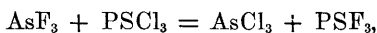XXXIV.—*On Thiophosphoryl Fluoride.*

By T. E. Thorpe, F.R.S., and J. W. Rodger, Associate of the Normal School of Science, S. Kensington.

In a short paper bearing the above title, published in the Transactions of the Society during the summer vacation of last year (Trans., 1888, **53**, 766), we announced the existence of a new gaseous substance of the formula PSF_3, to which we gave the name of *thiophosphoryl fluoride*. The present communication contains the results of the experiments which have served to establish the nature and composition of the new compound.

Arsenic trifluoride acts with great violence on phosphorus pentachloride, with the formation of phosphorus pentafluoride and arsenic trichloride (Thorpe, *Proc. Roy. Soc.*, **25**, 122). Phosphorus trichloride mixes with arsenic trifluoride, and on gently warming, the mixture evolves the gaseous phosphorus trifluoride (Moissan, *Ann. Chim. Phys.* [6], **6**, 433).

The behaviour of thiophosphoryl chloride with arsenic trifluoride is however very different. If arsenic trifluoride is dropped into phosphorus thiochloride in the cold, or if a mixture of the two compounds is boiled under ordinary pressures, no action takes place. When, however, the mixture is heated in a sealed glass tube at 150°, arsenious sulphide separates, and on cooling and opening the tube considerable quantities of gas are evolved. The nature of the gaseous product varies with the relative proportions of the arsenic fluoride and phosphorus thiochloride. If the reacting substances are heated in the proportions demanded by the equation—

$$AsF_3 + PSCl_3 = AsCl_3 + PSF_3,$$

analysis shows that about $\frac{1}{6}$th of the gas produced consists of thiophosphoryl fluoride, the remainder being made up of the fluorides of phosphorus and silicon. As the amount of the thiophosphoryl chloride is increased relatively to that of the arsenic fluoride, larger proportions of phosphorus thiofluoride are produced, until when four equivalents of thiophosphoryl chloride are used to one equivalent of arsenic fluoride, the gas evolved is *spontaneously inflammable*, and exhibits in general the characteristic features of the pure thiophosphoryl fluoride. It was found impossible, however, to entirely prevent the formation of silicon tetrafluoride and phosphorus trifluoride by this means, and although our subsequent experience with the gas has enabled us to devise a method for separating these

compounds from thiophosphoryl fluoride, it was evident from the relatively large quantity of arsenious sulphide invariably produced, that the method, even apart from the manipulative difficulties of working with sealed tubes containing gas under pressure, was neither a convenient nor an economical mode of preparing the new substance.

If arsenic trifluoride is heated with phosphorus pentasulphide in a sealed glass tube, the gas evolved consists mainly of silicon tetrafluoride. Lead fluoride, however, readily reacts, on heating it with phosphorus pentasulphide, producing thiophosphoryl fluoride in considerable quantity—

$$P_2S_5 + 3PbF_2 = 3PbS + 2PSF_3.$$
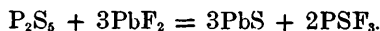
A mixture of red phosphorus, sulphur, and lead fluoride also gives rise to thiophosphoryl fluoride, but if the materials are used in the proportions required by the above equation, the reaction is extremely violent. It may, however, be moderated by using a large excess of lead fluoride. The mixture should be placed in a thin layer in a glass tube of narrow bore and which is gradually heated from behind forwards, so that the gaseous product as it is formed passes over the cold anterior portions of the tube and materials.

Bismuth trifluoride may be used instead of lead fluoride in the reaction, but in this case a brass tube must be employed, as the temperature at which the gas is evolved is considerably higher, and large quantities of phosphorus trifluoride are apt to be simultaneously formed.

On the whole, we found that the most convenient method is to heat a mixture of lead fluoride and phosphorus pentasulphide, but in order that the gas shall be obtained pure, certain precautions are absolutely necessary. Thiophosphoryl fluoride is readily altered by contact with air and moisture: hence it is necessary that the materials should be perfectly anhydrous, and that every trace of free oxygen should be absent. Moreover, as the gas is readily decomposed by heat, it is desirable that it should be produced at the lowest possible temperature. The best method of procedure is as follows : A quantity of freshly prepared phosphorus pentasulphide, made from washed and perfectly dry amorphous phosphorus and powdered roll sulphur, is quickly pounded with the requisite quantity of pure freshly fused lead fluoride, and the mixture is placed in a thin uniform layer in a dry leaden or " composition " tube, open at both ends. One end of the tube is fitted with a caoutchouc cork and glass delivery tube, whilst the other is attached to an apparatus yielding a supply of pure dry nitrogen. The air within the tube is rapidly swept out by the dry nitrogen, and the tube is gently heated in order to get rid of any sulphuretted hydrogen produced by the action of

