrome wire are shown at H. The inside or primary heater was wound over $\frac{1}{2}$

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inch of asbestos sheet and carried current of approximately 12 amps. A layer of asbestos lagging was placed over the primary heater and then the secondary or auxiliary heater was put in place. The auxiliary heater carried current of approximately 10 amps. A final insulation of asbestos l_{E}^{1} inches thick was added over the second heater. Both heaters were operated from a 110 volt a.c. source.

While the cell was functioning the primary heater was left on. To control the temperature within a range of 240° - 250° a resistance was connected in series with the heater and reduced the current in the primary circuit to 8 amps. As hydrofluoric acid was removed by the electrolysis the melting point of the electrolyte was raised. Thus it was necessary to raise the operating temperature gradually to maintain the proper current flow.

The electrodes were connected to the 110 volt d.c. mains and to a motor generator (which operated at 15 volts) through a rheostat and an ammeter. The current could be drawn from either source.

The charge required for the generator was about 35 pounds of KF. HF. Both heaters were turned on during the fusing process after which, only the primary heater was needed. A frothy mass usually floated to the surface and was removed

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before operating the cell. When the cell was properly charged the diaphragm assembly was put in place. The diaphragm, being at room temperature, caused some of the electrolyte to solidify and a short time was required before the whole mass was again molten. The 110 volt d.c. current was turned on and approximately 15 amps. put through the cell. At first, traces of water in the electrolyte were electrolyzed and the cell did not conduct properly. During this time it was not possible to operate the cell with the motor-generator as the oxygen, produced by the electrolysis of the traces of water, caused polarization of the anode which could only be overcome by using the higher voltage. The motorgenerator was used when the cell was functioning normally. The cell was aperated at 25 amps. and 10 volts at a current density of 1.18 amps. per square inch.

As mentioned previously hydrofluoric acid is removed by electrolysis and the melting point of the electrolyte is raised. When the operating temperature became too high (260°) hydrofluoric acid was introduced into the molten electrolyte until its melting point was reduced to 240°. Since the hydrofluoric acid usually contained traces of water, it was necessary to electrolyze this water before the operation of the cell again became normal.

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The cell was not allowed to cool to the point where the electrolyte completely solidified. When it was necessary to cool the cell the diaphragm was removed and the large container was emptied. Or, another practice was to place a thin copper vessel in the electrolyte which could buckle and take up the strain caused by the solidification of the charge. If this were not done the outer vessel would split at the welded seam.

Time did not permit accurate measurements of the current effeciency or fluorine output. An accurate record was kept of the volume of SF_6 produced over several long runs of about 8 to 10 hours each. Calculations showed that at least 10 litres of fluorine per hour were produced. Actually some of the fluorine was used up in the production of lower fluorides which were not considered in the calculations. For this reason the figure of 10 litres per hour is conservative.

Although meeting most of the requirements for the present work, this generator had two serious faults - insulating material could fall into the electrolyte - conduction frequently stopped for no apparent reason. A third design of generator similar to the above was constructed and will be described by Mr. F. P. Lossing in his report on work done in connection with sulfur fluorides. With this modified design

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the operational difficulties have largely been eliminated, and quantities of fluorine up to ten and twelve litres per hour may be obtained conveniently.

The fluorine produced by the first generator was not purified, but led directly to the reaction vessel. The chief impurities were HF and carbon fluorides.

The fluorine from the second generator was passed over dried KF contained in a horizontal copper vessel 2 inches in diameter and 15 inches in length. This procedure was not entirely satisfactory as KF is not available in anhydrous form but as KF.2H₂O. It is very difficult to remove all the water of hydration from the KF, and in pulverizing the dried lumps, moisture is taken up. NaF was not readily available for this purpose.

When the third generator was used the fluorine was passed through a copper trap kept at 0° and through a series of four glass traps cooled with liquid air. The copper - to glass connection was made gas-tight with sealing wax. As long as the joint was perfectly dry and gas-tight, fluorine did not seriously attack the wax. Much of the HF was removed in the copper trap as the melting point of HF is - 83° and its boiling point 19°. The remainder of the HF and most of the carbon fluorides were removed in the glass traps. Fluorine

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has a melting point of - 220° and boils at - 187°. The liquid air used was chiefly oxygen which boils at - 183°, thus fluorine passed through the traps and contained a minimum of impurities.

(b) Sulfur

-U.S.P. sublimed sulfur was used in the first experiments. In later work the same kind of sulfur, carefully dried in an oven at 110° was used.

(c) Platinized Asbestos

Pulverized asbestos was moistened with a one percent solution of platinic chloride and then heated to dryness in a platinum dish. This material was used as a catalyst in some of the experiments.

Apparatus

In the first preparations of sulfur hexafluoride the fluorine from the V type generator was passed directly over sulfur in a horizontal copper vessel 1 inch inside diameter and 10 inches in length. The reaction products were led to the top of a column of KOH pellets in a glass tube $l\frac{1}{2}$ inches in diameter and 20 inches in length (Figure 4). The connecting tubes of the column were of glass. The tube next to the reaction chamber was badly etched and had to be replaced frequently. A is a glass trap fitted with ground joints and cooled in liquid air. When sufficient product had solidified in A, the trap was transferred to a series of purification bubblers which contained alcohol (B),



water (C) and concentrated sulfuric asid (D) respectively. The stopcock on the side-arm of A was closed and the trap was warmed carefully. This was done by supporting the trap above the liquid air with a clamp and raising it slightly from

time to time so that vapour was slowly and steadily evolved. The apparatus was open to the atmosphere at H which permitted the gases from A to force their way through the purification train and to solidify in trap E which was cooled in liquid air. When A reached room temperature and gas no longer passed through the bubblers, the stopcock at H was closed, the pump __started and stopcock T opened slightly. The bubbling now proceeded and as soon as the pressure in A was slightly below atmospheric, the stopcock on the side-arm of this trap was opened. With experience this operation could be started without a large surge of air through the system. After 15 or 20 minutes the last traces of products were swept out of A and the purification train into E. The stopcock on E was now closed and the whole system evacuated as indicated by the closed-end manometer M. Further purification was effected by fractionating the materials using the traps E, F and G. The first and last fractions were discarded and the remainder stored in the bulb S.

Shortly after work with the above apparatus had been started, it was found that $S_2 F_{10}$ was produced along with SF_6 and that the former was toxic. A new purification apparatus was constructed to separate out pure S_2F_{10} (Figure 5). The reaction products were

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led directly from the reaction vessel into a trap cooled in liquid air, without passing through a KOH column. The purification was achieved by forcing the gas through a bubbler train in the manner previously. described. The train consisted of a series of traps containing concentrated KOH solution A and B, water C, and concentrated sulfuris acid E. This apparatus was used in much the same manner as the first one and sublimations and fractionations were carried out using traps H, J, K and L.

Actually trap D was not introduced until a much later date when analyses of solutions A, B and C were carried out. This empty trap prevented sulfuric acid from reaching the first traps should the movement of the gases be momentarily reversed. At a later date the side tube was attached to the storage volume S, but for convenience is put in this diagram.

Considerable trouble was caused by the clogging of the lower end of the entry tube of bubbler A. This was overcome by using a T tube fitted with a glass rod that could be used to dislodge the deposit. (Figure 6).



Once the problem of purifying the S₂F₁₀ was overcome, much effort was directed to producing the compound in larger quantities. During this period the writer worked in co-operation with Mr. J.T. Hugill.

An apparatus was constructed to carry out the fluerination of sulfur at the temperature of dry ice. (Figure 7.) The inner vessel was a copper cylinder closed at the bottom and filled with a dry ice-acetone mixture.



The outer vessel was of glass fitted with an inlet and two outlets as shown. The lower outlet permitted any liquid that formed to escape; the upper outlet was for gases. Sulfur was supported on a corrugated copper screen. Fluorine and nitrogen were fed in at the inlet and any products were collected in liquid air traps.

On carrying out the reaction of fluorine and sulfur in a glass vessel the surface of the sulfur appeared molten. This suggested passing fluorine through molten sulfur and a glass apparatus was designed as shown in Figure 8. The sulfur vessel was fitted with a cold water jacket to prevent sulfur from vaporizing into the trap containing the products. The sulfur was heated above its melting point in an oil bath. Since a back pressure in the fluorine generator could cause an explosion the reaction vessel was evacuated by an aspirator until this danger was overcome. The pressure in the aspirator line was indicated by an open-end manometer. The products were collected in a trap cooled with liquid air.

Another apparatus (Figure \$) was designed so that sulfur vapour could be fluorinated. The apparatus was made of glass and requires no explanation. The sulfur was vaporized by heating in an oil bath. The centre trap kept at 0° prevented sulfur from reaching the trap containing the reaction products.

The next step was to try fluorinating a compound

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containing two sulfur atoms in the hope of producing S₂F₁₀. Fluovine was first passed over S₂Cl₂ (technical grade) in a horizontal tube. Since S2F10 could have dissolved in the S₂Cl₂ a glass apparatus (Figure 10) was constructed in which S2Cl2 vapour could be blown into a reaction chamber by a stream of undried nitrogen. The quantity of S₂Cl₂ was adjusted by regulating the flow of nitrogen with a flowmeter (Figure 10) and by controlling the temperature of the S2Cl2. For a calculated flow of fluorine of 165 cc. per minute, 60 cc. of Nitrogen per minute were passed over S2Cl2 at 20°. The reaction vessel was electrically heated and insulated with asbestos. The temperature was determined by ther-The reaction vessel was used unpacked as well as mocouples. when packed with glass chips or copper turnings. Lower temperatures were required when the reaction chamber was packed.

Attempts were made to prepare S_2F_{10} from SF_6 by pyrolyzing the latter in a quartz tube. The apparatus was very simple and a diagram is not shown. A quartz tube was electrically wound and insulated with asbestos. The temperature of the tube was indicated by thermocouples and was regulated by suitable rheostats in the heater circuit. Pure SF_6 was stored in a small tank and allowed to pass through the pyrolysis tube at a definite rate, indicated by a flow-meter. The products were collected in a liquid-air trap as in previous

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experiments.

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 SF_6 and hydrogen were passed over platinized asbestos using an apparatus shown in Figure 11. The temperature of the experiments were low so that a glass apparatus could be used. The catalyst was placed in the centre tube and its temperature regulated by an electrical heating circuit. A thermocouple was used to indicate the temperature within the vessel. SF_6 and hydrogen were metered into the reaction vessel at rates of 25 cc. per minute and 12.5 cc. per minute respectively. The reaction products were collected in a liquid air trap. Other catalysts tried were nickel and activated alumina.



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An attempt was made to react SF_6 with sulfur. Some sulfur was placed in a 250 cc. steel bomb fitted with a valve and pressure gauge. The bomb was evacuated, cooled in liquid air and 13 litres of pure SF_6 were condensed into it. The bomb was allowed to come to room temperature and then heated to 230°.

A study was made of the stability of S_2F_{10} . An apparatus (Figure 12) was constructed to determine the decomposition temperature of the compound. The system was connected to the purification apparatus and a sample of pure S_2F_{10} was condensed into one of the bulbs. The U tube was heated by means of a glycerol bath to a desired temperature. Pure S_2F_{10} was condensed from one bulb at room temperature into the other held at 0°, at various temperatures of the U tube. Decomposition interfered with this transfer and thus indicated when the decomposition temperature was reached.

It was desirable to know the effect of fluorine on S_2F_{10} . For this investigation a glass apparatus was constructed as shown in Figure 13. The traps were detachable and fitted with stopcocks so they could be weighed at room temperature. The S_2F_{10} was forced into the fluorine stream by a flow of nitrogen (25 cc. per minute). The quantities of material used were small hence the traps were small, - approximately 25 cc.. The fluorinating chamber was about 40 cc. in valume

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and was heated with a glycerol bath to any desired temperature. The gases from the heated vessel were cooled by passing them through a tube kept at 0° and were then collected in a liquid air trap. Transfers were made through the fluorine stream at regular temperature intervals of the fluorinating vessel. After each transfer the trap finally containing the S_2F_{10} was allowed to come to the temperature of dry ice - and then evacuated. Any SF6 that was formed was pumped off and any remaining S_2F_{10} was weighed. When a sufficiently high temperature was reached the sample of S_2F_{10} lost weight. This indicated it was attacked by fluorine or decomposed at the elevated temperatures.

It was noticed the yield of S₂F₁₀ was greater when the reaction vessel was copper rather than glass. Thus various salts were mixed with the sulfur before fluorination, in an attempt to improve the yield. Shortly after this time Mr. J.T. Hugill went on active service and the writer worked in co-operation with Mr. F.P. Lossing. A new type of reaction vessel was designed (Figure 14) and used in much of the work involving mixtures of sulfur and salts (stable to fluorine). The reaction tube was a heavy copper pipe 1 inch inside diameter and 30 inches in length. The inlet and outlet tubes passed through fittings which were threaded to fit the ends of the reaction vessel. It was fitted with a small copper tube,

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Fig. 14.

(closed on one end) into which a thermocouple could be thrust to measure the temperature of the reaction vessel at various points over its entire length. The copper vessel was surrounded by a metal cylinder 6 inches in diameter, that was waxed on at the ends. The outer container held ice and water to cool the reaction vessel during some of the experiments.

Density determinations on the gases were made using a glass bulb fitted with a ground joint and stop-cock. The bulb was calibrated using boiled distilled water. The pressures were calculated from measurements made on a mercury manometer with a cathetometer.

The first toxicity tests were carried out by the Biochemistry Department of McGill University. The animals were exposed in closed chambers in which the gases were circulated with a mechanically operated fan. The gas to be tested was displaced from the sample tube with mercury and forced into the chamber. The volumes of the chambers used were 10 litres, 29 litres and 110 litres.

