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THE EVOLUTION OF FLUORINE IN SUPERPHOSPHATE PRODUCTION AND ITS ABSORPTION

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The recovery of fluorine from the processing of phosphate rock with sulphuric acid is an important part of the operation. There is an increasing vigilance of national and local authorities, as well as the general public, towards atmospheric pollution caused by chemical factories. From the economic point of view, the fertilizer manufacturer should realise the commercial potentialities of the element and, with proper development of methods of recovery and utilisation, it should turn from a liability to a source of profit.

Little work has been published on the evolution or absorption of the gases. Absorption systems at present in use work reasonably well but a rational design, based on chemical engineering principles, should be aimed at.

With these points in mind, a programme of work was carried out in the laboratory and the summary of this forms the basis of the paper. For convenience the paper can be divided into six sections.

- Section 1. Development of an analytical method for fluorine estimation.
- Section 2. Qualitative and quantitative aspects of gas evolution in a small laboratory mixer.
- Section 3. The constitution of solutions of fluosilicic acid with special reference to the solubility of silica.
- Section 4. The vapour pressures of solutions of fluosilicic acid at various temperatures and concentrations.
- Section 5. The absorption of silicon tetrafluoride
 - a) in water droplets,
 - b) in a thin film of flowing water

Each of these topics is discussed separately, together with the experimental methods used.

SECTION 1.

The estimation of fluoride.

Although fluorine is a very reactive element its estimation is difficult. At an early stage of the work, it was necessary to investigate the methods available, and to standardise on one of them.

Willard and Winter (1), in their classical paper, used thorium nitrate for titrating fluoride in the presence of equal volumes of water and alcohol; the pH value was adjusted with HCl to a point which was judged by the colour of a zirconium-alizarin indicator.

Later, Reynolds and Hill (2) showed that the end-point was more clearly defined if the solution was buffered, and if the alcohol was omitted. Half-neutralised monochloroacetic acid, giving a pH value of approximately 2.8, was used by the above workers. (In the present work the same buffer was used, and solutions gave an average pH of 2.8 after titration.)

Probably the most comprehensive review of fluoride analysis is that by H.A. Williams (3) in 1948; this covers all aspects of the literature up to that date, and describes a new etching test for micro-quantities, also the titration of microgram quantities.

According to several published papers, the thorium nitrate is standardised against a solution of pure fluoride. In the present work a known quantity of pure fluoride was taken, acidified, and steam-distilled in the presence of glass wool, and the distillate was used for standardising the thorium tetranitrate.

There are two reasons why this method is to be preferred:

1) The actual state of the fluorine in the distillate is uncertain (some of it may be present as fluosilicic acid and some as hydrofluoric acid), and it is more satisfactory to use the fluoride during the preliminary titration with thorium nitrate under conditions which are as close as possible to those during an estimation.

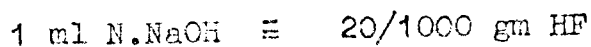
2) The recovery errors are, to some extent, compensated.

The method adopted thus resolves itself into six distinct parts.

A. Preparation of standard solution of the alkali fluoride.

There is no need to isolate the solid fluoride, and the solution can be used directly for distillation.

Aqueous hydrofluoric acid was weighed in a polythene weighing bottle, the contents were washed out into a platinum dish with about 20 ml distilled water, 6 drops of phenolphthalein added, and the solution titrated with standard sodium hydroxide in the cold to the first appearance of a permanent pink colour.



This estimation is accurate and probably gives the best standard fluoride.

SECTION 2.

Qualitative and quantitative aspects of the gas evolution.

In some cases, in the literature, it is stated that a mixture of silicon tetrafluoride, hydrogen fluoride and carbon dioxide is evolved during the manufacture of superphosphate. It would be possible for the silicon tetrafluoride to contain a relatively large amount of hydrogen fluoride, and for silica still to be deposited on hydrolysis with water, though the amount would be reduced by reaction with the hydrogen fluoride.

As will be shown later in this paper, the sampling of gases evolved from a den is a difficult matter, so that the problem was investigated with a small laboratory mixer. It was aimed to imitate production practice as far as possible, so that qualitative and quantitative experiments could be carried out.