z 2

atmospheric moisture on the phosphorus pentasulphide.   When the tube is completely filled with nitrogen, the current of this gas is stopped and the leaden tube is heated from behind forwards by a small Bunsen flame.   The reaction begins at about 170°, and as it is advisable to keep the temperature as low as possible consistent with the production of the gas, it should not exceed 250°.   The gas is collected over dry mercury and may be stored in a glass gas-holder. The gas-holder should contain a few fragments of quicklime, the pores of which should be freed from air by passing small quantities of dry nitrogen into the gas-holder and repeatedly exhausting by means of the Sprengel pump.   The thiophosphoryl fluoride is not allowed to pass into the holder until a sample is wholly absorbed by a dilute solution of potash or ammonia.   In order to get rid of the small quantity of nitrogen adhering to the lime, as soon as two or three cubic centimetres of gas have entered the holder, the latter is connected with the Sprengel pump and the gas and nitrogen sucked out, this operation being repeated twice or thrice.   The rest of the gas is passed into the holder, and after standing for a day or so over the lime, which removes the phosphorus fluoride and any traces of silicon tetrafluoride, is pure thiophosphoryl fluoride.

Determination of Vapour-density.—A bulb of about 240 c.c. capacity and fitted with tubes and stopcocks, as seen in Fig. 1, after being

FIG. 1.
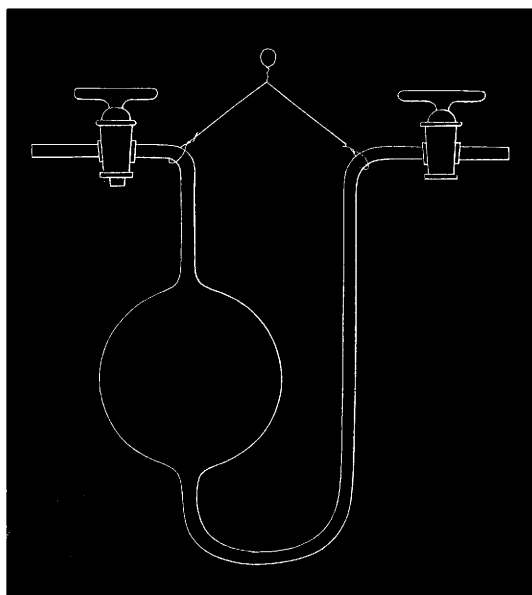
cleaned and weighed, is placed in a bath of water and filled with dry nitrogen. The bulb is then connected with a small mercury gas-holder, containing thiophosphoryl fluoride, made and purified as above described, and the nitrogen is slowly displaced from below upwards by the thiophosphoryl fluoride. The exit-tube of the bulb is attached to a piece of glass tubing, which dips a short way under mercury, so as to cut off the direct connection with the air. The bulb is immersed in the bath nearly to the level of the stopcocks, and a current of cold water, carrying with it a stream of air-bubbles. is allowed to enter at the bottom of the bath, and flow away at an open-ing near the top. The stream of air-bubbles is sufficiently strong to keep the mass of the water in circulation, and thus tends to render the bath of uniform temperature. When all the gas has passed over, the cocks of the bulb are turned, the tube dipping under the mercury removed, one cock momentarily opened to equalise the pressure, and the temperature of the bath and the height of the barometer noted. The dried bulb, after standing in the balance-case for about an hour, is then re-weighed.

To determine the amount of the residual nitrogen, the entry-tube of the bulb (both stopcocks being closed) is connected by means of caoutchouc tubing with a large burette containing a dilute solution of pure caustic potash. The potash is caused to fill the caoutchouc tube and the entry-tube of the bulb up to the stopcock. The stopcock is next opened and the potash allowed to enter the bulb. The gas is slowly absorbed, the bulb being meanwhile immersed in a vessel of water at a constant temperature. When the absorption is complete and the contents of the bulb are brought to the temperature of the water, the levels of the liquid in the bulb and burette are equalised, and the burette reading taken. The burette is then raised, and the stopcock of the exit-tube of the bulb is carefully opened. The level of the potash solution within the bulb rises until it reaches the stop-cock, which is then closed, when the levels are again equalised and a second reading on the burette taken. The difference between the two readings gives directly the volume of the residual nitrogen at the temperature of the bath and under the atmospheric pressure.

The details of two experiments carried out in this way are as follows : —

I.

Capacity of bulb at $15.8°$ and 776 mm.......	239·86 c.c.
Weight of bulb in air at $17.1°$ and 771 mm...	59·7543 grams.
Weight of bulb in air at $17.0°$ and 771 mm. filled with gas and residual nitrogen at $10.7°$ and 771 mm.	60·3954 ,,
Volume of residual nitrogen at $11.3°$ and 771 mm................................	78·9 c.c.
Reduced weight of gas and residual nitrogen	0·9372 gram.
Weight of nitrogen	0·0964 ,,
Weight of thiophosphoryl fluoride......	0·8408 ,,
Volume of gas + residual nitrogen at $0°$ and 760 mm................................	234·15 c.c.
Volume of residual nitrogen at $0°$ and 760 mm.	76·86 c.c.
Volume of thiophosphoryl fluoride	157·29 ,,
157·29 c.c. of thiophosphoryl fluoride weigh .	0·8408 gram.
1000 c.c. of thiophosphoryl fluoride weigh...	5·3455 ,,

Vapour-density $(H = 1) = 59.66$.

II.