In later work a flow system was designed and used in this laboratory (Figure 15).



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The chamber C was a glass cylinder about 2 litres in volume. The diameter of the charcoal tube B was such as to require a flow of 720 ccm. per minute regulated by the flowmeter F. A was a calibrated burette into which a known quantity of S2F10 was measured and then diluted with air to 100 cc., in the burette. Mercury was then run in the side tube at such a rate as to force the S₂F₁₀ - air mixture into the air stream in exactly one hour. In phosgene experiments a drop of oil was placed on the exposed mercury in the manometer and gas burette. To produce a gas mixture of 1/5000 of SgF10 and air, the bulb E containing S2F10 was held at 20°, (vapour pressure of S2F10, 550 mm). The burette was filled to 11.6 cc., with mercury in the side tube at the level necessary to make up the balance of current atmospheric pressure. The top stop-cock on the burette was closed and the S2F10 in the line was condensed back into E. Air was run into the burette to 100 cc., volume at atmospheric pressure. The air and S2F10 were allowed to stand for several hours to permit complete diffusion. The air stream as measured by F was adjusted to 720 cc., per minute and when the burette was emptied in one hour the concentration of S2F10 in the air stream was 1/5000. The charcoal of suggestions of the C.W.5 variety, was carefully packed in B to a depth of 5 cm. A space velocity of 720 cc., per minute was equivalent to 32 litres per minute through a service canister.

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RESULTS AND DISCUSSION

I. Preparations using Sulfur and Fluorine

(a) At ordinary temperatures

The first samples of sulfur hexafluoride were prepared using the V type generator and the purification apparatus shown in Figure 4. Fluorine was passed over the sulfur in a copper tube (Figure 4) and the reaction proceeded spontaneously. The temperature of the reaction vessel reached approximately 50°. The gaseous products could have been sulfur vapour, traces of sulfur-dioxide, fluorine, hydrogen fluoride and fluorides of sulfur, chief of which was sulfur hexafluoride. All these gases with the exception of SF6 and sulfur vapour react with KOH. The existence of S₂F₁₀ was not known at this time. Reaction of the gases with the KOH was quite violent and considerable heat was produced. A heavy liquid formed in the KOH pellets and caused clogging in the column. This made it necessary to change the purification apparatus to the design shown in Figure 5.

At the temperature of liquid air sulfur hexafluoride is a white solid. It sublimes at - 63.8° to a colorless, odorless and inert gas. In the first preparation the sample was small and only the first part of one termined from the following.

Volume of density bulb 319.9 cc.

Weight of bulb and hexafluoride = 102.1285 gm.Weight of bulb= 101.3277 gm.Weight of sulfur hexafluoride0.8006 gm.

at 331 mm. pressure and 23.6° Applying the ideal gas law and using the relation

$$PV = \frac{g}{M} RT$$

the Molecular weight = 149.75 (correct 146.1). This sample was considered sufficiently pure for preliminary toxicity tests.

To test the toxicity of sulfur hexafluoride five mice were exposed to a concentration of one part in 1000 of sulfur hexafluoride to air. The mice showed no discomfort for the first half hour. At the end of an hour the mice were removed from the gas chamber and appeared to be uncomfortable. After one and a half hours in the fresh air one mouse was dead. In two and a half hours all the mice were dead.

A second sample of sulfur hexafluoride was prepared and being a larger sample both the first and last fractions were discarded. The molecular weight was determined in the same manner as for the first sample and was 143.2. This sample was tested for toxicity using the same concentrations and conditions as for the first sample. The second sample was not toxic. A toxicity test was repeated on the first preparation and the results were identical with the first test. However, the treatment of the two samples differed. In the first preparation the higher boiling fraction was retained but in the second it was discarded. The molecular weight of the first preparation was higher than of the second, indicating the presence of a high molecular weight fraction in the former. It was recalled that during the fractionation of the first preparation after the white solid had sublimed (SF_6) a small drop of liquid remained momentarily in the bottom of the bulb. This liquid was considered to be the heavy molecular weight fraction.

A third large sample of impure SF_6 was prepared with every precaution to retain all of the liquid fraction. In this case the impure SF_6 was fractionated from a bulb at the temperature of dry ice into one at the temperature of liquid air. A molecular weight determination was performed on the heavy fraction and it was refractionated. The molecular weights during three fractionations were as follows:

Fractionation	Molecular weight
l	196.4
2	211.4
3	253 ,9

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A fourth sample was prepared and the high molecular weight fraction was fractionated three times giving the following molecular weights.

Fractionation	Molecular weight
1	247.8
2	252.9
3	252.6

A search through the literature revealed that disulfur decafluoride had been reported by Denbigh and Whytlaw-Gray (14) (15) and its molecular weight was 254.

The second generator was now in operation and a 2 gram sample of S_2F_{10} was prepared. Extensive toxicity tests were carried out to determine the merits of the compound as a lethal agent. The results of these tests will be given in a later section.

All subsequent effort was directed towards finding a method of preparing larger quantities of S_2F_{10} . For this reason the properties and physical constants of S_2F_{10} were not rigorously determined. The values of the melting point, boiling point, and vapour pressures of S_2F_{10} prepared, agreed with those reported by Denbigh and Whytlaw-Gray (14) (15). Thus the identity of the compound was established. Since the vapour pressure of SF_6 is approximately 400 mm. at dry-ice acetone temperatures and that of S_2F_{10} is negligible, a very efficient separation could be performed at that

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temperature. To determine the ratio of S_2F_{10} to SF_6 the gases were fractionated and expanded into calibrated volumes. The purity of the gases was shown by molecular weight determinations. Calculations showed that, on the average, in the first preparations the S_2F_{10} made up approximately one percent by volume of the S_2F_{10} and SF_6 gas mixture.

(b) At the temperatures of dry-ice and acetone.

It was thought that by reacting the fluorine and sulfur at - 78° the reactivity of the fluorine would be reduced, producing more S_2F_{10} and less SF_6 . With the apparatus shown in Figure 7 a fluorine stream of 165 cc. per minute diluted with 100 cc. per minute of nitrogen was used. At this temperature no increase in the ratio of S_2F_{10} to SF_6 was noted.

(c) Fluorine and liquid sulfur.

The possibility of the reaction taking place in the liquid phase suggested passing fluorine through liquid sulfur. The apparatus used is shown in Figure 8. The flow rates of fluorine and nitrogen were the same as in the previous experiment. The results were not distinctly different and there was no definite increase in the quantities of S2F10 produced.

II. Preparations using Sulfur Compounds and Fluorine

(a) Fluorine and sulfur chloride.

Denbigh and Whytlaw-Gray measured the parachor of S_2F_{10} and from it deduce that a sulfur-sulfur bond exists in the molecule. This suggested fluorinating compounds containing two sulfur atoms, for example S_2Cl_2 . The apparatus was previously described and shown in Figure 10. For a calculated flow of fluorine of 165 cc. per minute, 60 cc. of nitrogen per minute were passed over the S_2Cl_2 at 20°. Fluorine did not react appreciably with S_2Cl_2 at room temperature. It was necessary to raise the temperature of the reaction vessel to 400° before all the fluorine was made to react. When the reaction chamber was packed with glass chips or copper turnings a temperature of 200° was sufficient to cause the fluorine to react completely. In these experiments SF_6 was produced but no S_2F_{10} .

When fluorine escapes from a tube it will ignite a gas jet since hydrocarbon gases ignite on contact with fluorine. This principle was used in the detection of leaks in the generator and in the fluorine line. In the above experiment when the reaction vessel was at room temperature sufficient fluorine passed through the apparatus to ignite a gas jet at the exit of the liquid-air trap.

(b) Fluorine and Carbon disulfide

Fluorination of CS2 produced an explosion and this

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reaction was discarded.

(C) Fluorine and sulfur monofluoride

Mr. E. J. Wiggins prepared S_2F_2 according to the method of Centnenszwer and Strenk (11) (12) in the hope of fluorinating it to S_2F_{10} . The S_2F_2 decomposed as rapidly as it was formed leaving a deposit of sulfur in the apparatus and the plan.was abandoned.

III. Decomposition of SF6

(a) Pyrolysis

When SF₆ was passed through a quartz tube it did not decompose until the tube was heated to redness. The products of the decomposition reacted with the quartz probably producing SiF₄. Sulfur was deposited in the cooler part of the tube. No S₂F₁₀ was produced. Since there was apparently no way of controlling the decomposition, the plan was abandoned.

(b) Hydrogen and catalysts

 SF_6 and Hydrogen were passed over platinized asbestos in an apparatus shown in Figure 11. At a temperature of 200° the SF6 was reduced to sulfur and the HF produced absorbed in KF. It was not possible to control this reaction to produce any intermediate products between sulfur and SF_6 . Other catalysts used were Nickel pellets and activated alumina but a temperature of 400° was necessary to cause a reduction. Again, no intermediates were detected. (c) Sulfur and Sulfur hexafluoride

Sulfur and SF_6 were placed in a bomb, and the temperature was raised to 230° - pressures up to 100 atmospheres were produced. There was no reaction.

IV. Experiments on S₂F₁₀

(a) Thermal decomposition

To determine the decomposition temperature of S2F10 the apparatus shown in Figure 12 was used. At room temperature the vapour pressure of S_2F_{10} is 600 mm. and at 0° it is 230 mm. Decomposition produced SF6 which interferred with the transfer of S_2F_{10} from the bulb at room temperature to the one at 0°. The transfers were difficult when the U tube approached 200° and impossible at 215°. A molecular weight determination of the products indicated SF6 was produced. There was a slight deposit of sulfur in the apparatus. This work was not pursued further and from the information obtained, it was not possible to suggest a mechanism of the decomposition. A slow decomposition may take place at lower temperatures.

(b) Storage

S2F10 was stored in a glass bulb for a month. On removal its molecular weight was 252, indicating no decomposition had taken place. A toxicity test showed the sample to be as toxic as before storage.

(c) Stability in fluorine

To determine whether S2F10 was an intermediate in the

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formation of SF_6 , it was exposed to fluorine at different temperatures, using the apparatus shown in Figure 13. There was no indication of fluorine attacking S_2F_{10} until the fluorinating chamber reached a temperature of 200°. At higher temperatures the rate of the reaction increased. This indicates that S_2F_{10} is stable in fluorine up to temperatures approaching its decomposition temperature.

V. Fluorination of Sulfur and Salt Mixtures

Various salts were mixed with the sulfur before fluorination. Since using a copper vessel seemed to produce slightly improved yields of S_2F_{10} , various copper salts were mixed with the sulfur. These included powdered CuO, CuS, and CuF₂ in dilutions up to equal weights of sulfur and salt. There was no marked increase in the yield of S_2F_{10} .

For a time the writer worked on another problem. In the interests of continuity several developments during that period are mentioned here. The problem has received the attention of workers in other laboratories and their most significant findings influenced the course of the work at McGill.

Alexander, working in the C.W. establishment of the National Research Council, Ottawa, found that - NaHF₂ mixed with the sulfur produced a marked increase in the yield of S_2F_{10} . Schneider in the same laboratory, carried out experiments using NaF, NaHF₂, KHF₂, KF.3HF, cryolite and CuF₂ in various proportions with the sulfur. The yield of S_2F_{10} was not consistent with the amount of diluent used in each case, but was increased by NaHF₂, KHF₂, KF.3HF and cryolite. The average high yields of S_2F_{10} reported, were 12.5 % by volume or 20.0% by weight of the purified gases. NaF and CuF_2 were not found effective in increasing the yield of S_2F_{10} .

Burg working at the University of Southern California prepared S_2F_{10} by passing fluorine diluted with nitrogen over sulfur. The reaction vessel was of copper, one inch inside diameter and 30 inches in length - cooled in an air blast. The best yield of S_2F_{10} was produced by a fluorine flow of 5.0 litres per hour diluted with ten times the volume of nitrogen. In this experiment the yield based on sulfur is not definitely known. However for a flow of 4.6 litres per hour of fluorine and 40 litres per hour of nitrogen the yield of S_2F_{10} was 9.0% based on the sulfur used. The results of Schneider's work and of Burg's work are not comparable since the data of the former gives the yield on the products collected (SF₆ and S_2F_{10}) while the data of the latter gives yields on the amount of sulfur used. It will be shown later, that as much as 50% of the sulfur could have been used to produce lower fluorides.

F. P. Lossing at McGill found that careful drying of

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the sulfur improved the yield of S_2F_{10} , and that KF was more effective as a diluent than KHF₂. These salts were carefully dried and powdered. When the fluorine was diluted with nitrogen and the sulfur with KF the yield was again improved. For example using a mixture of 75 grams of KF with 5 grams of sulfur and 165 cc. per minute of fluorine diluted with 300 cc. per minute of dried nitrogen the yield of S_2F_{10} (based on the S_2F_{10} and SF_6 produced) was 24% by weight. CaF₂ was much less effective in improving the yield of S_2F_{10} than the above salts. NaF was as effective as KF.

The work reported below was done by six people working in three groups of two on eight hour shifts. They were J.C. Arnell, J. Davis, F.P. Lossing, L. Siminovitch, A.P. Stewart and the writer. There was a request from the C.W. establishment, National Research Council, Ottawa, for 60 gm. of pure S2F10. During the preparation of this material, the procedures were varied to clear up two problems. (1) To develop a system of analysis which would account for all the sulfur used ie. for the lower fluorides as well as the SF6 and S2F10.