When sulphuric acid reacts with phosphate rock to form superphosphate, a considerable evolution of heat occurs from the reaction, and the temperature of the mass rises rapidly to $75^{\circ} - 80^{\circ}\text{C}$., the exact temperature depending on the heat losses to the surroundings and the concentration of the acid. The partial pressure of water above the slurry is considerable, while that of the sulphuric acid is negligible. In the Broadfield superphosphate plant, a stream of cold air is used to ventilate the den; this cools the gas mixture, some condensation of water occurs, and subsequent reaction of water with the tetrafluoride takes place. It was found, from preliminary laboratory experiments, that by keeping the gases well above their dew-point reaction seemed to be avoided.

Observations on the plant being available, the following variables could be held constant, and bearing a known relation to plant conditions, during an experiment:

1. Temperature of the reaction.
2. Sieve grading of rock.
3. Type of rock.
4. Acid/rock ratio.
5. Concentration of sulphuric acid.
6. Reaction time.
7. Air flow over the reacting mass.

In laboratory experiments it was found very difficult to absorb the acidic gases quantitatively in water, and this was finally overcome by passing through heated sodium hydroxide pellets, which resulted in good absorption.

The 'organic' smell persisted in the gas after passage through solid caustic soda, but efforts to detect fluorine or silica in this exit gas were unsuccessful; it was shown that the constituent giving the smell could be absorbed by silica gel or charcoal, but an increase in weight of the absorption tube was not always detectable.

B. Steam-distillation of the fluoride with sulphuric acid.

60% perchloric acid and concentrated sulphuric acid gave identical results with sodium fluoride solution, provided the temperature did not rise above 145°C in the distillation. The steam-distillation equipment consisted of standard items, with ground glass joints to avoid the use of rubber. Material which is only slowly decomposed with sulphuric acid can be fused with sodium hydroxide pellets in a silver crucible; it is then necessary to add extra sulphuric acid for the distillation; the presence of sodium sulphate helps in the attainment of the required temperature. (Owing to some risk of explosion, it was desired to avoid the use of perchloric acid).

C. Titration of aliquots of the distillate with thorium nitrate.

Phenolphthalein was added to 50 ml water, and N/10 NaOH was run in to a definite pink colour; 13 drops of alizarin indicator were added, and thorium nitrate run in until a definite pink colour was formed. (With N/25 thorium nitrate about 5 drops were required.) This constituted the control, and unknown fluoride solutions were titrated to this colour after they had been made up to 50 ml with water.

D. Construction of the calibration curve.

It is found that a plot of fluorine content against volume of thorium nitrate required gives a slightly curved line, which is the calibration curve for the nitrate solution.

E. Distillation of the unknown fluoride.

F. Titration of distillate E with thorium nitrate.

Finally, the amount of fluorine was read off from the calibration curve.

It was shown, by the distillation of a solution of fluoride containing a small amount of sodium sulphite, that the presence of sulphur dioxide in the distillate can lead to serious errors. From a similar experiment using sodium carbonate and fluoride it was concluded that carbon dioxide does not effect the fluoride-thorium end-point.

The presence of sulphur dioxide in gases from fertilizer driers can thus cause error in estimating the fluorine content, and the sulphite should be oxidised to sulphate before the determination.

We have found that the use of chrome azurol as an indicator, as described by Milton et al (4), and in "Industrial Fluorosis" (5), is satisfactory for small quantities of fluoride.

The method described above is satisfactory, but discovery of a good method of estimating fluoride which does not depend on a thorium nitrate titration would be an advance.

Fig. 1 shows the general arrangement of the apparatus and Fig. 2 shows the type of mixer used.

Fig. 1.

Fig. 2.

To exclude any possible reaction between glass and reagents, the reaction vessel was made of lead-lined stainless steel, with mild steel backing flange; the top of the pot and tube connections were of 'Monel'. A graphite-impregnated asbestos tape was used for the stirring gland, lubricated with a graphite paste. The Monel stirrer had 3 blades arranged spirally, the bottom blade reaching to the bottom of the reaction vessel.

A Monel tube was used as absorber, with the caustic soda pellets; the heating sleeve could be slipped off. Any water vapour escaping the caustic soda pellets was absorbed in magnesium perchlorate tubes. The temperature of the air thermostat was kept approximately the same throughout by means of a small fan.