Capacity of bulb at $15.8°$ and 776 mm.......	239·86 c.c.
Weight of bulb in air at $15.6°$ and 778 mm...	59·7282 grams.
Weight of bulb in air at 15.1 and 778 mm. filled with gas and residual nitrogen at $7.7°$ and 778 mm......................	60·5274 ,,
Volume of residual nitrogen at $9.6°$ and 777 mm................................	43·4 c.c.
Reduced weight of gas and residual nitrogen	1·0995 gram.
Weight of nitrogen	0·0538 ,,
Weight of thiophosphoryl fluoride	1·0457 ,,
Volume of gas + residual nitrogen at $0°$ and 760 mm.	238·81 c.c.
Volume of residual nitrogen at $0°$ and 760 mm.	42·86 ,,
	195·95 ,,
195·95 c.c. of thiophosphoryl fluoride weigh .	1·0457 gram
1000 c.c. of thiophosphoryl fluoride weigh...	5·3355 ,,

Vapour-density $(H = 1) = 59.56$.

The calculated vapour-density of PSF_3 is 60·0.

Analysis of Thiophosphoryl Fluoride.—The solution of the gas in the dilute potash was transferred to a 500 c.c. measuring flask, and the bulb carefully washed out and bromine-water added to the liquid until the colour persisted after repeated shaking, when the solution was diluted to the mark. In order to determine the *sulphur*, an aliquot portion of the solution was acidified with hydrochloric acid and mixed with barium chloride and the barium sulphate weighed. To obtain the amount of *phosphorus*, a second aliquot portion of the liquid was treated with ammonium molybdate solution in the usual manner, and the precipitate converted into magnesium ammonium phosphate and weighed as pyrophosphate. The results were as follows :—

I. One-fifth of a solution containing 0·8408 gram of gas gave 0·3223 gram barium sulphate.

A second fifth gave 0·1557 gram magnesium pyrophosphate.

II. One-fifth of a solution containing 1·0457 gram of gas gave 0·3992 gram barium sulphate.

A second fifth gave 0·1924 gram magnesium pyrophosphate.

	Calculated for PSF_3.	Found.	
		I.	II.
Phosphorus	25·83	25·85	25·69
Sulphur	26·66	26·32	26·22
Fluorine	47·51	—	—
	100·000		

Properties of Thiophosphoryl Fluoride.—At ordinary temperatures thiophosphoryl fluoride is a transparent, colourless gas, which, under the application of about 10 to 11 atmospheres pressure, condenses to a colourless liquid. Neither the gas nor the liquid acts to any appreciable extent on dry glass at ordinary temperatures. In air or oxygen the gas is spontaneously inflammable, and its oxidation products have a disagreeable, irritating smell, in which that of sulphur dioxide can readily be detected. Under the action of heat or the electric spark the gas is readily decomposed, with the separation of sulphur and phosphorus and the formation of phosphorus fluorides. If the decomposition be effected in a glass tube heated to a sufficiently high temperature, the gaseous product eventually consists entirely of silicon tetrafluoride.

Thiophosphoryl fluoride has no action on mercury, oil of vitriol, carbon bisulphide, or benzene. In ether, it is soluble to some extent, and the solution burns with a greenish flame. The gas is not readily dissolved by water, and dilute solutions of potash, soda, and ammonia

dissolve it only with comparative slowness. It unites with gaseous ammonia to form a white solid, and is completely absorbed by peroxide of lead. If passed over gently heated sodium the metal takes fire, and burns with a red flame, and the residual mass in presence of water evolves spontaneously inflammable phosphuretted hydrogen.

As certain of these reactions are of considerable interest, we have studied them in detail.

Action of Air on Thiophosphoryl Fluoride.—In contact with air, pure thiophosphoryl fluoride is speedily decomposed, the nature of the appearances attending the decomposition varying to a great extent with the conditions under which the admixture takes place.

If a very slow stream of the pure gas be allowed to issue from a narrow platinum jet into the air, a white fume is instantly formed. No indication of flame is evident in daylight if the stream is sufficiently slow, but in the dark, the white fume is seen to be traversed in the vicinity of the jet by a blue, flickering flame. On increasing the current of the issuing gas the blue, flickering flame becomes more pronounced, and eventually travels back to the orifice of the jet, and ignites the stream. If the supply of gas is maintained, the gas continues to burn, giving off copious white fumes. The flame is greyish-green in colour, and is tipped with a faintly luminous dull yellow portion, a light-blue zone occurring close to the platinum jet.

If, instead of allowing the gas to issue from a jet, a considerable bulk be suddenly permitted to come in contact with the air, the appearance is considerably modified. When the delivery tube of an apparatus in which the gas is being generated dips beneath the surface of mercury, and is surrounded by a piece of wide glass tubing about 6 inches long, open top and bottom, and with its lower end under the mercury, the wide tube becomes gradually filled with the gas, which is prevented from combining rapidly with the oxygen of the air by a layer of decomposition products formed from the first bubbles of the gas which entered the tube. When the tube is nearly filled with the gas, which may be ascertained by noting the position of the layer of fume which roughly indicates the line of separation of the gas and air, on lifting its lower end out of the trough the gas quickly falls down on to the surface of the mercury, combination rapidly takes place, accompanied first of all by a beautiful blue flash of light followed by the greyish-green flame observed in the case of a jet of the gas. The shape of the flame indicates that the gas has spread itself for a considerable way over the surface of the mercury before combination ensues. If the layer of fume be allowed to rise above the top of the tube, the gas is no longer protected from the action of the air, and takes fire from above and burns with the greyish-green flame.