(2) To find the best conditions for the production of S_2F_{10} . This concerned the proportion and nature of the salt used to dilute the sulfur, the dilution of the fluorine with nitrogen and the temperature of the reaction vessel.

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To save time, the SF_6 and S_2F_{10} were not fractionated, as in the first part of the work, to determine the ratio of the two gases. The products of the run were purified and expanded into the storage volume. When the gas composition was uniform, a sample was weighed in the density bulb. Knowing the volume of the manifold, and of the storage bulb it was possible to calculate the volume and pressure of these two gases for each run. At the same time a sample was taken for a density determination. From the density, the percentage of S_2F_{10} and SF_6 in the whole sample was calculated. The weight of sulfur in the SF_6 and S_2F_{10} was also calculated.

From previous experience S_2F_2 was known to be very unstable and decomposed rapidly leaving a deposit of sulfur. In the early part of the runs a yellowish band appeared in the upper part of the first traps. This may have been sulfur produced by the decomposition of S_2F_2 as the products left the reaction vessel. Most of the runs were continued until all the sulfur was used and fluorine escaped from the collecting traps. Under these conditions the sulfur produced by the decomposition of S_2F_2 would be fluorinated chiefly to SF_6 as in the ordinary fluorination of sulfur. At the end of the runs there was no yellowish band in the traps and there was

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no evidence of sulfur in the traps or purification train. This indicated that at the end of the runs there was little or no S_2F_3 in the products of the fluorination process. However, it does not preclude the possibility that S_2F_2 was present during the course of the fluorination.

The lower fluorides react with NaOH solution according to the following equations (11) (12) (13).

 $2S_2F_2 + 6NaOH - 4NaF + Na_2SO_3 + 3S + 3H_2O_4$

 $SF_4 + 6NaOH - 4NaF + Na_2SO_3 + 3H_2O.$

The Na₂SO₃ and S are equivalent to the lower fluorides but under the conditions of the fluorination the second reaction is considered to account almost completely for the lower fluorides. The method of analysis did not include an oxidation of free sulfur to sulfate. Once the procedure of analysis was known to be satisfactory for sulfites the sulfur accounted for was approximately 100% of the sulfur used. This indicates there had been little free sulfur present and confirms the previous statement that little or no S_2F_2 was present in the reactio: products as analyzed.

The Na_2SO_3 was oxidized to Na_2SO_4 by H_2O_2 and then precipitated by $BaCl_2$ as $BaSO_4$. Since BaF_2 is insoluble, fluorides interfered with the precipitation of the $BaSO_4$. An attempt was made to precipitate the sulfate as benzidine hydrogen sulfate by the benzidine hydrochloride method (23) (24) (25) (26). This method did not prove satisfactory in the presence of fluorides and was discarded. The final procedure was based on a method developed by A.A. Borkovskii and N.A. Porfir'ev at Zavodskaya Laboratories (27). The method depends on the presence of B (OH)₃ to fix the fluoride as BF_4^{\pm} ion which prevents the formation of insoluble BaF_2 . In the work of Borkovskii, et al, 3 cc. of concentrated HCl and 3 gm. of B(OH)₃ were added to a one gram sample of NaF (containing sulfate), in 200 cc. of water. The accuracy of the determination depends on the concentration of HCl and B(OH)₃.

To test this method of analysis a series of solutions containing the following quantities of materials were made up:

Weight in grams of	1.	2.	3.
Na ₂ SO4	0.1585	0.1585	0.1585
Na2SO3	0.0997	0.0997	0.0997
KF 2HoO	0.7856	1.8030	2,3118

The samples were diluted to 300 cc. and treated with 2 cc. of concentrated HCl and 2 cc. of a solution of H_2O_2 . The solutions were boiled for half an hour to destroy any excess peroxide. 2 gm. of B(OH)₃ were added to each sample and the sulfate was precipitated with a slight excess of BaCl₂ solution (40 mg./litre). The weights of the precipitates were: 1. 2. 3. 0.2867 gm. 0.2991 gm. 0.4081 gm.

(correct 0.4390 gm.)

If only the original sulfate had been precipitated the weights of the precipitates would have been approximately 0.26 gm. It would appear that the oxidation of Na₂SO₃ to Na₂SO₄ was incomplete. In addition there must have been BaF₂ precipitated as there was an increase in the weight of the precipitates with increasing fluoride ion concentration. This indicates that insufficient $B(OH)_3$ had been added.

A second series of solutions was made up as follows:

Weight in grams of	1.	2.	3.
Na2S04	0.1746	0.1746	0.1746
Na2SO3	0.1449	0.1449	0.1449
KF.2H ₂ 0	1.0170	1.5255	2.0340

These samples were treated as before except that 5 cc. of concentrated H_2O_2 were added to each and 4 gm.. of $B(OH)_3$. The weights of the precipitates were:

> 1. 2. 3. 0.5213 gm. 0.5545 gm. 0.7982 gm.

> > (correct 0.5552 gm.)

These results indicate that as in the previous series of solutions, oxidation of the sodium sulfite was incomplete and insufficient B(OH)3 had been added.

A new supply of H_2O_2 was used containing at least 30% peroxide. As mentioned previously the unknown solutions that were to be analyzed were saturated with NaF. The third solutions were made up as follows:

Weight	in	grams	of	1.	2.
Na_2SO_4				0.3765	0.3765
Na2SO3				0.9859	9.9859
Naf				saturated	saturated

To each sample was added 2 cc. of concentrated HCl and 5 cc. of concentrated H_2O_2 . 4 gm. of B(OH)₃ was added to sample No.1 and 2 gm. to sample No.2. Precipitations were carried out as previously giving the following weights:

1. 2.

2.2045 gm. 2.2003 gm.

(correct -2.443 gm.)

This indicates that the oxidation of sodium sulfite was incomplete and that BaF₂ was not precipitated.

A fourth solution was made up as follows:

Weight in grams of	1.
Na2 50 4	0.1882
Na ₂ S03	0.4930
Naf	saturated

To this sample was added 1 cc. of concentrated HCl and 5 cc. of concentrated H_2O_2 . Sample was boiled for half an hour and then 4 gm. of $B(OH)_3$ were added. The precipitate in this case weighed 1.2151 gm. (correct - 1.2210 gm.). Further tests indicated that this method of analysis was satisfactory.

The procedure finally adopted was as follows. The KOH and water solutions of the purification train were removed from their containers and made up to 1000 cc. in a volumetric flask. A 50 cc. aliquot part was removed and

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neutralized with HCl using phenolphthalsin as an indicator. One cc. of concentrated HCl was added in excess. Five cc. of concentrated H_2O_2 were added and the solution was made up to 300 cc. After boiling the solution for half an hour, 4 gm. of B(OH)₃ were added, and BaSO₄ was precipitated with BaCl₂ solution (40 mg./ litre). The solution was filtered using a sintered glass filtering crucible. The precipitate was washed with 10 cc. of water and 10 cc. of acetone - then dried in an oven at 120° before final weighing.

To study the conditions under which S_2F_{10} could best be produced, a series of experiments was performed in which the flow rate of fluorine was kept as uniform as possible by adjusting the electrolyzing current to 10 amp. The flow rate of the nitrogen was shown by a flow meter, and varied from 100 cc. to 500 cc. per minute. NaF was used because it was simpler to dry than KF. The proportions of sulfur and salt were varied. In a few experiments the reaction tube was placed in a cooling bath of ice and water.

In all the experiments the salt and sulfur were carefully dried before being placed in the reaction vessel. The nitrogen was dried by passing it through a column of KOH pellets and two scrubbers containing concentrated sulfuric acid. The fluorine was purified as previously described. The amount of sulfur used was calculated by weighing either the charged reaction tube, or the sulfur and salt mixture, before and after fluorination. The first procedure was preferred as it was difficult to charge and unload the tube

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without losing some of the solid. When the reaction tube was surrounded by the metal container of the ice-bath, it was necessary to use the second procedure. In each experiment temperatures were taken at half-hour intervals at four points within the reaction tube by means of thermocouples. (Fig.14). Position No.1 was one-quarter of the way down the tube from the fluorine entrance and position No.4 was next to the exit tube. When the fluorine stream was diluted with nitrogen there was danger of some of the products being blown through the collecting trap. Several liquid-air traps were used (up to six) in series and in parallel, to prevent the loss of products. When high flow rates of nitrogen were used the last liquid-air trap was packed with small pieces of copper screen as an extra precaution against loss of products. In most cases the reaction was run to completion, i.e. until the temperatures within the reaction tube indicated that the sulfur had all been fluorinated. When high flow rates of nitrogen were used, fluorine could be detected at the exit of the liquid air traps some time before the temperature within the tube indicated that the reaction with sulfur was complete. When all the sulfur was fluorinated the generator was stopped and nitrogen passed through the reaction tube and liquid-air traps for approximately one hour. This served to remove all the products from the reaction tube and to clear the fluorine from the liquid-air traps. If the reaction tube had been cooled during the fluorination, the ice and water were removed from the outer container and the tube was heated to drive out all the products during the clearing-

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out process. The products were now put through the purification train. The S_2F_{10} and SF_6 were freed of CF_4 by pumping on the solid condensed in liquid air. They were then expanded into calibrated volumes and a density determination made. The average molecular weight was then calculated as well as yields based on sulfur. The bubbler solutions were analyzed as previously described.

The following are representative data:

Run No.30

Ratio of NaF to sulfur - 75 grams to 5 grams.

Nitrogen - 300 cc. per minute.

Weight of reaction tube before fluorination 1715.38 gm. Weight of reaction tube after fluorination 1710.87 gm.

Sulfur used 4.51 gm.

Time started 12:10

Temperatures and positions of thermocouples.

Time	<u>1</u>	2	3	<u>4</u>
12:30	56°	60 °	50°	40°
1:20	52°	68°	58°	48°
2:00	40°	44 °	46°	41°
2:30	37°	38°	37 °	36°
2:50	36°	36 °	36°	36°
3:10	28°	28°	29°	28°
	•		,	

Time stopped 3:10.

Nitrogen was passed through tube for 50 minutes after turning off the fluorine generator.

Analysis of S2F10 and SF6

	•
Volume	5835 cc.
Pressure	183.7 mm.
Temperature	299.9° K.
Weight	0.8917 grams
Average molecula:	r weight 174.6 (26.5% S ₂ F ₁₀)
Weight of S ₂ F ₁₀	3.86 grams
	- representing 21.6% of sulfur used
Weight of SF ₆	6.18 grams
	- representing 30.0% of sulfur used

Analysis of lower fluorides

Weight of precipitate of BaSO₄ - 1.502 gm. for a 50 cc. aliquot part of 1000 cc. sample representing 2.065 gm. of sulfur or 45.8% of sulfur used. Total sulfur accounted for: 97.4% of sulfur used.

It is noted that as the reaction proceeded, a temperature gradient gradually moved along the reaction tube. This indicated a rapid reaction of the fluorine with sulfur which produced local heating. The temperature peak progressed along the tube as the sulfur was fluorinated.

In the following tables, the most significant data from the series of runs made during the progress of the work are recorded. In some runs the generator failed to function properly or the apparatus leaked. The data of such runs are omitted.



TABLE I

Run No.	Nitrogen cc./min.	NaF t. 5 gm.S	Sulfur used	Time of run	Max. Temp	%S as • ^S 2 ^F 10	% S as SF6	% S as SF4+ S ₂ F2	Total Sulfur analyzed
3	0	0	5	in min.) 180	-	0	63.8	15.5	79.3
4	0	0	5	240	-	0	69.6	14.5	84.1
5	0	0	5	165	-	0	73.1	14.2	87.3
7	100	0	5	180	68	4.2	56.8	15.5	76.4
1 1	100	0	5	220	70	4.72	30.2	8.32	43.2
16	250	75	1.83	60	45	16.6	23.7	20.7	60.0
17	250	75	4.5	120	68	24.0	25.4	26.2	75.6
12	300	75	3.82	120	64	24.1	22.4	27.6	74.2
21	300	75 3	2.78	80	53	11.9	12.9	49.6	74.4
25	300	50	4.72	115	55	21.6	15.5	25.7	62.8
26	300	50	2.10	60	?	16.6	17.3	83.8	117.7
27	300	50	3.74	120	68	16.1	38 .6	42.5	97.2



TABLE II (reaction tube uncooled)

Run No•	Nitrogen cc./min.	NaF to 5 gm.S	Sulfur used (j	Time of run in min.)	Max. Temp.	% S as ^S 2 ^F 10	% S as SF ₆	% S as SF4+ S ₂ F2	Total Sulfur a	nalyzed
42	0	75	5.0	120	40°	3.5	33 . 2	25.3	62.0	
43	100	75	5.0	230	20	15.7	18. 3	61.8	95.8	
44	200	75	4.9	165	16	9.6	13.4	70.0	93 . 1	
54	200	75	4.81	160	40	20.3	24.9	50.4	95.6	
56	200	75	5.0	160	16	19.9	35.1	49.5	104.4	
45	300	75	4.95	150	20	17.5	11.1	63.1	91.7	
50	300	75	4.97	210	18	24.1	18.2	55.3	97.6	
49	400	75	4.83	190	18	17.2	16 .0	67.3	100.5	
55	400	75	4.99	225	12	18.7	18.1	64.7	101.5	
51	500	75	4.90	160	36	14.5	15.1	67.8	97.4	

TABLE III (reaction tube cooled)

N ₂ cc. per min.	NaF to 5 gm_S	% S as S ₂ F10	% S as SF6	% S as SF ₄ + S ₂ F ₂	Total Sulfur	analyzed
0	75	5.0	58.2	29.2	92.5	
100	75	12.6	35,8	44.3	92.7	
200	75	12.3	28;0	50 .7	91.0	
300	75	18.4	26.9	53 . 5	98. 8	
400	75	17.8	23.2	58,5	99.4	
500	75	16.7	25.0	53 . 3	95.0	
Ng cc. per min.	<u>T</u> NaF to 5 gm.S	ABLE V % S as ^S 2 ^F 10	(average % S as SF ₆	of III) % S as SF ₄ + S ₂ F ₂	Total Sulfur	analyzed
0	75	3,5	33,2	25.3	62.0	
100	75	15.7	18.3	61.8	95.8	
200	75	16.6	24.5	56.6	97 . 7	
300	75	20.8	14.6	59.2	94.6	
400	75	18 .0	17.0	66.0	101.0	
500	75	14.5	15.1	67.8	97.4	

TABLE IV (average of II)

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The average molecular weights used in Table I were not accurately determined due to an error in technique. The purified samples containing S₂F₁₀ and SF₆ were expanded from the fractionation bulbs into the storage bulb. After the gases had diffused, they were expanded into the density bulb. In this procedure S_2F_{10} went into the storage volume last, and thus filled the manifold. In the expansion for the density determination, S₂F₁₀ from the manifold entered the density bulb first. A considerable time was required for the gases to diffuse completely, and in many cases insufficient time had been allowed. This meant that the values of the gas densities were too large and that the calculated yield of S_2F_{10} was too large. Also the lower fluoride analysis had not been worked out completely and the sulfur balance in the earlier runs was not satisfactory.