Compressed air was passed through calcium chloride and sodium hydroxide tubes before entering the glass heat exchanger. A steady flow of two litres/hour was obtained.

Experimental technique.

The Monel absorber, charged with sodium hydroxide pellets, was weighed, also the perchlorate tubes, so that a material balance on the reaction could be constructed. A charge of 100 gm Morocco rock was placed in the reaction vessel, and the temperature of the air thermostat was adjusted to the estimated den temperature, and left to come to thermal equilibrium for an hour. Referring to Fig. 1; with tap 1 closed, tap 2 open, tap 3 was slowly opened and the sulphuric acid allowed slowly to run in. The gases generated in the reaction vessel displaced the air, and a check on the flowmeter showed how to regulate tap 3. The small rubber bulb on the dropping funnel was used for forcing the sulphuric acid in, and to prevent any gas escaping this way. After the initial reaction, tap 2 was closed and the reaction allowed to continue for about 5 minutes; tap 1 was opened, and the needle valve adjusted so that the rate of flow of 2 litres/hr. was registered on the flowmeter at the end of the absorption train. After one hour, tap 1 was closed, the air flow was stopped, and the apparatus allowed to cool. The heating sleeve was slipped

off the absorber and, when cool, the latter was reweighed with the perchlorate tube.

Water was added to the absorber; the tube was re-stoppered and cooled under the tap, and washed out into a volumetric flask. It appeared that, if the tube was washed out when hot, silica was deposited, and it was necessary to avoid this. No silica was deposited if the tube was allowed to cool before washing.

Analysis of the solution.

The solution contained sodium carbonate, fluoride, silicate and unchanged hydroxide. Carbonate content was estimated by the method described by Haslam (6); this method was checked by synthetic mixtures of sodium carbonate, fluoride, and silicofluoride, and gave good results. It was also used for estimating the carbonate content of the phosphate rock used. 6N or concentrated hydrochloric acid, or 40% phosphoric acid, were found to give good results with rock; sulphuric acid tended to coat the particles with gypsum or anhydrite, and this prevented complete attack. Sulphuric acid could however be used for the estimation of the carbonate from the absorber, as there was no solid present.

The fluoride content was estimated by distillation with sulphuric acid, followed by titration with thorium nitrate solution.

Although the estimation of silicon in the presence of fluorine is difficult, it was found that the method described by Brabson et al (7) was very satisfactory and it was used in the present work. In this the fluorine is taken up into a complex compound by the addition of boric acid, and the silicon is precipitated as the oxine salt of molybdisilicic acid. Unfortunately phosphorus forms a similar compound, and the accurate estimation of the silicon content of phosphate rock is very difficult by this method. Recently Huré and Ortis (8) have shown that separation of silicomolybdic acid from the phosphorus compound is possible, using ethyl acetate as solvent and working in the pH range 1 - 1.4; the silicon can then be determined colorimetrically.

The Moroccan phosphate rock used had the following analysis:

Chemical	=	Sieve analysis -
P ₂ O ₅	33.9%	Through 240 ⁺ B.S.S. 30.9%
Calcium	37.41%	" 200 ⁺ B.S.S. 31.0%
Sulphate	1.94%	" 170 ⁺ B.S.S. 31.7%
Silicon	0.392%	" 150 ⁺ B.S.S. 34.4%
Fluorine	4.2%	" 120 ⁺ B.S.S. 44.4%
CO ₂	3.7%	" 100 ⁺ B.S.S. 54.8%
		" 72 ⁺ B.S.S. 79.5%
		" 60 ⁺ B.S.S. 88.7%
		" 36 ⁺ B.S.S. 98.9%
		" 22 ⁺ B.S.S. 99.6%

Material balances.

The superphosphate prepared in the mixer was weighed and analysed for P₂O₅; since the P₂O₅ content of the rock was known, also the loss in weight, and the amount of sulphuric acid added, a material balance could be calculated. Fluorine was estimated in the superphosphate, and a material balance could also be done for this element.

Some results are given in Table 1.

Table 1.