The action of air upon thiophosphoryl fluoride may be further illustrated by rapidly mixing a small quantity of the gas contained in a glass vessel with a large excess of air.   For this purpose a small glass gas-holder provided with a stopcock at the top and tubulus at the bottom is filled with mercury and placed in the trough, the tubulus being open, and a few cubic centimetres of the gas are next introduced. If the cock is now opened the mercury falls, and air rapidly enters the gas-holder.   White fumes are at once formed, and increase in quantity with the amount of air until, when a certain volume has been introduced, a sharp explosion takes place accompanied by light and heat, and the mercury is forcibly ejected from the cylinder.

Action of Oxygen on Thiophosphoryl Fluoride.—When a quantity of thiophosphoryl fluoride is passed into a confined volume of oxygen contained in a eudiometer standing over mercury, the fluoride, being about four times heavier than the oxygen, collects on the surface of the mercury, and burns quietly with a yellow flame, and a white fume is produced which quickly settles on the sides of the eudiometer. If the oxygen is passed into the gas, combination is more rapid, and a much denser deposit settles.   When, however, the gas is gradually passed into the oxygen, that is, in a slow stream of small bubbles, the behaviour of the two gases is considerably altered.   The first few bubbles on reaching the oxygen inflame, giving a blue flash of light. As oxidation products collect on the surface of the mercury, more bubbles may be added without any signs of combination until when a certain amount of gas has accumulated in the oxygen, a bright-yellow flash is seen to traverse the gaseous mixture, and is followed by a smart detonation.   On adding more of the fluoride, a second detonation may be obtained either spontaneously or by increasing the pressure of the mixture.   As a rule, a third explosion cannot be obtained either by agitating the gases or by increasing the pressure on them, even although oxygen may still be in excess.   Dry oxygen and thiophosphoryl fluoride may in fact exist together in presence of a sufficient quantity of oxidation products, apparently without inter-action, provided all traces of moisture are carefully excluded from the mixture.   If lead fluoride is heated with phosphorus pentasulphide which has been kept in a bottle for some time, with no special pains to exclude air from the apparatus, gas is evolved which can be mixed with excess of dry oxygen without the slightest change taking place, even when the eudiometer is gently heated.   The mixture, however, at once inflames on exposure to the air.   That it is the moisture in the air which serves to start the reaction is proved by the fact that on passing fragments of blotting-paper moistened with water into the mixture of gas and oxygen their explosive union instantly follows.

These facts render it difficult to experimentally determine the

exact chemical nature of the action of oxygen upon the gas. We have, however, made the attempt. A measured quantity of thiophosphoryl fluoride was passed into a small graduated tube containing a known volume of dry oxygen gas (from three to five times the volume of the fluoride) standing over mercury. After combination had taken place, and it had been ascertained that all the thiophosphoryl fluoride had been oxidised, the apparatus was allowed to cool down to the temperature of the air, and the volume of the mixed gases was determined. These were then treated either by lead peroxide or by a strong solution of potash, which absorbs the products of combustion; the residual gas is pure oxygen, and its volume represents the amount which has taken no part in the reaction. The original volume of the oxygen and of the thiophosphoryl fluoride, together with the volume of the products and of the residual oxygen being known, it is easy to calculate the amount of oxygen which is required to oxidise a definite volume of the gas as well as the volume of the products formed and the contraction which has ensued.

From the mode in which the thiophosphoryl fluoride is passed into the oxygen it is difficult to introduce it in a uniform stream, but when this is effected the first bubbles of gas take fire and the rest explodes as already described; in such cases the amount of oxygen used and the amount of products formed are always greater than when the gas is passed up in quantity and burned, either entirely or in part, without explosion.

The results obtained are as follows; for the sake of simplicity the ratios only of the volumes are given :—

Action of Oxygen on PSF$_3$.

No. of expt.		Gas.	Products formed.	Oxygen used.	Contraction.
I	Gas has stood over lime; part burns; part explodes	1	1·535	1·29	0·755
II	Same gas as I; all burns quietly	1	1·433	1·143	0·7105
III	Gas made in "compo" tube; part burns; part explodes.	1	1·372	1·219	0·8457
IV	Same gas as III; all explodes	1	1·492	1·259	0·7675
Va	Same gas; all explodes but one little bubble.........	1	1·596	1·209	0·6126
Vb	Products of Va are sparked; bubble is thus combined..	1	1·444	1·209	0·7649
VI	Same gas. Eudiometer is heated by bunsen........	1	1·39	1·096	0·71

Rejecting VI, as in that case the tube was heated, and Va, as the

little bubble of gas evidently did not combine spontaneously, and only did so in passing the electric spark, Vb, the values are—