To obtain reproducible densities a side-tube was attached to the storage bulb. The S_2F_{10} and SF_6 from each run were condensed into this side-tube and the stopcock on the storage bulb closed. The gases were allowed to expand into the storage bulb from the side-tube. Since the sidetube was small compared to the storage volume (20 cc. to 6 litres), and the opening of the side-tube was large, the diffusion process was complete in a short time. After two hours the gases were expanded into the density bulb, and the usual calculations made.

The data of Tables II and III were calculated from

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correct density determinations. In addition, the lower fluoride analysis was sufficiently accurate to make the sulfur balance satisfactory. The discrepancies in the sulfur balance were often due to errors in calculating the quantity of sulfur used. The difficulties of weighing the sulfur and salt mixture have already been indicated. The runs listed in Table II were made with the reaction tube uncooled, whereas the runs listed in Table III were made with the reaction vessel cooled in an ice bath. Tables IV and V are made up from Tables II and III respectively. They show the average yields of S_2F_{10} , SF_6 and lower fluorides at various flow rates of nitrogen, and are calculated on the basis of sulfur used.

The data of Table I cannot be considered important because of the errors in the gas density determinations and the lower fluoride analysis. Some general statements may be made concerning the information as listed. Dilution of fluorine with nitrogen favoured the production of S_2F_{10} . The higher nitrogen flow rates produced the best yields of S_2F_{10} . Dilution of the fluorine with nitrogen in conjunction with mixing the sulfur with NaF greatly increased the yield of S_2F_{10} . At the same time the yield of SF_6 was reduced and the yield of lower fluorides was increased. For reasons previously discussed the lower fluorides will be considered as chiefly made up of SF_4 .

The data of Tables II and III can be most conveniently represented by plotting the data of Tables IV and V (Fig.16). The circles represent the various products

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when the reaction tube was cooled with an ice bath. The triangles represent the products when the reaction tube was not cooled. The experiments on which these data are based are too few to enable one to draw definite conclusions, but possible mechanisms of the reaction may be discussed.





When pure fluorine reacts with sulfur the reaction is so violent that a faint blue flame appears on the surface of the sulfur. Locally, the temperature of the reaction may reach many hundred degrees. All the sulfur fluorides might possibly be produced in the ordinary fluorination of sulfur, but the average life of many of them would be very short. At the temperature of the reaction they would be immediately fluorinated, for the most part, to SF_6 which is the end point of the fluorination. If the temperature of the reaction were reduced, some of the lower fluorides might escape from the high temperature region. Since S_2F_{10} decomposes at temperatures as low as 160° (Laidler - N.R.C.Ottawa) temperature control is an important factor in the production of the compound.

The flow of nitrogen may remove the products from the seat of the reaction more quickly so that more lower fluorides appear in the products. The lower fluorides should increase with increasing flow rates and this is actually the case as represented in Figure 16.

The effect of adding salt to the sulfur may be catalytic, or it may serve to conduct heat away from the points of the reaction and thus increase the life of the lower fluorides sufficiently to permit them to escape. The catalyst theory is supported by the fact that only certain salts increase the yield of S_2F_{10} , but certain discrepancies in the results of different investigators make this view less definite. For example, Schneider found that NaF was less effective than KHF₂ in increasing the yield of S_2F_{10} , whereas at McGill the reverse was true. Similarly, if the conduction of heat away from the points of reaction was the only factor in increasing the yield of S_2F_{10} , one would not consider the nature of the salt to be important. Actually NaF improves the yield of S_2F_{10} and CaF₂, a very similar compound, does not. The data

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of Figure 16 are based on a salt mixture of 75 grams of NaF to 5 grams of sulfur. The effect of the proportion of the salt in the reaction mixture cannot be discussed since the number of experiments in which the sulfur to salt ratio was varied are too few. However, when the reaction tube was cooled with an ice bath the yield of S_2F_{10} was slightly increased, the SF₄ considerably increased and the SF₆ considerably decreased. This is in agreement with the previous deduction that a lower reaction temperature favoured the formation of the lower fluorides.

The sulfur fluorides in order of decreasing stability are SF6, S₂F₁₀, SF4 and S₂F₂ - which is also in order of decreasing fluorine content per mole of sulfur. A mechanism representing the formation of S_2 F₁₀ and SF6 may involve the lower fluorides. At ordinary temperatures sulfur probably exists as S₈ chains. When sulfur is fluorinated the sulfur atoms may be stripped from the chains one at a time and fluorinated to SF₂, SF₄ and SF6. Of this series SF4 and SF6 are known to be stable, especially the latter. Occasionally two sulfur atoms may be stripped from the chain and fluorinated progressively from-S₂F₂ through S₂F₄, S₂F₆, S₂F₈ to S₂F₁₀ and perhaps to 2SF₆. An equilibrium system of these steps could be represented as follows:

 $s_2 + F_2 \rightleftharpoons s_2 F_2 + F_2 \rightleftharpoons s_2 F_4 + F_2 \rightleftharpoons s_2 F_6 + F_2 \rightleftharpoons s_2 F_8 \rightleftharpoons$ $s_2 F_{10} + F_2 \rightleftharpoons 2 SF_6$

From whatever equilibrium conditions exist a certain quantity of S_2F_{10} may be obtained. Of the equilibrium

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series S2F2, S2F10 and SF6 are known to exist. Since the trends of the curves in Figure 16 are towards constant values, the equilibrium has apparently been displaced to a maximum. Under the conditions studied the reaction has proceeded to a limiting value, where the maximum of S_2F_{10} was produced. The slope of the S_2F_{10} curve at the right hand end in the uncooled series depends on one experiment. There is no reason for believing that there is a maximum in this graph. It would be much better to consider it as nearly parallel to the abscissa as is the case with the other curves. Attention is again drawn to the fact that although S2F2 was not definitely identified in the reaction products, there is no reason to suppose it did not exist at some point in the course of the reaction. Under the conditions of the experiments the lower fluorides were predominantly SF_4 , as previously indicated.

Two less probable reactions are:

 $SF_6 + SF_4 \longrightarrow S_2F_{10}$

 $2 \operatorname{SF}_4^* \longrightarrow \operatorname{S}_2 \operatorname{F}_8 + \operatorname{F}_2 \longrightarrow \operatorname{S}_2 \operatorname{F}_{10}$

Both reactions would no doubt require some activation. Activation is possible at the reaction centres, but once these products leave the seat of the reaction, under the conditions used, it is doubtful whether there was much opportunity for them to react. SF_6 is very stable and SF_4 , although much less stable, may not be active enough to react with SF_6 at ordinary temperatures. Similarly, SF_4 would require special treatment

to proceed to S_2F_8 and hence to S_2F_{10} . Before discarding these proposals four groups of experiments should be done.

(1) The S_2F_{10} should be removed from the reaction products and an attempt made to react the SF_6 and SF_4 . The latter products could be condensed into a bomb and allowed to come to room temperature or even heated. The change in volumes in this reaction indicates that increasing the pressure would shift the equilibrium towards S_2F_{10} . An active surface may be necessary to make the reaction possible.

(2) SF₄ could be separated from the reaction products and condensed into a bomb along with some fluorine. The reaction could proceed to S_2F_{10} or SF₆, more probably the latter. This experiment would indicate the nature of the equilibrium conditions. If only SF₆ were produced and no S_2F_{10} it would appear that the reaction proceeded directly to SF₆.

(3) The SF4 could be separated from the reaction products and routed through a reaction tube in which the ordinary fluorination of sulfur was taking place. Under these conditions SF4 might be made to react as indicated in the above equations.

(4) S2F2 should be prepared again and an attempt made to fluorinate it to S2F10. With the present experience in handling sulfur fluorides the plan may be much more successful.

Much more information is needed before a satisfactory explanation of the results obtained is possible. At

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present only a general statement can be given. The yield of S_2F_{10} is increased in the sulfur-fluorine reaction by diluting the fluorine with nitrogen and by mixing the sulfur with certain fluorides.

VI TOXICITY TESTS

Toxicity tests were carried out with the cooperation of Dr. R. Noble of the Department of Biochemistry. Tests have been performed on mice, rats, guinea pigs and cats to determine the minimum concentration of fatal doses.

The toxicity tests on mice were performed in a ten-litre chamber. The gas was measured into sample tubes at the temperature and pressure necessary to produce the desired concentration in the chamber. The sample was forced into the chamber with mercury. The increase in pressure was not sufficient to affect the results of the tests. To produce a concentration of 1/1000 in 10 litres required 12.7 cc. of gas at 65.8 cm. pressure and room temperature. For rats and guinea pigs a 29-litre chamber was used and for cats a 110-litre chamber. The volume of these chambers was such that over a period of one hour, the oxygen content was not sufficiently reduced to cause any discomfort to the animals.

For S₂F₁₀ mixed with air the results using five mice for each test were as follows:

TABLE VI

<u>Concentration</u>	Time of Exposure	Mortality	Time of death
1/10,000	30 min.	100%	133 min.
1/10,000	30 min.	100%	127 min.
1/100,000	60 min.	100%	5 hrs.
1/200,000	60 min.	60%	48 hrs.
1/500,000	60 min.	20%	48 hrs.

Using other species of animals the following results were obtained:

TABLE VII

Species	<u>Concentration</u>	Time of Exposure	Mortality	<u>Time of</u> <u>Death</u>
Rats	1/50,000	60 min.	100%	102 min.
	1/100,000	60 min.	100%	278 min.
	1/200,000	60 min.	none	-
Guinea pigs	1/35,000	60 min.	100%	120 min.
	1/50,000	60 min.	100%	193 min.
	1/100,000	60 min.	none	-
Cats	1/50,000	60 min.	100%	278 min.
	1/100,000	60 min.	none	-

Animals which were exposed and did not die were killed and examined at increasing intervals of time after exposure. That is, if five rats were used and all survived, one would be examined each day or at various intervals to determine the nature of the physiological effect. Fluid seemed to remain in the lungs. It was thought that by using several exposures the effect would prove cumulative. Rats were exposed to a concentration of $S_{2}F_{10}$ of 1/200,000 for one hour each day, for four consecutive days. Although they were definitely affected, there were no fatalities.

To compare the toxicity of S_2F_{10} with other known poisonous gases one may use Haber's formula: ct = W, where c is the concentration in milligrams per cubic meter, t the time of exposure in minutes, and W the product of mortality or lethal index.

Prentiss (28) lists the lethal index according to American data for some common poisonous gases, for

example: phosgene 5,000 chloropicrin 20,000 chlorine 56,000 hydrocyanic acid 2,000

These results are for dogs and mice. From experiments conducted on mice using S_2F_{10} the lethal index calculated for an exposure of 60 minutes in a concentration of 1/200,000 (60% mortality) is 3,000. Prentiss (28) points out that, for longer periods of exposure and reduced concentrations, the lethal index increases. Thus the lethal index

for S_2F_{10} calculated for larger concentrations and for short exposure periods would be expected to be smaller. The lethal index given above is calculated for conditions showing a larger lethal index (i.e., lower toxicity).

Marked differences in toxicity data are found in the literature. Slight variations in the technique of various investigators may account for some of the discrepancies. Changes in the concentration of the gas being tested may take place when the animals are exposed in closed chembers. Some of the material is absorbed by the respiration of the animals, some by adsorption on the walls of the container or on the fur and skin of the animals. R. L. McIntosh and the writer made an elementary analysis of concentration changes brought about by absorption of the poisonous materials by the respiration of the animals in closed chambers. The analysis proceeds as follows:

Let V be the volume of the chamber in cc.

v - the lung volume in cc. breathed per animal per second.

n - the number of animals.

Co - the initial concentration of toxic material in weight per cc.

- the fraction of toxic material retained in the lung on each breath.