Series No.	1	2	3	4	5	6	7	8
Temp. (°C.)	85	100	58	95	58	80	75	62
Acid % w/wH ₂ SO ₄	71.5	71.5	46.0	74.6	60.0	67.5	67.5	63.8
gm. F evolved	0.873(1)	1.08	0.053	1.026	0.145	0.91	0.767	0.313
gm. Si evolved	0.318(2)	0.3873	-	0.376	0.0538	0.3265	0.282	0.1122
F/Si atoms	4.05 (3)	4.07	-	4.0	3.98	4.10	4.0	4.12
gm CO ₂ evolved	2.71	2.63	3.22	2.56	2.89	2.71	2.81	2.97
gm F in super.	3.34	3.04	4.15	3.15	3.93	3.19	3.32	3.98
Error in F balance (%)	0.3	2.2	-	0.5	2.8	2.4	2.6	2.4
No. of expts. in each series	13	5	3	7	4	3	6	5

Notes : (1) ±0.093 (2) ±0.04 (3) ±0.10

The figures given are based on 100 gm Morocco phosphate rock of the analysis given above. In all cases Acid/Rock = 0.6 gms H₂SO₄ per gm. rock.

Arithmetic mean figures are given, but the standard deviation was calculated for the first series.

$$\text{Standard deviation} = \sqrt{\frac{(x - \bar{x})^2}{N - 1}}$$

where x = observed value.

\bar{x} = arithmetic mean.

N = number of observations.

The fluorine balances were satisfactory in these experiments. When acid of about 70% H₂SO₄ was used, 19-23% of the fluorine originally present in the rock was evolved; in a Broadfield plant, with acid/rock = 0.64, the figure is about 25%. From the experiments, it appears that not all the carbon dioxide is evolved after one hour in the den and, from other results, which showed that about 23% of the P₂O₅ of the rock was unreacted after one hour, it appears that attack on the apatite and evolution of the CO₂ takes place almost

proportionally to one another. From the amounts of silicon and fluorine evolved it was possible to calculate whether any free hydrogen fluoride was evolved during the reaction between rock and sulphuric acid.

$$\begin{aligned} \text{In the gas : } \frac{F}{Si} &= \frac{\text{Wt. of fluorine}}{\text{Atomic wt. of fluorine}} \times \frac{\text{Atomic wt. of silicon}}{\text{Wt. of silicon}} \\ &= \frac{28}{19} \frac{\text{Wt. of fluorine}}{\text{Wt. of silicon}} \end{aligned}$$

In no experiment was there evidence of an appreciable amount of hydrogen fluoride; the values of F/Si range on both sides of 4.0, within the limits of experimental error. The average, 4.05, instead of 4.0 required for SiF₄, proves that the fluorine was practically all present as silicon tetrafluoride.

Figure 3 shows a plot of % fluorine evolved from rock against concentration of sulphuric acid used. All figures are for Moroccan rock with 0.6 gm H₂SO₄ per gm. rock. In each experiment, the temperature in the mixer was that to be expected on the large scale with acid of the concentration used. The temperatures were found by means of preliminary experiments carried out in a Dewar flask, and varied from 58°C with acid of 46% H₂SO₄ to 95°C with acid of 75% H₂SO₄. Points were also found to lie on a smooth curve if % fluorine evolved from rock was plotted against the temperature of reaction.

Fig. 3.

It is seen that fluorine evolution rises sharply between 63 and 70% w/w H₂SO₄ whilst above 70% w/w it tends to a steady value of about 25% of the total present in the rock.

An attempt was made to increase the fluorine evolution from the rock by mixing it with various proportions of dry sand or precipitated silica before reaction with the acid. In no case was the fluorine evolution appreciably increased.

Now that the composition of the gases from rock and acid, and some of the factors which governed their evolution, had been established, attention was given to the constitution of fluosilicic acid.

SECTION 3.

Constitution of fluosilicic acid.

Tannanaev (9) found that more silica may be present in fluosilicic acid (giving it a higher Si/F ratio) than the formula H_2SiF_6 indicates. S.M. Thomsen (10) agreed with this conclusion, and found that silica-saturated fluosilicic acid approaches a composition H_2SiF_6, SiF_4 which he called fluodisilicic acid.

In the above papers, the source of the fluosilicic acid used is not clear. AS acid prepared from silica and hydrofluoric might well be different from that obtained by the hydrolysis of silicon tetrafluoride (as occurs in superphosphate wash-towers) the whole matter was re-investigated.