	Gas.	Pro-ducts.	Oxygen.	Contrac-tion.	Gas.	Pro-ducts.	Oxygen.	Contrac-tion.
I...........	1	1·53	1·29	0·75	4	6·14	5·16	3·05
II...........	1	1·43	1·14	0·71	4	5·73	4·57	2·84
III...........	1	1·37	1·22	0·85	4	5·49	4·88	3·38
IV...........	1	1·50	1·26	0·77	4	5·97	5·04	3·07
Vb...........	1	1·44	1·21	0·76	4	5·78	4·84	3·06
Mean values..	1	1·45	1·22	0·76	4	5·82	4·90	3·07
Rejecting III—								
Mean values..	1	1·475	1·225	0·747	4	5·905	4·903	3·00

These results are not very concordant, and the reason of their discrepancy will be evident from what follows.   The numbers, however, at once serve to show that the reaction between thiophosphoryl fluoride and oxygen is not in accordance with the equation—

$$PSF_3 + O_3 = POF_3 + SO_2.$$
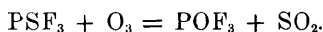
In this equation, 5 vols. of mixed gases condense to form 4 vols. of products; the contraction being one-fifth of the initial volume.

The numbers on the whole tend to show that 4 vols. of gas require 5 vols. of oxygen and give 6 vols. of gaseous products with a contraction of 3 vols., but it will be observed that certain of the experiments differ considerably from these values.   What probably takes place is, that a portion of the gas is acted upon by oxygen thus :—

$$PSF_3 + O_2 = PF_3 + SO_2,$$
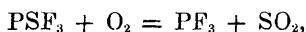
and that at the high temperature the phosphorus trifluoride is converted partly into phosphoryl fluoride and partly into phosphorus pentafluoride in the manner already indicated by Moissan :—

$$5PF_3 + O_5 = 3PF_5 + P_2O_5,$$
$$PF_3 + O = POF_3,$$
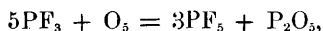
the ratio of these products being dependent upon the conditions under which the reaction takes place.

As phosphorus pentoxide and sulphur dioxide are unquestionably products of the action of oxygen upon the gas, the reaction in all probability tends towards the equation—

$$5PSF_3 + O_{15} = 3PF_5 + P_2O_5 + 5SO_2,$$

which implies that 4 vols. of the gas require 6 vols. of oxygen and

yield 6·4 vols. of products.   If a portion of thiophosphoryl fluoride
was decomposed only into the trifluoride and sulphur dioxide, which
is highly probable, less oxygen would be needed and a less volume of
combustion products would be obtained, which is exactly what is
observed.   It is noteworthy that in all cases in which the decomposi-
tion took place with violent explosion, that is, at a high temperature,
the amount of oxygen used and the volume of combustion products
formed was greatest.

On introducing a flame of thiophosphoryl fluoride burning in air
into an atmosphere of oxygen, the flame becomes reduced in size and
much more luminous.   Its colour changes from greyish-green to
bright yellow, and dense, white fumes are given off.   The solution of
the products formed smells strongly of sulphur dioxide, and gives the
reactions of phosphoric acid.

In some respects the behaviour of thiophosphoryl fluoride with
oxygen resembles that of phosphorus trifluoride as observed by
Moissan.   Moissan found that a strong spark was necessary to effect
the union of the trifluoride with oxygen, and that in presence of an
excess of oxygen, which acts as an inert gas, the explosion was not
produced.   When the amount of oxygen was double that necessary
to produce the oxyfluoride, the two gases only combined by the pro-
longed action of the spark without detonation or incandescence.
Moissan also found that a mixture of 1 vol. of the trifluoride with
half a volume of oxygen, which detonated violently on passing a
sufficiently strong electric spark, did not ignite by contact with an
ordinary gas flame.   The temperature was not sufficiently high to
effect the combination.   On bringing the oxyhydrogen flame in
contact with the mixture contained in a wide tube, combustion was
produced and the flame descended, but without explosion, to the
bottom of the tube.   These experiments show that the oxyfluoride is
only produced at a relatively high temperature, and serve to
strengthen the improbability that this gas is formed at all events in
any large quantities during the combustion of thiophosphoryl fluoride
in air or in oxygen.

Thiophosphoryl fluoride cannot be burned with safety from a jet in
a closed apparatus through which a current of dry air or oxygen is
passing.   The flame is liable to be extinguished by a current of air
or oxygen sufficiently powerful to carry over the products into the
absorption-tubes.   As a rule, the gas speedily relights itself, but not
before sufficient unburnt gas has escaped to form a spontaneously
explosive mixture.   We made two attempts to burn the gas in a
closed space, and in each case the apparatus was shattered by
explosion.