As a first approximation we may consider the n

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animals to breathe in unison. Then the amount of toxic material remaining at the end of the first breath is

$$Co - n \propto v Co$$
(1)

and the concentration

$$C_{1} = \frac{CO \nabla - n \sim \nabla CO}{\nabla} = C \left(1 - \frac{n \sim \nabla}{\nabla}\right) \quad (2)$$

On the second breath $n \propto v \cdot \theta_1$ is absorbed provided we assume that \propto does not change with concentration and the concentration remaining is (3)

$$C_1 - \frac{n \cdot \nabla C_1}{V} = C_2 = C_1 \left(1 - \frac{n \cdot \nabla V}{V}\right) = Co \left(1 - \frac{n \cdot \nabla V}{V}\right)^2$$

and so on for each breath, whence

$$B_{y} = Co \left(1 - \frac{n \propto v}{v}\right)^{y}$$
 (4)

where C_y is the concentration of the yth breath, and y is the number of breaths. The arithmetic mean of the concentration is given by the sum of all the concentrations divided by the total number of concentrations, that is, $y = \frac{y + \cos(1 - \frac{n \cdot e \cdot v}{V}) + \cos(1 - \frac{n \cdot \infty \cdot v}{V})^2}{\sqrt{y}}$ etc. (5)

or
$$Ca = \frac{Co (1 - (1 - \frac{n \propto v}{V})^{y})}{y \frac{n \propto v}{V}}$$
 (6)

If the animals are not assumed to be breathing in unison, the breathing may be considered as continuous and the following relationship holds:
It is apparent that reliable results can only be obtained by using large chambers and short runs. With large numbers of animals or large animals the errors could be great. In the next group of toxicity tests the flow system (Figure 15) was used to overcome the above problem.

In the flow system higher concentrations were used, for example 1/1000 to 1/5000 and exposure times were reduced by stages to 30 seconds. In these short exposures precise values of the concentration are not known for two reasons. First, a finite time is required for the concentration in the chamber to build up to a constant value, as pointed out in an American secret document E.A.TR.109. Second, a time lag is involved before S_2F_{10} reaches the chamber. However, the objections may be disregarded if the experiments are made comparative, that is, if a toxic substance whose lethal index is known is tested in the same manner, and the results compared. Purified phosgene was used to make this comparison.

Mice and guinea pigs were used in these tests and the results are arranged in the following tables.

TABLE X (using charcoal)

Species	Concentration	Time of exposure		Result
Mice	1/5000	1 hour	no	deaths
Mice	1/1000	l hour	no	deaths
Mice	1/1000	1 ¹ / ₂ hours	no	deaths
Mice	1/1000	2 hours	no	deaths.

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From Table X it would appear that charcoal of the C W 5 variety provided adequate protection and that there was no breakdown even after a two hour test. Since the mice are affected by a concentration of a few parts per million, any leak there may have been was immeasurably small. Etching of the glass next to the carbon indicated a decomposition of S_2F_{10} with probable production of HF or SF_4 .

TABLE XI (without charcoal)

Species	Concentration	Time of exposure	Time of death	Mortality
Mice Mice Mice Mice Mice Mice Mice Mice	1/1000 1/1000 1/1000 1/5000 1/5000 1/5000 1/5000 1/5000	5 min. 2 min. 30 sec. 1 hour 2 min. 1 min. 45 sec. 30 sec.	80 min. 100 min. 120 min. 50 min. 120 min. 4 hours 12 hours no deaths	100% 100% 100% 100% 100%
Guinea pigs Guinea pigs	1/1000	5 min. 2 min	4 hours	100%
Guinea pigs Guinea	1/1000	l min.	no deaths	-
pigs	1/1000	30 sec.	no deaths	-

Another test was carried out exposing ten mice to a concentration of 1/1000 for two minutes with Dr. Noble present to dissect the mice at regular intervals after exposure. It was found that immediately after exposure the lungs appeared normal but with increasing time they became enlarged, inflamed and flooded with fluid. It was also noticed in tests using high concentrations and short exposures that mice, usually quite active, flattened out on the bottom of the chamber gasping for breath as soon as the S_2F_{10} reached them. They never appeared to move normally after this first lull in their movements and death followed a few violent actions suggesting convulsions.

To compare S_2F_{10} with a known toxic substance similar tests were made using pure phosgene. Results are given in the following table.

TABLE XII

Species	Concentration	Time of exposure	Time of <u>Madeath</u>	ortality
Mice	1/1000	l min.	20-24 hrs.	100%
Mice	1/1000	30 sec.	no deaths	-
Mice	1/5000	45 sec.	no deaths	-

From tables XI and XII it is apparent that S_2F_{10} is more toxic than phosgene. Taking the lethal index = ct, the lethal index for S_2F_{10} is 1700. With mice using phosgene the mortality product is 5200, as listed by E.A.T.R.109 reports, and from the above table is calculated as 4500. By comparison $\frac{4500}{5200} = \frac{1700}{x}$ where x is 1900 for S_2F_{10} . Thus S_2F_{10} is approximately three times as toxic as phosgene from a comparison of the above lethal indices.

Toxicity tests on S_2F_{10} have been conducted by McLean at the University of Chicago and the above results have been confirmed.

DISULFUR DECAFLUORIDE AS A WAR GAS

One is impressed by the favourable characteristics of $S_{2F_{10}}$ as a chemical warfare agent.

(1) Lethal index - indicates a greater toxicity than the gases now used and studied.

(2) Inertness to chemicals and heat.

(a) Only slightly attacked by concentrated KOH.

(b) No reaction with concentrated H_2SO_4 .

(c) Not hydrolyzed.

(d) No reaction with fluorine up to the decomposition temperature.

(e) Stable at least up to 160°.

(3) Can be stored as a liquid at room temperature (boiling point 29°). The vapour pressure is sufficiently high to make its dispersal rapid and simple.

(4) Clear liquid, colourless vapour, and in low concentrations, sufficient to be lethal, is odourless.

(5) High molecular weight - 254 - making for greater persistence.

(6) Penetration tests conducted at the National Research Council, Ottawa, show that with a service canister, the effluent gases become irrespirable in one-third the time compared to other gases.

It is hoped that with continued effort, production difficulties will be solved and that this compound will prove to be of great importance as an agent of chemical warfare.

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PART II

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THICKENERS FOR MUSTARD

evolve gases which would build up excess pressure in the containers. No completely satisfactory polymer has been found for either of the above requirements with impure mustard. Polyvinyl acetate has shown some promise as a suitable thickening agent and has been studied in some detail. The Shawinigan Chemical Co. Ltd. produces a series of polyvinyl acetates under the trade name of Gelvas which are graded according to the degree of polymerization. The availability of these materials has prompted the present investigation.

In this work, data on the viscosities of crude mustard (HS) thickened with Gelva and stored in glass, are presented. Storage tests with these materials in contact with metal are in progress. The results of these experiments will be given in incomplete form.

Review of Previous Work

The problems related to the thickening of crude mustard have been investigated for the past few years. Since the data are confidential the literature on the subject is strictly limited. In Canada such information is obtainable only at the National Research Council Library.

One of the most recent reports is by R.G.W. Norrish, Cambridge, England. This report lists the types of polymers studied as thickening agents for mustard. Long chain hydrocarbons and their chlorinated products seem suitable for spraying solutions. In the group of polyvinyl de-

-2-

rivatives, polyvinyl acetate shows particular promise as a thickener. The study of cellulose derivatives has only just begun. The results from a study of glycols have not been encouraging.

From a list of reports to the National Research Council of Canada only a few are of particular interest to the present work. The viscosity of a solution of a chlorinated rubber and crude mustard (RR/322 35D) increased on storage and finally settled to a gel. Vinyl acetate was used as a thickener (RR/322/42B) and storage trials in glass and steel under ordinary and "climatic" (140°F) conditions are not complete. The viscosity of crude mustard thickened with benzyl cellulose decreased considerably on storage (RR/322151). No satisfactory results were obtained from the use of methylated starches as thickeners (RR/322/63). Report numbers are shown in brackets.

A. E. Childs has carried out storage tests on thickened mustard at 60°. This treatment is termed accelerated ageing or "climatic storage." According to this report there is some doubt as to whether the behaviour observed under these unnaturally severe climatic conditions provides a valid basis for deduction about the probable behaviour at lower temperatures. The present work seems to verify this statement. Childs reports markedly greater instability of many chargings in steel containers, as compared with their behaviour in glass or varnished containers, and suggests

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heterogeneous catalysis by iron compounds. Results of a study of heterogeneous catalysis in this laboratory are reported in a later section.

EXPERIMENTAL

<u>Materials</u>. The crude mustard used throughout this work is an English product, made by the sulfur dichloride process, and is designated as HS. Ethylene is passed into a solution of sulphur dichloride in carbon tetrachloride. When the reaction is complete the carbon tetrachloride is "stripped off" until only approximately 15% remains. The product is a black liquid of density nearly 1.3 at 10°. Due to the nature of the process HS contains, in addition to mustard and carbon tetrachloride, small amounts of sulfur chlorides, colloidal sulfur, water, and iron compounds resulting from plant corrosion. A slow decomposition of HS produces additional impurities, namely hydrochloric acid, 1:2:2' trichlordiethyl sulfide, chlorethylchlorvinylsulfides, and other unidentified compounds.

The polyvinyl acetates (Gelvas) for this project were obtained from Shawinigan Chemicals Ltd. These compounds are graded on the basis of their viscosity, when a molecular weight of vinyl acetate is made up to one litre in benzene at 20°. Such a solution of Gelva 15 has a viscosity of approximately 15 centipoises at 20°. The Gelva numbers were checked by experiment, and the following results were obtained:

<u>Gelva No</u> .	n in centipoises
100	104
60	62
45	52
30	30.5
15	13.6

For the calibration of the viscometers a series of solutions of chlorinated rubber (Parlon) in methyl salicylate was used. The viscosities of these solutions were determined with an Ostwald viscometer, standardized with distilled water at the same temperature (10°). These values were checked using a modified Ostwald viscometer, standardized with a 95% glycerol and water solution. These viscosities are given in Table I, and shown graphically in Figure 1.

Table I

% Parl

246789

on	Viscosity	10°
	.13	
	•35	
	•75	
	1.15	
	1.62	
	2.45	
	3.41	
	4.86	
	7.07	
	10.32	



For the work on metal ageing, 30 gauge iron wire, 99.8% pure (Merck and Co.) was used.

<u>Apparatus</u>. A design of viscometer suitable for handling vesicant materials was adopted for this work. Such a viscometer is described in a report by A. E. Childs. The viscometer proper is illustrated in Figure 2.



It consists of a capillary U tube (1 min. I.D.) approximately 8 cm. across, 33 cm. long in the straight portion, of which 30 cm. is graduated in cm., except for gaps at the lower end of one limb and at the upper end of the other, where detailed graduation is not required in practice. The ends of the U tube are fitted with standard taper ground joints. Projections near the upper ends of the instrument facilitate binding the ground joints to the glass-manifold or to the covering caps. Graduation marks are etched on the instrument with hydrofluoric acid. The length of the curved portion of the capillary from marks 0 to 0 is measured by means of fine iron wire. The manifold is connected through stopcocks 3 and 4 to a vacuum line, in conjunction with a six litre bulb, B and a manometer, M.

The viscosity of the charging is determined by causing the whole thread to move a measured distance under gravity. The ends of the thread remain in the two straight portions of the capillary, so that their surface tension effects, being opposed, are largely if not entirely balanced out at low speeds, and do not significantly diminish the motive pressure. If s be the distance moved by the thread in time t, h the head at time t, l length of thread, and γ the viscosity of the charging, the differential equation for the motion is:

$$\frac{ds}{dt} = \frac{1}{2} \frac{dh}{dt} = \frac{k}{\sqrt{1}} (p + h)$$
(1)

where p is pressure in excess of gravity in cm. of charging, ρ is the density of the charging and k is the constant of the instrument. Integration yields the formula:

$$\int = \frac{2k\rho t}{1 \log e \frac{p+h_1}{p+h_2}} = \frac{0.869 \ k\rho t}{1.\log_{10} \frac{p+h_1}{p+h_2}}$$
(2)

where h, and h2 are initial and final heads, or approximately

$$\gamma = \frac{k\rho t}{1} \div \left[\frac{p+h}{s} - \frac{1}{3} \frac{s}{p+h} \right]$$
(3)

where \overline{h} , the mean head = 1/2 ($h_1 + h_2$) and s the distance moved = 1/2 ($h_1 - h_2$), the approximation being valid within 1% provided that,

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$$\frac{s}{p+h}$$
 < 0.54 (i.e.) s < 0.35 (p + h₁)

Omitting the second term in the bracket in (3), the expression:

$$\gamma \doteq \frac{\mathbf{k} \rho \mathbf{t}}{1 \mathbf{s}} \quad (\mathbf{p} + \mathbf{\bar{h}}) \tag{4}$$

is obtained which is valid within 2% provided s $\langle 0.2 (p+h_1)$. If m_i and mg are the distances from the zero of the initial and final marks on the left arm of the instrument and m_i and mg' the corresponding distances on the right hand arm and c if the known length of the curved part of the capillary between the zero marks, then

$$s = m_{1} - m_{2}$$

$$h_{1} = m_{1} - m_{1}'$$

$$h_{2} = m_{2} - m_{2}'$$

$$\overline{m} = 1/2 (m_{1} + m_{2})$$

$$m' = 1/2 (m_{1} + m_{2}')$$

$$\frac{1}{h} = c + \overline{m} + \overline{m}'$$

$$h = m - m'$$

$$\beta = \frac{h}{s} - \frac{0.333}{h/s}$$

Also

and equation (4) gives $\gamma = \frac{k + t}{1}$ (5) From this it follows that the constant of the instrument is

 $k = \frac{1}{\sqrt{t\beta}}$. Using a solution of known viscosity such as described above the constant k may be evaluated for each instrument.