The silicon tetrafluoride required for this work was prepared from fluosilicic acid and concentrated sulphuric acid (11). The apparatus was constructed so that the two liquids could be dropped into a column packed with glass beads, spent liquid withdrawn from the base, and the gas stored over paraffin until required. When it was desired to use some of the gas, paraffin could be run in to the reservoir at a constant rate by means of a Mariotte bottle, thus displacing the SiF_4 at any rate required.

Fluosilicic acid was prepared in the laboratory by passing the tetrafluoride, prepared in the way described above, into water. If silicon tetrafluoride was passed directly into water the delivery tube quickly became blocked with silica. Mercury was therefore used as a seal, and the gas bubbled through this before passing into the water layer above.

Table 2 shows the collected figures for a number of analyses of fluosilicic acid. The total silicon was estimated by the method described by Brabson et al (7).

Table. 2.

(See next page.)

Samples A, B, E and F were prepared in the laboratory, and C and D were from the recirculation unit at a wash-tower.

The atomic ratios F/Si, based on lines c and d, show that the solutions approximate much more closely to the complex H_2SiF_6, SiF_4 than to H_2SiF_6 . Unfortunately the ratios estimated do not enable a definite formula for the acid to be put forward. A complex of the type H_2SiF_6, SiF_4 could also be regarded as $H_2Si_2F_{10}$ (or $HSiF_5$) and the latter regarded as SiF_4, HF , although the acid behaves as a dibasic acid in many ways. If the extra silicon is present as the oxide, the acid could be formulated as $5H_2SiF_6, SiO_2$, which also has F/Si ratio of 5.0.

The presence of 'extra' silica in fluosilicic acid was further confirmed by material balances on sodium and potassium silicofluoride precipitations. By precipitating fluosilicic acid with the equiv-lent quantity of alkali chloride and filtering, it was found that the 'extra' silica came through into the filtrate, where part of it was precipitated. This 'extra' silica must be present in the filtrate as a colloidal solution or hydrosol of silicic acid. It is well known that the hydrosol is more stable if small amounts of hydrochloric acid or sodium hydroxide are present.

Hydrochloric acid is a reaction product,



and this stabilises the colloidal silica in a certain range. However, precipitation of silica also occurred on adding a small quantity of concentrated hydrochloric acid to the filtrate and shaking for a few minutes.

Iler (12) has recently pointed out that gelling of silicic acid in the pH range 1 to 3 is catalysed by the presence of fluoride ions, and this is probably an additional factor which influences the precipitation of the colloid.

The course of the hydrolysis of the tetrafluoride with water was investigated further by comparing the amount of silica precipitated during the hydrolysis with that remaining in solution as the acid complex.

Table 3.

	Run.No.4.	Run No.5.
a SiO ₂ pptd. from solution during hydrolysis	0.3437 gm.	0.4534 gm.
b SiO ₂ present in filtrate	1.441 gm.	1.530 gm.
c Total SiO ₂	1.7847 gm.	1.9834 gm.
d F present in filtrate, by Willard and Winter estimation	2.222 gm.	2.500 gm.
e F/Si atoms : for overall reaction		
i.e. $\frac{\text{Wt. of F}}{\text{A.W. of F}} \times \frac{\text{M.W. of SiO}_2}{\text{Wt. of SiO}_2}$	3.94	3.98
f Required for SiF ₄ F/Si	4.0	4.0
g Error between theoretical and found	1.5%	0.5%
h F/Si (atoms) in filtrate	4.88	5.15
i Required for H ₂ SiF ₆ , SiF ₄ F/Si	5.0	5.0
j Required for H ₂ SiF ₆ F/Si	6.0	6.0

The above figures show, line e, that the gas used was SiF₄; it contained no free hydrogen fluoride, which, if present, would have accounted for the low precipitation of silica. Line h shows that the composition of the filtrate agrees well with the formula H₂SiF₆, SiF₄, as had been found in the previous section with concentrated fluosilicic acid.