These experiments on the behaviour of thiophosphoryl fluoride in

contact with air or oxygen are interesting as illustrating the extreme instability of the gas. Its ignition temperature is evidently very low, and a very slight alteration of the conditions under which it is presented to oxygen serves to determine whether the heat evolved by the spontaneous combination of a part of the gas suffices to ignite the remainder. On allowing a slow stream of the pure gas to issue into the air from a narrow jet, combination is seen to take place, but it is only when the current is increased that the rise of temperature is sufficient to ignite it. The cooling action of the air is sufficient to prevent any flame. Even when a considerable volume of the gas is poured out into the air, an appreciable lapse of time occurs before the temperature from the heat of combination is high enough to ignite the rest of the gas. We have on several occasions partially filled the empty space in a mercury trough with the gas without any flame resulting, but on gently blowing upon the mixture the whole has immediately ignited. Small quantities of indifferent gases greatly influence the temperature of ignition, and in some cases, as in the experiments with oxygen, entirely prevent the spontaneous oxidation of the gas. If the amounts of the diluent substances are considerable, the mixture of oxygen and thiophosphoryl fluoride may be subjected to a relatively high temperature without appreciable change. On sending an excess of the fluoride into a confined volume of air, partial combination at once ensues, but even on passing electric sparks through the mixture for some time, oxygen still exists uncombined. If the amount of the indifferent gas is small, a very slight cause will determine the explosive union of oxygen and thiophosphoryl fluoride; thus, if the mixture be shaken, or if its tension be suddenly increased, combination at once ensues with explosion. The mixture may also be detonated by bringing a drop of water into it. Gas containing a slight admixture of the products of combustion may issue into the air in a rapid stream with no appearance of flame, but if a test-tube containing warm water is held in the current it is ignited; on withdrawing the warm tube, the flame is at once extinguished, but reappears when the tube is again brought into the stream.

As might be expected from the low-ignition temperature, and from the ease with which the flame is extinguished, its temperature is very low. It is probably one of the coldest flames known. Our hands have frequently been surrounded by it without any too inconvenient sensation of heat.

Action of Water on Thiophosphoryl Fluoride.—If a stream of thiophosphoryl fluoride is sent through water, comparatively little of the gas is absorbed. The bubbles rise to the surface, and take fire immediately on reaching the air, forming rings of white smoke. In

order that any appreciable quantity may be dissolved, the gas must be shaken with the water for some time. The solution is acid to test-paper, smells of sulphuretted hydrogen, and gives the reactions for phosphoric and hydrofluoric acids. The decomposition is in accordance with the equation—

$$PSF_3 + 4H_2O = H_2S + H_3PO_4 + 3HF.$$

If the solution is effected in a vessel of flint-glass, the liquid at once becomes black, owing to the action of the hydrofluoric acid and sulphuretted hydrogen upon the lead silicate.

Action of Alkaline Solutions upon Thiophosphoryl Fluoride.—Thiophosphoryl fluoride is more readily dissolved by a solution of potash or soda than by water, but it is only by acting upon a confined volume of the gas, and frequently shaking the liquid, that large quantities can be absorbed.

Wurtz (*Ann. Chem. Phys.* [3], **20,** 472) has shown that alkaline solutions react on thiophosphoryl chloride, $PSCl_3$, with the formation of a thiophosphate and a chloride. Thus with soda—

$$PSCl_3 + 6NaHO = Na_3PSO_3 + 3NaCl + 3H_2O.$$

Analogy would appear to indicate that thiophosphoryl fluoride would behave in a similar manner.

Berthelot, arguing from the heat of solution of phosphorus trifluoride in alkaline solutions, has inferred the existence of a fluophosphoric acid. And it is, of course, possible that this compound might be formed from thiophosphoryl fluoride.

In order to ascertain the exact nature of the decomposition, a quantity of the gas was dissolved in pure soda solution, contact with glass being carefully avoided, and the solution was slowly evaporated in a large platinum dish. As crystals were formed, the mother-liquors were decanted, and the successive fractions, after being washed with a little water, were dried and analysed. The first fraction was found to consist of almost pure sodium fluoride, and the succeeding fractions contained gradually increasing quantities of sodium thiophosphate. The decomposition by alkaline solutions is strictly analogous to that of thiophosphoryl chloride as described by Wurtz :—

$$PSF_3 + 6NaHO = Na_3PSO_3 + 3NaF + 3H_2O$$
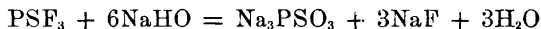
Action of Ammonia on Thiophosphoryl Fluoride.—If ammonia gas is passed into a confined volume of thiophosphoryl fluoride the two gases immediately combine, heat is evolved, and a white solid substance is formed. To determine quantitatively the volume ratios of the gases taking part in the reaction, measured quantities of dry ammonia were passed into a measured amount of thiophosphoryl fluoride and the

contraction was noted. Ammonia sufficient to condense part of the gas is added first of all, and after cooling and noting the volume more is added until all the gas has entered into combination.