When the viscosity becomes very high, and times of flow under gravity are correspondingly slow, it is convenient to supplement the head due to gravity with a suitable air pressure. This can be done very accurately by using the volume B. After the adjustment of the pressure in the reservoir to the desired value, this pressure can be applied practically instantaneously to the charging by opening the appropriate stopcocks. In practice however, this procedure is hardly necessary for the degree of accuracy which is significant in this work. With sufficient precision the volume between stopcocks 3 and 4 (called a doser) alone can be employed to obtain a calculated auxiliary motive pressure as follows:

The temperature in the funnels of the U tube is not of course uniform, since they are not immersed in the thermostat, but trial shows that the temperature distribution under steady conditions of experiment is sufficiently constant for the necessary reproducibility. The funnels in fact have each a fairly constant "effective" corrected volume, $\frac{V}{T} \left(= \int \frac{dV}{T} \right)$ which need not be known. In consequence, it follows by application of the gas-law pv = kt, that if the pressure present initially on both sides of the U tube (excluding any that may be due to saturated vapour) is po, and the atmospheric pressure is P, (po being $\langle p$), then n successive doses of air introduced on one side will produce an excess pressure p on that side such that

 $\log (P - po - p) = \log (P - po) + n \log (1-x)$ (6) where x is a small constant determined by the calibration, and for small n,

$$p \doteq n x (P - po) \tag{7}$$

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with an error of +50 (n-1)x % (no error for n = 1). It is convenient to express the barometric pressure P and also po (and hence p) in cm. head of the charging by multiplying the number of mm. of mercury by $\frac{13.6}{7}$ where ρ is the density of the charging.

The accuracy of result, for relative measurements of viscosity, depends upon the accuracy of definition of t, 1, (p+h), and (p+h2). Greater than 1% accuracy is not to be expected, nor would it be significant in this work. The viscosities under consideration are such that the time t can easily be kept well over 30 seconds so that the error devolves essentially upon the other three measurements. If the length of the curved and ungraduated portion of the U tube is nearly half that of the graduated straight portion of each limb, the relative error of definition of 1 remains always less than that of the logarithmic term involving (p+h1) and (p+h2). Now the maximum value for the thread movement s is the length of one straight limb. With this or any other fixed value of s, (p+h1) should be three or four times as large, if other considerations permit. There is no appreciable advantage in accuracy to be gained by making $(p+h_1)$ larger than this, but if it is convenient to make $(p+h_1) > 5$ s there is then, as already noted, the slight advantage that the simplified formula (4) may be used instead of (3). If on the other hand (as for instance

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p = 0 and gravity alone is used as the motive force) the possible value of $(p+h_1)$ is limited, then there is an optimum value of s for accuracy, viz. s= 0.36 $(p+h_1)$ and in practice $(\frac{s}{p+h_1})$ should lie between 0.3 and 0.36. Under these conditions if δ h represents the probable error of definition of $(p+h_1)$ and $(p+h_2)$, the consequent relative error in γ would be approximately 3.7 $\delta(\frac{h}{p+h_1})$ or 1.2 $\frac{\delta}{s}$. The precision of definition of $(p+h_2)$ and $(p+h_2)$ is about + 1 mm.

The viscosity of a 10% Parlon and methyl salicylate solution was measured with both an Ostwald and a U tube viscometer. The results were in agreement within 1%. Duplicate measurements of viscosity on a single charging agree within 1% or less. Using two U tube viscometers to measure the viscosity of a 6.7% Gelva 30 and HS solution at 10°, the results obtained were 5.71 poise, and 5.70 poises. This accuracy and precision justifies the use of this design of instrument.

To obtain the viscosities of the solutions the viscometers were attached to the manifold as shown in Figure 2 with the U tube submerged in a water bath kept at 10°. This bath was a Pyrex jar 45 cm. tall and 25 cm. in diameter, connected to a cooling coil (packed in ice) through a rotary pump. The water in the bath was stirred vigorously and by regulating the rate of flow through the cooling coil the bath could be uniformly maintained within a few hundredths of a degree of the desired temperature. Three other constant temperature water baths regulated at 25°, 45°, and 60° were used for storing the charged viscometers. The water levels in the baths were maintained by constant level devices. In addition, a constant temperature air bath regulated at 60° was used to store solutions in glass-stoppered bottles.

At a later date, approximately 40 cc. samples of the thickened solutions were placed in wide-mouthed, glass-stoppered bottles, of 125 cc. capacity. Each bottle was immersed to the neck in an oil bath. There was thus no possibility of distillation or condensation within the bottle. Three oil baths, thermostatically controlled to 30°, 45°, and 60° were used. In addition a series of samples was kept at room temperature approximately 20°. Samples for viscosity measurements were removed at the appropriate times.

For the metal ageing, calculated lengths of wife for each sample were wound in loose coils, and immersed in the HS solution. An A ratio of 1.5 has been used, where A is the area of metal exposed, and V is the volume of liquid. The A ratio of the S.C:I 500 lb. and 1000 lb. weapons is \overline{V} 4.0 (S.G.Mason, Experimental Station, Suffield - private communication). While the A ratio of 1.5 is not that used \overline{V} in actual practice, it is sufficiently high to indicate the effect of the iron on the solutions.

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Since polyvinyl acetates dissolve in HS with difficulty, a system of mercury-seal, glass stirrers was devised. The Gelvas required from six to twenty-four hours to go into solution depending on the concentrations and the Gelva number.

Technique

The charging is introduced into the viscometer by means of a pipette fitted with an aspirator bulb. The charge (which normally consists of approximately 1 cc.) is placed at the orifice of the capillary portion of the U tube so that it may drain down in a continuous thread without air inclusions. When the thread reaches the second zero mark the viscometer is placed in a horizontal position and the excess material is wiped out with a piece of twisted "Kleenex." The viscometer is then attached to the manifold with rubber bands and the thread permitted to come to rest. In this way the walls of the capillary are wetted by the charging.

The thread is brought up the left arm of the U tube by closing stopcock 2 and opening stopcocks 3 and 4 to a slightly reduced pressure. The rate of rise of the thread is regulated by the vacuum system so that it is similar to the rate of fall of the thread under gravity. This requires that its rate of rise increase during its movement upwards. When the right-hand meniscus of the thread passes the zero mark the position of the upper men-

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iscus is recorded. It is more convenient to determine the position of the upper meniscus in this manner than when the thread is moving downward, because then, the film in the wake of the thread obscures the meniscus. The thread is allowed to progress past these points a few millimeters and stopcocks 2, 3 and 4 are reversed. When the lower meniscus passes the zero mark a stop-watch is started. The thread is allowed to fall until the lefthand meniscus reaches a predetermined point (usually 20 cm.) when the stop-watch is stopped and the position of the right-hand meniscus recorded.

In the case of the calibrating solutions (Parlon and methyl salicylate) the viscometers are cleaned with carbon tetrachloride, acetone and water in the order given. Before further use the viscometers are placed in a chromic acid bath for twelve hours, then carefully washed with distilled water and dried.

Acetone is used to remove the bulk of the mustard chargings from the viscometers. This operation greatly reduces the time required for decontamination by concentrated nitric acid. As above the viscometers are cleaned in chromic acid, washed and dried.

RESULTS

The thickened solutions of mustard are required to have a viscosity of approximately six poises at 10°. To determine the amount of polyvinylacetate which would produce this viscosity, a series of solutions of each Gelva in HS was made up varying in concentrations from 1% to 10% by weight. The viscosities of these solutions are listed in Table II and shown graphically in Figure 3.

<u>v</u>	iscosit	ies of	Gelva	in HS	solutions	-Poises	at	10°
% Gelv	a	,		Gel	.va Number		-	
by wei	ght.	15	<u>30</u>	<u>45</u>	<u>60</u>	100		
1	0.	20 0.	24 0	.30	0.27	0.32		
2	Ο.	35 0.	45 0	.67	0.76	0.86		
3	0.	58 0.	94 1	.36	1.44	2.00		
4	Ο.	91 1.	65 2	2.53	2.78	3.85		
5	1.	35 2.	81 4	.67	5.15	7.88		
6	1.	86 4.	46 6	8.88	7.29	13.75		
7	2.	90 6	71 11	.75	12.25	23.70		
8	4.	32 10.	60 18	3.75	20.55			
9	5.	68 -	· ·					
10	7.	80 -						

TABLE II

Some of the higher viscosities were not determined as they are of no interest in the present work. Increasing the concentration of each type of polyvinyl acetate causes an increase in the viscosity of the solution, gradual at first but rising rapidly at higher concentrations. The effect of Gelva number is clearly shown in Figure 4, where each curve represents one concentration. In every case the Gelva of higher polymer number forms a more viscous solution than a lower polymer number for the same concentration. This follows as a direct consequence of the standardization of the Gelvas. At low concentrations this relation is almost linear but at higher concentrations there are marked deviations from this regularity.



Solutions of each Gelva in HS were made up to give viscosities of approximately 6 poises at 10°, placed in viscometers and set to age in the constant temperature baths. The solution containing Gelva 45 was put in three viscometers placed in baths at 25°, 45° and 60°. Solutions containing Gelva 15, 30, 60 and 100 were also placed in the 60° storage bath. The viscosities of these solutions measured at 10° at intervals of a few days over a period of some weeks are listed in Table III and shown graphically in Figure 5.

	<u>(a)</u>	Aged	in	Viscom	eters	in Water Ba	<u>ath 60</u> °
Time				Gelv	a Numi	ber	
in days	15	<u>30</u>	<u>45</u>	60	100	Gelva 45	Gelva 45
0	6.0	5.8	5.2	5.5	5.8	5.3	5.2
2	5.5	4.3	3.3	3.8	4.2	4.4	5.0
4	4.9	3.5	2.8	3.1	3.5	4.1	4.7
-6	4.8	3.5	2.6	2.9	3.1	3.7	4.3
8	4.7	3.0	2.5	2.8	3.0	3.8	4.2
12	4.4		2.2	2.5	2.6	3.6	4.3
15	4.2		2.1	2.3	2.5	3.7	4.5
18	4.1		2.0	2.3	2.4	3.5	5.4
25	3.8		1.8	2.3	2.2	3.2	9.5

TABLE III



The viscosity of all solutions at each of the three temperatures shows a definite decrease for several days, notably more rapid at the higher temperature. Solutions containing Gelvas 30, 45, 60 and 100 have very comparable rates and degrees of decrease of viscosity at 60°. Figure 6 shows the effect of storing three solutions of Gelva 45 in HS at three different temperatures.



At 25° after 12 days, the viscosity began to increase and exceeded its original value after 18 days. The viscometer at 45° acquired some impurity which made further observations impossible. At 60° the viscosity has shown no increase from the lowest value recorded to date. Previously in this work doubt was expressed as to whether the behaviour observed under "climatic storage" conditions provides a valid basis for deduction about the probable behaviour at lower temperatures. The above data indicate that such deductions are not possible. Further evidence on this point will follow. The decrease in viscosity was attributed to hydrolysis of the polyvinyl acetate by traces of hydrochloric acid present in the crude mustard. To offset this hydrolysis, acetic anhydride was added in increasing amounts to a series of solutions of Gelva 45 in HS, made up so that each final solution had a viscosity of approximately six poises at 10°. The compositions and viscosities of these solutions are listed below.

<u>% Gelva 45</u>	% Acetic Anhydride	Viscosity 10° i	n poises
5.94	7	C A	
5.98	2	0.4 6.9	
6.12	~ 3	6.9	
6.26	4	7.1	
6.40	5	7.3	

Table IV-a lists the viscosities of these solutions measured at intervals of a few days over a period of two weeks.

TABLE IVa

Viscosities of "Stabilized" Gelva in HS Solutions -Poises at 10 (a) Aged in Viscometers in Water Bath at $6\overline{0^{\circ}}$ Percent Acetic Anhydride Time in days 1 2 3 <u>4</u> <u>5</u> 0 6.3 6.7 6.9 7.1 7.4 1 7.1 7.3 6.4 6.9 6.9 З 6.4 7.1 7.1 7.3 7.5 7.1 :6 5.5 7.0 7.4 7.7 7.2 11 4.4 6.7 7.4 6.4 13 7.3 4.0 7.5 6.2 6.6 15 3.7 7.2 7.4 6.6 6.0

Solutions "stabilized" with 2%, 3% and 4% of acetic anhydride show only slight changes in viscosity but a concentration of 1% of the anhydride seems insufficient as a definite decrease in viscosity has occurred. The decrease in viscosity of the solution containing 5% anhydride seems inconsistent and will not be accepted unless verified by future experiments. While the charged viscometers were stored in the 60° bath there was a slight distillation from the U tube up into the caps and for this reason a series of solutions was stored in glass-stoppered bottles in an air bath regulated at the same temperature. The viscosities of these solutions were measured at intervals over a period of seventy-seven days (Table IVb).

Viscosities of	*Stabi	lized	Gelva	in <u>HS</u>	Solution	ns - Poises
	ĩ	*.	•			<u>at 10°</u>
		Perc	ent ac	etic a	nhydride	
Time in days	<u>1</u>	2	<u>3</u>	<u>4</u>	<u>5</u>	
0 7 13 15 20 26 30	6.3 5.8 5.4 5.1 3.9 3.2 3.4	6.7 6.8 6.4 6.0 5.6 5.7	6.9 7.0 6.7 6.9 6.4 6.4 6.5	7.1 7.2 7.0 7.0 6.8 6.7	7.4 7.5 7.1 7.3 7.4 7.4 7.3	
55 77	3.3 3.3	5.6 5.6	6.0 6.0	6.7 6.6	6.7 6.7	

TABLE IVD

Since the viscometers had to be charged, cleaned and decontaminated for each measurement, fewer observations were made. The results are not strikingly different from those of Table IVa except that the solution containing 5% anhydride was regular and the one containing 1% decreased less than formerly. The samples were aged at 60° for 30 days, during which time the change in viscosity of the solutions containing 3, 4 and 5% acetic anhydride was very slight. The samples were then aged at room temperature for 45 days more. During this period the samples containing 4% and 5% acetic anhydride have not changed appreciably. At the 55 day point, a new viscometer was used to measure the 5% anhydride sample. The value obtained has been duplicated after 22 days, which indicates that the solution is unchanged. From these observations one might conclude that the hydrolysis suggested above has been offset by the addition of acetic anhydride.