The amounts of silica precipitated and remaining in solution can now be correlated with the equations:-

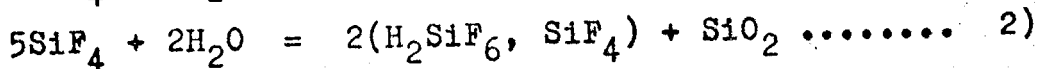
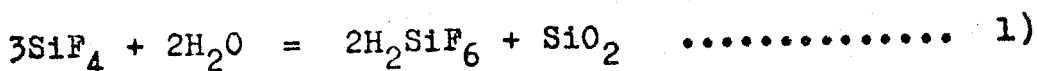


Table 4:

	<u>Run No. 1</u>	<u>Run No. 2</u>
Percentage of total Si present found in precipitate	19.3	22.8
F present (by titration) - gm	2.21	2.50
Concn. of acid prepared (% H ₂ SiF ₆)	0.558	0.631

According to equation 1 the percentage of the total Si in the precipitate would be 100:3 = 33.3, whereas according to equation 2 it would be 100:5 = 20.

It is thus shown that the hydrolysis of silicon tetrafluoride proceeds according to equation 2 rather than equation 1. The results of Run No. 1 agree with the calculated results better than those of No. 2, but agreement in the latter case is within errors likely in this type of work.

Later, a solution obtained by absorption of SiF₄ from air in a wetted-wall column was analysed immediately on its formation and at intervals thereafter with the following results:

<u>Time of analysis</u>	<u>F/Si atomic ratio</u>
Immediately	4.43
After one week	4.68
After three weeks	4.82
After four weeks	4.85

It appears that the Si content of the solution falls with standing, and that the F/Si ratio of 5.0 previously observed is probably a steady value, reached after some weeks. The ratio first observed here would correspond with the H₂SiF₆, 3.6 SiF₄ or H₂ SiF₆, 0.36 SiO₂. Taking account of these figures and the final value of the F/Si ratio, it seems more likely that the compound present after standing for a long enough time is H₂SiF₆, SiF₄, and that equation 2 should be :-

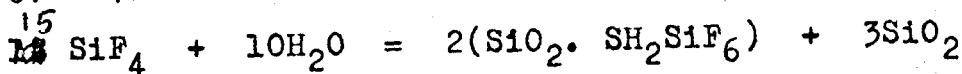


Table 2.

	A	B	C	D	E	F
a H_2SiF_6 content calculated from acidimetric titration	19.55gm	24.32gm	19.57gm	31.5gm	6.558gm	6.631gm
b F content from acidimetric titration	15.5gm	19.25gm	15.5 gm	24.95gm	0.441gm	0.50 gm
c F content by Willard and Winter estimation	15.8gm	18.90gm	15.4 gm	25.1 gm	0.444gm	0.50 gm
d SiO_2 content (gravimetrically)	9.95gm	11.62gm	10.0 gm	16.0 gm	0.288gm	6.306gm
e F/Si atoms	5.02	5.14	4.9	4.95	4.88	5.15
f Req'd. for $\text{H}_2\text{SiF}_6, \text{SiF}_4$	5.0	5.0	5.3	5.0	5.0	5.0
g Req'd. for H_2SiF_6	6.0	6.0	6.0	6.0	6.0	6.0

SECTION 4.

Vapour pressures of fluosilicic acid.

For work on the absorption of silicon tetrafluoride in water, it was necessary to know the vapour pressures above solutions of various concentrations of the acid over a temperature range. Since the anhydrous acid does not exist, it would be expected that, above solutions of fluosilicic acid, there would at equilibrium be a) water vapour, b) hydrogen fluoride, c) silicon tetrafluoride.

Concentrations of these were determined at 25°C, 40°C, 75°C, by a transpiration method. A known volume of air was blown through three saturators containing the acid, and acid gases were removed from the exit air by caustic soda pellets in a weighed tube. The saturators were of Monel, as any glass would have been attacked by the acid.

It was found that the partial pressures of HF and SiF₄ were small when the concentration was below 25% H₂SiF₆, but that they rose quickly in the region of 30 - 35% w/w.

Fig. 4.

This figure shows the equilibrium values of P_{SiF₄} over solutions of fluosilicic acid at 25°, 40°, 75°C. At 40°C the curve has been extrapolated, and, since only one value could be measured at 25°C, a line of similar slope to that at 40° has been assumed.