The following are the numbers obtained in two consecutive trials: the volumes are reduced to standard temperature and pressure :—

Original volume of ammonia gas.............. 39·07 c.c.
    ,,   ,,   thiophosphoryl fluoride..... 7·51 ,,

After 1st admixture—
Residual vol. of NH_3 .. 18·52 c.c. NH_3 used.... 20·55 c.c.
    ,,   ,, PSF_3.. 2·34 ,, PSF_3 ,, ... 5·17 ,,

After 2nd admixture—
Residual vol. of NH_3 .. 7·51 c.c. Total NH_3 used 31·02 c.c.
Excess of NH_3 added.. 0·74 ,, PSF_3 ,, 7·51 ,,

1st admixture..... 1 vol. of PSF_3 condenses 3·98 vols. NH_3.
2nd ,, ... 1 ,, ,, 4·13 ,,

One molecule of thiophosphoryl fluoride appears, therefore, to combine with 4 mols. of ammonia to form a solid product. In this respect its behaviour is analogous to that of thiophosphoryl chloride, $PSCl_3$. Gladstone and Holmes (*Chem. Soc. J.*, **18**, 7) found that this substance could not absorb more than four equivalents of ammonia, and they were of opinion that the reaction was in accordance with the equation—

$$PSCl_3 + 4NH_3 = 2NH_4Cl + P(NH_2)_2ClS.$$

Schiff, on the other hand, represents the reaction on the supposition that *thiophosphotriamide*, $PS(NH_2)_3$, is formed,

$$PSCl_3 + 6NH_3 = 3NH_4Cl + PS(NH_2)_3,$$
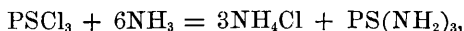
although no analytical data are given in support of this view of the action (*Ann. Chim. Pharm.*, **101**, 292).

If a reaction corresponding to Schiff's equation took place in the case of thiophosphoryl fluoride. 6 vols. of ammonia ought to be condensed. The volume ratios actually observed support the idea that the action of ammonia gas on thiophosphoryl fluoride may be represented by the equation—

$$PSF_3 + 4NH_3 = 2NH_4F + P(NH_2)_2SF,$$

and if the analogy between Gladstone and Holmes's compound is assumed to hold good, the product, excluding the ammonium fluoride, should be acted upon by water with the formation of thiophosphodiamic acid and hydrofluoric acid, thus :—

$$P(NH_2)_2SF + H_2O = HF + P(NH_2)_2HSO.$$
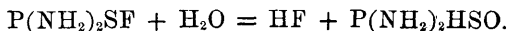
In order to obtain further evidence on this point, we passed about half a litre of thiophosphoryl fluoride into a small flask into which a stream of dry ammonia gas was also being led. The solid compound settled on the bottom and sides of the flask as a white, compact crust, which speedily deliquesced on exposure to the air. When freshly prepared it has no smell of ammonia. It dissolves readily in water, giving a slightly alkaline solution, in which no trace of phosphoric acid or hydrosulphuric acid can be detected in the cold. With metallic salts it gives reactions which in some cases correspond with and in others differ from those obtained by Gladstone and Holmes with the solution of the compound obtained by the action of ammonia on thiophosphoryl chloride. Both solutions give precipitates with salts of mercury, copper, silver, lead, and tin, and no precipitate with those of barium and iron. On the other hand, the thiophosphoryl fluoride compound gives no precipitates with salts of zinc, cadmium, nickel, and cobalt, in which respect it differs from the thiophosphoryl chloride compound. Gladstone and Holmes (*loc. cit.*) found that the precipitates obtained from the thiophosphoryl chloride compound consisted of salts of *thiophosphodiamic acid*, $H(NH_2)_2PSO$.

On adding copper sulphate solution to a solution of the thiophosphoryl fluoride compound the liquid remains perfectly clear for a short time. A yellowish-white precipitate gradually forms which rapidly darkens in colour and is ultimately transformed into copper sulphide. On filtering, the clear liquid slowly deposits a crystalline salt of a pale greenish-blue colour: it is insoluble in water, both hot and cold, but readily dissolves in dilute hydrochloric acid solution. The salt is only very gradually formed, and many weeks are required to obtain an amount sufficient for analysis. On examination it was found to be a double salt of copper phosphate and copper silicofluoride, of the formula $Cu_3P_2O_8,CuSiF_6$.

0·3226 gram salt gave 0·1756 CuO and 0·1217 $Mg_2P_2O_7$.

	Found.	Calculated.
Copper	43·15	43·41
Phosphorus	10·61	10·53

The formation of this compound is easily accounted for. All the sulphur is removed as copper sulphide and the amidated phosphoric acid is gradually decomposed, with the deposition of the light green double salt, by the hydrofluosilicic acid gradually formed by the action of the hydrofluoric acid on the glass vessel. It is worthy of note that in the double salt the phosphorus bears the same ratio to fluorine that it does in the thiophosphoryl fluoride from which it was derived.