To study the effect of hydrochloric acid as the hydrolyzing agent pure mustard was obtained by vacuum distillation of HS. An all-glass apparatus was used and the mustard that distilled over between 65° and 75° at a few millimeters pressure was water white in color and almost oderless. To the pure H, 15% of carbon tetrachloride and 6% of Gelva 45 were added. Three 10 cc. samples were placed in glass-stoppered bottles the first of which served as a control. A drop of concentrated hydrochloric acid was added to the second and a drop of water to the third. Both were stirred thoroughly. These samples were stored in the air bath at 60° and their viscosities measured at 10° at intervals over a period of 8 days are listed in Table V and shown graphically in Figure 7.

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TABLE	v

chlorid (poises	les of Gelva 45 in le in the presence at 10°) aged in a	of water and HCl air bath at 60°	
<u>Time</u> in days	Gelva 45+h+CCl4	Gelva 45+H+H ₂ 0	Gelva 45+H+HCl
0 1	2.98 3.01	3.80 3.78	3.35 2.59
2	3.07	3.86 5.77	2.53
4 6	3.23 3.14	3.85	2.87
8	3.76	4.26	3.21



The control and the sample containing water have increased in viscosity, the former to a somewhat greater extent. The sample containing hydrochloric acid shows a definite decrease in viscosity, followed by an increase which will probably continue.

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Table VI illustrates results similar to those obtained previously on "unstabilized" and "stabilized" Gelva in HS solutions.

TABLE VI - Glass Storage

Viscosities of "Unstabilized" Gelva in HS solutions -Poises at 10°

	Ge	lva 1	Gelva 45									
<u>Time</u> in days	Room Temp.	<u>30</u> °	<u>45°</u>	<u>60°</u>	Room Temp.	<u>30°</u>	<u>45°</u>	<u>60°</u>				
0 1 2 4 5 8 12 30 31	6.7 6.3 6.4	6.7 6.7 7.0 6.4 6.2	6.7 6.1 6.0 6.0	6.7 6.0 5.2 4.8 3.9	5.4 5.2 5.2 4.8	5.4 5.3 5.0 4.5 3.6	5.4 4.7 4.3 3.5 2.6	5.4 5.1 3.5 3.0 2.3				

Viscosities of "Stabilized" Gelva in HS Solutions -Poises at 10°

	Ge	lv a 15	5	<u>Gelva 45</u>									
<u>Time</u> in days	Room Temp.	<u>30</u> °	<u>45</u> °	<u>60</u> °	Room Temp	<u>30</u> °	<u>45°</u>	<u>60</u> °					
0	4.5	4.5	4.5	4.5	3.8	3.8	3.8	3.8					
2		4.2	 4.4	4•⊥ 		3.8	3.9	3.8 					
4				4.3	3.8								
5		4.2	4, 4	4.4		3.8	3.9						
.8	4.5			4.3	3.8			3.7					
12			4.4			3.8	3.9						
30	4.6			4.5	3.8			3.3					
31		4.2	4.4			3.8	3.8	3.3					

For these ageing tests, only Gelvas 15 and 45 have been used. Each "stabilized" solution contains 5% of acetic anhydride. A slight sediment was formed in the "stabilized" Gelva 15 solutions. This would probably render them unsuitable for spraying purposes. No sediment was observed in the "stabilized" Gelva 45 solutions.

The addition of iron has changed the ageing trend of the "stabilized" solutions, and has increased the ageing rate of the "unstabilized" solutions. The results are given in Table VII.

TABLE V	II -	Metal	Storage
---------	------	-------	---------

Viscositi	es of	Unsta	bilize	d" Ge	<u>lva in</u>	HS So	lution	S
		Poi	ses at	10°				
	G	elva l	.5	•				
Time	Room				Room			· ·
in days	Temp.	30 °	45°	60°	Temp.	<u>30</u> °	<u>45</u> °	<u>60</u> °
	-	/	,	,		· ·		,
0	6.4	6.4	6.4	6.4	6.1	6.1	6.1	6.1
1	6.1			6 .2 .	6.0			4.7
2		5.9	6.0			5.6	5.6	
5	6.5	_ _ '		3.6	5.8			3.0
6		5.9	5.6			5.3	4.8	
12	6.5			7.1	5.6			3.2
13		5.9	5.3			5.1	4.0	

Viscosities of "Stabilized" Gelva in HS Solutions Poises at 10°

	G	elva	15	,	Ge			
<u>Time</u> In days	Room Temp	<u>30</u> °	<u>45</u> °	<u>60</u> °	Room Temp.	<u>30</u> °	<u>45</u> °	<u>60</u> °
0 1 2 5 6 12	5.5 6.1 5.8 6.0	5.5 6.5 6.6	5.5 6.7 7.9	5.5 7.4 13.3 X	6.6 6.9 7.6 7.8	6.6 7.1 7.5	6.6 7.8 9.0	6.6 8.0 13.0 X
13		8.3	X			10.7	13.0	

X - indicates viscosity greater than 15 poises

It will be noted that the effect is much greater in the case of the "stabilized" solutions.

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The viscosities have increased with time in each case, and more rapidly at the higher temperatures. A decrease in viscosity is first evident in the "unstabilized" solutions. After 12 days at 60°, an increase in viscosity is noted.

From the above, it seems that the presence of acetic anhydride increases the effect of the iron, possibly by increasing the rate of solution of the iron. If the action of the acetic anhydride on the thickened solutions is simply the removal of water, and not the displacement of an equilibrium, then drying of the HS and the polymer should yield stable solutions.

These data suggest the existence of two distinct reactions when Gelva is dissolved in HS; a hydrolysis reaction which takes place to a greater extent at "climatic storage" temperatures, and a gel formation which takes place preferably at or near room temperature. The hydrolysis reaction is related to the decrease in viscosity since a decrease does not occur in the presence of acetic anhydride. The gel formation has as yet been unexplained. Polyvinyl acetate does not gel when put into solution in benzene or many other common solvents, but the mustard molecule may be involved in setting up cross-linkages between the polyvinylacetate molecules to such an extent that a gel results. It is reasonable to assume that this cross-linkage cannot go on indefinitely, but must reach a limit. If this is true, diluting a thickened or partially gelled solution with crude mustard containing acetic anhydride should ultimately innibit gel formation.

If iron is excluded from the thickened solutions, then a satisfactory thickener, polyvinyl acetate, has been found. Thickened solutions have been kept stable for 77 days, by the addition of 5% of acetic anhydride. Mr. J. A. Morrison is continuing the work and if the freezing point of the "stabilized" solution is not appreciably higher than the freezing point of the unthickened HS, then a field trial is recommended.

ACKNOWLEDGMENT

The writer wishes to thank Mr. J. A. Morrison for his cooperation during the work on the above problem.

PART III

VOLUME ACTIVITY OF CERTAIN CHARCOALS

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VOLUME ACTIVITY OF CERTAIN CHARCOALS

INTRODUCTION

The British Government requires that the activity of canister charcoals meet certain specifications. Determination of the volume activity is a common test. The C.W. establishment, National Research Council, Ottawa, uses the British specifications in testing charcoals produced in Canada.

The C.W. establishment and the Physical Chemistry Department of McGill University performed tests on samples of charcoal. The tests in the two laboratories were made independently and then the results were compared.

EXPERIMENTAL

(a) Apparatus

The apparatus as used is shown in Figure 1. and was constructed according to specifications supplied by Major E.A. Flood of the C.W. establishment, National Research Council, Ottawa.



B and J are flowmeters working on the Venturi principle. A constriction is interposed in the tube along which the air is flowing and the difference in pressure on either side of the constriction gives a measure of the rate of flow.

Air enters the apparatus at A and passes through the constriction at B (2 cm. long 1 mm. bore). The rate of flow is shown on the gauge glass C. The large tube of the flowmeter D is of pyrex glass 1-1/2 inches in diameter and the gauge C is of small bore pyrex tubing.

The air stream is dried by passing it through two towers E and F filled with granular CaCl₂. On leaving the second drying tower, the air stream is divided into two parts by means of a piece of small bore tubing inserted into the main flow tube at G. The subsidiary air stream, the flow of which is controlled by the stopcock H, passes through the flowmeter J and then through a warming coil of copper tubing K to the carburetter L.

The carburetter L is a horizontal cylindrical vessel about 3-1/2 inches long by 1 inch inside diameter, with three vertical tubes as shown in the diagram. The centre tube is half inch bore and is fitted with a cork and a separating funnel M which serves as a reservoir for carbon tetrachloride; the stem of the funnel is drawn out to a fine jet which indicates the correct level of carbon tetrachloride in the carburetter. The two side tubes of the carburetter are of "Pyrex"(1/4 inch outside diameter) and one of them is bent to connect up with the heating coil K.

The heating coil and carburetter are suspended in a thermostat maintained at a constant temperature of 30°.

The main air stream and the subsidiary stream of air, laden with carbon tetrachloride vapour, meet at N and pass through a suitable mixing device 0 which consists of a tube loosely packed with glass wool and phosphorus pentoxide. The stream enters the jacket tube P which is 8 inches long and 1 inch inside diameter, in which the charcoal tube is suspended.

The charcoal tube Q of which an enlarged drawing is included with Figure 1 consists of a glass tube(1) 2 cm. bore and 12 cm. long. Near the bottom, a length of about 1 cm. of slightly narrower tubing(2) is fixed inside the main tube with de Khotinsky cement, and on the ridge so formed, a disc of fine silver or brass gauze(3) is also fixed by cement. A second piece of tubing 1 - 3 cm. long(4) which is a sliding fit inside the main tube, and a disc of fine gauze(5) is fixed to the lower end. A mark is etched on the glass of the main tube, such that the volume between the lower gauze disc and the mark is exactly 20 cc.

Three stoppers are used with the charcoal tube, one with a glass tube through it for use during the test, the remaining two being solid stoppers, one of which was fitted with a brass loop to suspend the tube while it is being weighed. The exit tube from the charcoal tube passes through both a large and a small rubber stopper, the smaller one of which is inserted into the charcoal tube while the larger cork holds the charcoal tube suspended in the outer jacket.

The air passing out of the charcoal tube flows through a piece of silica tubing R, of quarter inch bore and 12 inches long, which is heated to bright redness by a Bunsen burner.

The air stream then passes through a bubbler T containing

a fresh starch-potassium iodide solution (0.1% soluble starch and 0.5% KI), and then by way of a pressure regulator U and a control tap V to a cushioning volume X and finally to an aspirator.

Rubber connections were not used in the apparatus except for a one-holed stopper which held the charcoal tube in place. Rubber readily absorbs carbon tetrachloride thus this stopper was frequently replaced.

(b) Calibration

The first flowmeter D was calibrated to register a flow of one litre per minute. A known volume of air was displaced through it in the time required to produce the proper rate of flow.

Flowmeter J was constructed and calibrated to register 35 cc. of air per minute. This was done with a mercury burette.

In the calibration of the charcoal tube, the bottom was stoppered and water was run in from a burette. When the water had reached the bottom gauze, a further 20 cc. were added. The upper level indicated the position of the mark that was etched on the tube.

To charge the tube, charcoal is run in about 5 cc.. at a time. After each addition the tube is rotated and tapped both vertically and laterally until the charcoal is packed to a maximum specific gravity. The method of tapping is of great importance for unless maximum density is attained, the charcoal shows a low volume activity.

(c) Operation

The charcoal was dried to a constant weight at 110°, filled into the charcoal tube in the specified manner and the tube and contents weighed. A small quantity of starch-iodide solution was placed in the bubbler. When the silica tube had been sufficiently heated and the thermostat had reached its operating temperature the level of the carbon tetrachloride in the carburetter was adjusted, the aspirator turned on, and continued until a blue coloration appeared in the starch-iodide bubbler. The aspirator was then stopped, the charcoal tube removed immediately, stoppered and weighed.

The results are expressed as follows:-

Volume activity = $\frac{\text{Increase in weight of charcoal x 100}}{20}$

It has been found that the volume activity is not affected appreciably by the temperature of the charcoal nor by minor variations in the flow rate or the concentration, but it is adversely affected by the presence of moisture in the charcoal or in the air stream and by indifferent packing of the charcoal tube.

The carbon tetrachloride used was first washed with KOH solution, dried over P_2O_5 and finally distilled in a packed column rated at twenty-seven theoretical plates. The first and last thirds of the distillate were discarded.

RESULTS AND OBSERVATIONS

The preliminary runs were made with carbons of known volume activity. Reproducibility of the results was poor, and changes of the drying methods did not improve the agreement of successive determinations. The disagreement was traced to the method of filling the cell. The recommended method was discarded and the following technique substituted. The cell was accurately marked off in quarters, and the charcoal added in four portions. After each addition a light wooden plunger about six inches in length and made to fit the cell loosely, was dropped one quarter of the cell depth onto the surface of the charcoal a definite number of times(10). This gave a specific method of packing and the results became reproducible and of the same order as determined by the C.W. establishment, Ottawa. The values obtained with the recommended method of packing are given in Table. I.

The values of Table III proved to be satisfactory indicating that the technique of determining volume activities was properly acquired.

ACKNOWLEDGMENT

The writer wishes to thank Mr. J. Davis for his co-operation during the work on the above problem.

TABLE I

Run Number	C.W. Value	McGill Value	Weight of filling
3	13.6 13.6	9•3 8•8	10.8 gm. 10.6 gm.
6 7	13.6	10.9	10.6 gm. 11.1 gm.

The results obtained with samples of known volume activity, packed into the cell as described above are given in Table II.

TABLE II

Run Number	C.W. Value	McGill Value	filling
24	23.5	23+2	9•7 gm.
25	24.0	22.5	10.6 gm.
26	9•3	9.4	11.3 gm.
27	9.3	9.3	11,1 gm.

Values obtained for the samples of unknown volume activity are given in Table III.

TABLE III

			Weight of
Run Number	Sample Number	McGill Value	filling
l	1000	15.4	11.2 gm.
2	1000	15.6	10.9 gm.
1	1001	16.0	11.4 gm.
2	1001	16.1	11.3 gm.
3	1001	16.7	11.1 gm.
1	1002	16.2	11.2 gm.
2	1002	16.0	11.3 gm.
1	1003	14.8	11.1 gm.
2	1003	14.5	11.3 gm.

PART IV

IMPREGNATION OF CHARCOAL

BY NICKEL CARBONYL

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IMPREGNATION OF CHARCOAL BY NICKEL CARBONYL

INTRODUCTION

In a report by J. Davis (C.E. 51 - Nove. 25, 1940) it was stated that nickel carbonyl breaks down completely on an active carbon surface depositing nickel and liberating four molecules of carbon monoxide. It was suggested in that report that nickel carbonyl could be used to impregnate active carbon with nickel, which metal might act as a useful impregnant against arsine. A sample of carbon was impregnated using nickel carbonyl. Its service time against arsine was determined. X-ray photographs were taken of the charcoal to identify the form of the adsorbed nickel.

EXPERIMENTAL

I Materials

(a) Nickel Carbonyl

The Ni(CO)₄ was technical grade stored in a small cylinder. At toom temperature Ni(CO)₄ is a colourless, volatile liquid with vapour pressure 320 mm. Its melting point is -25° and boiling point is 43° .

(b) Arsine

Arsine was prepared by treating calcium arsenide with dilute nitric acid-drying the evolved gases, condensing them in liquid air and then pumping off the hydrogen. The gas used in service time tests was 99.6% pure arsine as shown by molecular weight determinations.

(c) Charcoal

English (A-87) unimpregnated charcoal was used in these

experiments. It was not dried.

II Apparatus

(a) Impregnating device.

The impregnating apparatus is shown in Figure 1. The carburetter and metering system is the same as described in part III



Pig. 1

of this thesis. This part of the apparatus was used in the experiments on volume activity and required slight alterations. The nickel carbonyl outlet valve H was fastened to a glass lead using heavy rubber tubing and sealing wax. This lead was attached to the carburetter D as well as a manometer M and a vacuum pump. Stopeceks: were so placed that the carburetter, coil and manometer could be evacuated. Ni(CO)₄ was condensed into the carburetter by cooling it with a dry-ice-acetone bath and then opening the valve of the cylinder. After sufficient Ni(CO)₄ had condensed into the carburetter the valve H was closed. Any non-condensable gas (probably carbon monoxide) was pumped off as indicated by the manometer. As in the volume activity experiments the air stream entered at 2 and was adjusted by a flowmeter, dried by two CaCl₂ columns and then divided into two parts. The major portion passed directly over the carbon. The minor portion was adjusted by a flowmeter, passed through a P_2O_5 drying tube and through the heater coil and carburetter. This stream now rejoined the main air stream so that a Ni(CO)₄air mixture flowed to the impregnating device proper.

The carbon was tumbled through the $Ni(CO)_4$ -air stream by a revolving tube E. This tumbling arrangement consisted of a 50 cm. glass tube. 2.5 cm.in diameter drawn down at each end. The tube could be separated into two sections by means of a large ground joint near one end. This facilitated filling the tube with carbon. Copper gauze and corks were used to confine the carbon in the drum and yet permit an air stream to pass through. Two ordinary rotating unions (C,C) of galvanized iron were attached by heavy rubber tubing to the glass drum. The unions were well greased and not tightly screwed together. They were supported by two clamps on each union to prevent the revolving motion from tightening or loosening the unions beyond the desired amount. As the unions were not perfectly machined the revolving caused some vibration and strain but this was

taken up by the rubber tubing which joined the iron stems of the unions to the glass drum. Only slight leaks occurred at the bearings and as this was inward it was not dangerous. A large driving wheel D, six inches in diameter, was attached to one of the unions on the end next the drum, which was made to rotate at a speed of about three times a second. The coupling stem at the exit end of the revolving tube was connected through nitric acid scrubbers to a cushioning volume and a water aspirator.

(b) Arsine apparatus.

The apparatus for the preparation of arsine is shown in Figure 2. It was constructed by Mr. F.P. Lossing whose work on arsine required certain parts of the apparatus, as shown, which are of no interest here.

 $Ca_{jAs_{2}}$ was placed in the flask A and a measured volume of dilute nitric acid was run in from the funnel D. Stopcocks were set so that the gases evolved passed through the drying tube G, the line I and condensed in trap 1.



that was surrounded with liquid air. A pump was used to remove hydrogen through C. When the reaction in the flask A was complete, the trap containing the arsine at liquid air temperature was evacuated as well as the line I. The manometer M indicated when all the hydrogen had been pumped off. The arsine was allowed to expand into the storage volumes J and samples were removed as required by condensing them in liquid air at U.

(c) The service-time apparatus.

The service-time apparatus was used by several previous workers and was loaned to perform the tests on the nickel impregnated charcoals. It consisted essentially of three parts, the breathing device (Fig. 3), the adsorption cell(Fig. 3) and the gas delivery system(Fig. 4). The breathing device was an adaptation of that designed by 0. Maass(1). The action of this apparatus will not be described here. The movement of the gases through the cell was intermittent and made to resemble that through a service canister in actual use. The adsorption cell used required a flow of 2 litres per minute to represent a flow of 16 litres per minute in a service canister.



The adsorption cell, (Fig. 3) was of glass and had a side arm inlet tube near the top and an outlet tube at the bottom. The charcoal was supported on a sintered glass disc fused into the wall of the cell to minimize the effect of chanelling of the gas-air mixture through the charcoal. The cell was closed with a ground glass stopper. The stopcocks served to make the gas-air stream go through the cell or to by-pass it.

The test-cell is as shown in Figure 3. The test paper was made by wetting filter paper with a saturated solution of mercuric chloride. The papers were used dry. Very low concentrations of arsine in air change this paper from white to yellow and, on continuous exposure to brown. The colour change is gradual. The service time was taken as the time when a fresh paper placed in the test cell became distinctly coloured in one minute. When it was necessary to change a test paper, the stream was by-passed around the cell and the run was not interrupted.

Figure 4 represents the system for producing desired concentrations of gas and air in a flow system. The arsine was



introduced into the evacuated system by transferring the solid, in a trap cooled with liquid air, from the arsine apparatus to the ground joint of trap G. The system was evacuated and the gas was either re-condensed in the bulb B or stored as a gas in the storage volume A. The burettes were filled with gas in the following manner. After they were filled with mercury, pressure was allowed to build up from the liquified gas in B. Stopcock T_{4} was opened and mercury was drained from the burette at Stopcock T_{6} , at a rate equal to its displacement by the vaporization of the gas.

The arsine concentration used was 1:100 for a flow of 2 litres per minute. Stopcocks T_2 and T_3 were adjusted to deliver mercury into the side tubes of the burettes to displace 10 cc. of gas per minute. The operation was to open stopcock T_4 to the air stream and stopcock T_1 to the burette on the left. In this way the gas was added to the air stream at 10 cc. per minute. The burettes were filled to a pressure about 1 cm. of mercury less than an atmosphere as the pressure of the air stream was reduced that amount by the resistance of the apparatus.

The air stream was drawn through the system by the breathing device, the rate being adjusted to 2 litres per minute. The air was bubbled through three bottles of diluted sulfuric acid to give it the desired relative humidity (58%). The gas and air were uniformly mixed by passing them through a tube packed with glass wool. The mixture was then passed through the adsorption cell.

RESULTS AND DISCUSSION

The speed of the revolving drum was adjusted so that when it was half filled, the carbon tumbled evenly and rapidly. 500 co. of air per minute were drawn through the carbon and 25 co. per minute passed over the $Ni(CO)_4$ at room temperature. Under these conditions 5% by weight of $Ni(CO)_4$ was deposited on the carbon in about an hour and a half. Before removing the carbon the system was flushed out with dry air for 15 minutes. The change of weight of the carbon was determined after removal from the drum and a sample of it tested qualitatively with dimethyl glyoxime.

Two samples of nickel impregnated carbon of 5% and 1% nickel by weight, were tested against arsine. The arsine concentration in air was 1:100 by volume and the relative humidity was 58%. A satisfactory impregnant, such as copper or silver, gives a service time for arsine of 35-40 minutes. For the two samples impregnated with nickel the service times were somewhat less than two minutes.

X-ray photographs were attempted on the 5% nickel sample by Dr. W.H. Barnes of the McGill Chemistry Department, using the powder method of analysis. No patterns were detected that could be interpreted to indicate the presence of any particular form of nickel.

At a later date Dr. W.H. Barnes and L. Williams of the McGill Chemistry Department, prepared nickel impregnated samples of carbon in the manner described above. They were unable to obtain X-ray photographs that could be interpreted to indicate the form of the nickel deposit on the carbon. By chemical tests it was inferred that the nickel was adsorbed as an amorphous deposit of oxide and carbonate. It was also found that the older deposits seemed to take up oxygen, water or carbon dioxide which reduced the nickel content.

The ease with which nickel carbonyl is exidized in the presence of even small amounts of air, particularly moist air, has been reported by many investigators, among them Berthelot(2) Lehrer and Loos(3) Bewar and Jones(4) Hatschek and Thorne(5,6,7,8) Garratt and Thompson(9) and Bawn(10). The work of these investigations indicates that the charcoal must be dry, theroughly outgassed, and the deposition must take place in the absence of air or moisture in order that nickel itself be deposited.

Under the conditions of the experiments conducted in this work the nickel as deposited by nickel carbonyl adsorption is not in a suitable form to improve the service time against arsine.

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The writer wishes to thank Dr. R.L. McIntosh for his copperation during the work of the above problem.

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SUMMARY

Disulfur decafluoride was prepared along with sulfur hexafluoride by the fluorination of sulfur. It was found that S_2F_{10} was toxic. Attempts to prepare S_2F_{10} included the fluorination of sulfur vapour, liquid sulfur, and S_2Cl_2 . SF_6 was pyrolyzed and also reduced by hydrogen in the presence of catalysts. S_2F_{10} was found to decompose on heating to 200° and to be stable in fluorine up to its decomposition temperature. It was found that the yield of S_2F_{10} was increased when sulfur was fluorinated in the presence of certain fluorides, particularly NaF. Toxicity tests showed that S_2F_{10} is more toxic than phosgene and is a potential agent of chemical warfare.

"Stabilized" and unstabilized solutions of Gelva in HS have been prepared and their viscosities measured over a period of time. Storage tests have been conducted at 25°, 45° and 60°. The addition of acetic anhydride to Gelva and mustard solutions has considerable merit in preventing hydrolysis of the polyvinyl acetate. The viscosity of solutions of polyvinyl acetate in HS "stabilized" by the addition of acetic anhydride was constant for 77 days at both 20° and 60°. The addition of iron wire to the solutions destroyed this stability. If iron is excluded from the solutions, a satisfactory thickener for HS has been found. The technique of determining volume activity has been outlined and the volume activity of certain charcoals has been determined.

Nickel carbonylwas adsorbed on carbon up to 5% by weight but did not improve the service-time against arsine as the deposit was an amorphous form of oxide and carbonate.

CLAIMS TO ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

A new type of insulation for the carbon anode in a fluorine generator has been used. It involves a lead seal with mica to provide the necessary insulation.

Apparatus was designed for the fluorination of liquid sulfur, sulfur vapour and S_2Cl_2 . Special apparatus was required for the stability study of S_2F_{10} in the presence of fluorine.

A flow system was built to determine toxicities of poisonous gases.

A method of packing charcoal in test cells was devised that gives reproducible results in absorption experiments.

A method of depositing nickel on carbon by the absorption and subsequent decomposition of nickel carbonyl was developed.

The contributions to knowledge were as follows:

(1) Disulfur decafluoride is a toxic substance, even more toxic than phosgene.

(2) S_2Cl_2 on fluorination passes to SF_6 .

(3) SF₆ is reduced by hydrogen to free sulfur, at temperatures as low as 200°, in the presence of platinized asbestos as a catalyst. (4) S_2F_{10} is stable up to temperatures approaching 200°.

(5) S_2F_{10} is stable in fluorine up to temperatures approaching its decomposition temperature.

(6) When sulfur is fluorinated in the presence of certain fluorides and the fluorine stream is diluted with nitrogen the yields of S_2F_{10} and other lower fluorides are increased and the yield of SF_6 is decreased.

(7) S_2F_{10} is readily adsorbed on a carbon surface and decomposes in a complex manner, not studied in any detail in this work.

(8) HS solutions thickened with polyvinyl acetate are stable in the presence of acetic anhydride provided iron is excluded from the solutions.

(9) Nickel, deposited on a carbon surface by nickel carbonyl in the presence of air, does not improve the service-time against arsine.