Action of Thiophosphoryl Fluoride on heated Glass.—When a quan-

tity of thiophosphoryl fluoride is heated in a glass tube, the gas, after a given temperature has been reached, deposits a yellow film on the glass, the volume begins steadily to decrease, and after a time becomes constant. The residual gas, after the action is complete, consists entirely of silicon tetrafluoride. The decomposition follows the equation—

$$4PSF_3 + 3Si = 3SiF_4 + P_4 + S_4,$$
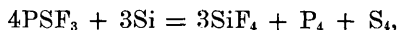
four volumes of the thiophosphoryl fluoride giving three of silicon tetrafluoride. A small measured quantity of thiophosphoryl fluoride was heated in a *cloche courbe* over mercury. After heating for about an hour the tube was allowed to cool and the volume of the residual gas noted. The results of two experiments carried out in this way were as follows :—

   I.   7·90 c.c. PSF_3 gave 5·95 c.c. SiF_4.
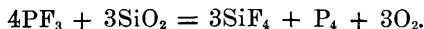   II. 11·39   ,,   ,,   8·81   ,,

Calculated from the equation—

          I .... 5·93 c.c.
          II................. 8·65 ,,

The sulphur is rapidly deposited from the heated gas which, indeed, appears first to decompose in accordance with the equation—

$$PSF_3 = PF_3 + S,$$
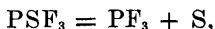
the phosphorus trifluoride then decomposing in the manner indicated by Moissan (*Ann. Chim. Phys.* [6], **6**, 464),

$$4PF_3 + 3SiO_2 = 3SiF_4 + P_4 + 3O_2.$$

A portion of the phosphorus combines with sulphur, whilst another part is oxidised and unites with the bases of the glass, forming pyrophosphates or metaphosphates. The deposit on the extreme upper part of the tube is yellow, and inflames on being heated in the air; it dissolves in water with separation of a little silica, and the solution smells of sulphuretted hydrogen, and gives the reactions for phosphoric acid.

Action of the Electric Spark and heated Platinum on Thiophosphoryl Fluoride.—If electric sparks are passed between platinum terminals in an atmosphere of thiophosphoryl fluoride, the gas is at once decomposed. A light yellow substance settles on the platinum wires and on the sides of the containing vessel, and the volume of the gas slowly diminishes. On heating a spiral of platinum to a low red heat in a confined volume of the gas, a cloud at once appears and a yellow film quickly settles on the cold sides of the tube. If the gas stands over

mercury a black sublimate of mercuric sulphide is also formed.   The platinum is rapidly attacked, and in two or three minutes falls to pieces, being converted into a black, brittle mass from the action of the phosphorus and sulphur.   The yellow deposit consists of sulphur and phosphorus, the former substance occurring in by far the larger quantity.   If moisture has been carefully excluded, the residual gas contains no trace of silicon ; although its volume is slightly less than that of the thiophosphoryl fluoride taken, it contains only phosphorus and fluorine.

It would thus appear that by the action of heat thiophosphoryl fluoride is quickly decomposed with separation of sulphur and formation of phosphorus trifluoride,

$$PSF_3 = PF_3 + S,$$
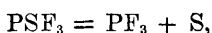
and that the phosphorus trifluoride, as already shown by Moissan (*loc. cit.*), is, by the further action of heat, gradually converted into phosphorus pentafluoride with separation of phosphorus—

$$5PF_3 = 3PF_5 + P_2.$$
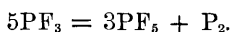
Spectrum of Thiophosphoryl Fluoride.—Professor J. Norman Lockyer was good enough to instruct Mr. Fowler to make some observations on this point for us.   A large end-on tube was carefully filled with dry nitrogen and placed in connection with an apparatus containing a mixture of lead fluoride and freshly made phosphorus sulphide.   The tube and apparatus were then exhausted by the Sprengel pump, and the whole filled with the thiophosphoryl fluoride which was then removed by the action of the pump : the filling was repeated once or twice, and the gas finally slowly pumped out until a spark at the lowest possible temperature would pass.   As soon as the spark begins to pass the spectrum is found to consist of lines characteristic of the fluorine spectrum as seen in silicon fluoride and boron fluoride.   After a time, as the pressure is reduced, lines of phosphorus appear and entirely displace the fluorine spectrum.   On further reducing the pressure, the phosphorus lines give place to a spectrum consisting entirely of sulphur flutings.   Thiophosphoryl fluoride is therefore dissociated at the lowest temperature of the spark.

Liquefaction of Thiophosphoryl Fluoride.—In the Cailletet apparatus, the gas is readily reduced to a colourless, transparent liquid.   By means of a specially constructed apparatus, in which we compared the reduction of the volume of hydrogen and of the gas by submitting both to the same pressure, we find the following relation between the temperature and pressure under which the liquefaction of thiophosphoryl fluoride takes place.

Temperatures.	Pressure in atmospheres.
3 8°	7·6
10·0	9·4
13·8	10·3
20·3	13·0

Addendum.—In the discussion which followed the reading of this paper, Professor Ramsay suggested that thiophosphoryl fluoride would probably be resolved by shock if treated in the same manner as carbon bisulphide vapour, *i.e.*, if a small quantity of mercuric fulminate was exploded in the gas. On making the experiment according to the method already described by one of us (Thorpe, " Decomposition of Carbon Disulphide by Shock," Trans., 1889, 220), a black deposit of mercuric sulphide was instantly produced by the explosion, and in quantity sufficient to show that the whole of the sulphur was thrown out of combination. It is, however, impossible to say definitely whether this result is the direct effect of the explosion or whether it is due to the action of the heated mercury vapour on the gas ; in other words, we have no means of knowing whether the action is purely chemical or is merely mechanical.