The strongest solution that can be produced in a gas absorption process is that in which the equilibrium partial pressure of the solute above the solution is equal to the initial partial pressure of the solute in the gas phase. From Fig. 4 it is seen that the vapour pressure of SiF₄ over a solution containing 32% w/w H₂SiF₆ is about 2.4 mms mercury at 75°C. This corresponds with $2.4 \times 100/760 = 0.32\%$ SiF₄ at atmospheric pressure, so that a gas stream entering a scrubbing system with an SiF₄ content over 0.3% can be made to form acid of at least 32% H₂SiF₆ so long as the temperature is not above 75°C. This was confirmed on a plant wash-tower when the whole of the liquid from the first section was re-circulated for a period of some hours.

The size of the scrubbing system required is dependent on the rate of absorption, which is dealt with in the next section.

SECTION 5.

Absorption of silicon tetrafluoride in water.

The rate of absorption of a solute from a gas stream by water is of course dependent on the area of the surface of contact. In the usual wash-towers for den gases, a large area of contact is formed by one or both of two methods, a) by splitting the water into drops by spraying it through nozzles, and b) by arranging wooden slats or other form of packing in a tower, and causing the water to flow over this in a thin film. In the experiments reported here both methods have been investigated; the work on droplets was of a preliminary nature, whereas that on a film of water was quantitative.

a) The course of the absorption of gas in a drop of liquid can probably be divided into three stages:

- i during the formation of the drop,
- ii during flight,
- iii during impact of the drop, and the collection on the wall or bottom of the tower.

Very little has been published on the absorption of gases in drops, and ammonia, carbon dioxide and oxygen have been the only gases used.

In the study of the absorption of carbon dioxide in liquid drops, Dixon and Russell (13) have shown that the rate of gas absorption in a drop during its period of formation may be high, especially when the time of formation is short, i.e. stage i cannot be ignored in comparison with stages ii and iii.

The drops from a commercial spray are generally very much smaller than can be produced in the laboratory, and the fact that the initial state inside the drops is different may well be important. In the case of a drop from a commercial spray, the liquid is probably in much more turbulent motion than in a drop falling freely from a jet or nozzle. This turbulence undoubtedly promotes gas absorption, as fresh surface is continuously exposed for mass transfer to take place.

It was obvious that, in these experiments, the rate of drop formation should remain constant for a series of runs. We were not interested in investigating the speeds of absorption with drops that had formed at different rates, and for the experiments the rate was standardised at 100 drops/min ($\pm 2\%$). The rate of air flow was also standardised, while the rate of SiF_4 flow was varied, so that the concentration of SiF_4 in the air stream was varied over a range. The drops fell from a nozzle which was surrounded by a shield, through which a stream of pure air was passed, so that the conditions of formation had ended before the drop entered the SiF_4 - air stream.

When using water as absorbing liquid, it was found that the concentration of H_2SiF_6 in the solution leaving the apparatus increased, with increasing partial pressure of SiF_4 in the gas phase, until this reached about 80 gms of mercury, when the concentration of H_2SiF_6 was about 1.0%. Further increase in the partial pressure of SiF_4 , however, resulted in practically no further increase in the H_2SiF_6 concentration. Since the equilibrium SiF_4 pressure of such a solution is negligible, it was obvious that some other factor was coming in to bring absorption to a standstill. When a 4% solution of sodium hydroxide was used instead of water, absorption proceeded to a slightly higher SiF_6 concentration, but at this again came to a standstill.

The above results, together with visual observations made during the experiments, suggested that a silica coating was formed round the drop, sealing off the liquid within from the gas phase. The result of the following experiment illustrates the stability of such a film:

A microscope slide was covered by a thin layer of vaseline by spreading a small quantity of it on the slide, and then gently warming it to the melting point. On cooling, the film of vaseline was almost transparent, and water formed stable drops on it. (photograph a). The drops were then placed for about a minute in a current of air carrying SiF_4 , after which the drops had an outside coating of precipitated silica (photograph b). It was possible to halve one of these drops by a razor blade. The inside of the drop was liquid, and was removed by a small strip of filter paper; the stable shell which remained is seen in photograph c.

Fig. 5.

As regards unpacked wash-towers for the absorption of SiF_4 , it is evident from the above that height is of little advantage, since drops will be coated before they have fallen far. A system which might be worth trying is to have splash-bars at 18 inch intervals in a tower, with the object of breaking up the coated droplets. The bars might be in the form of equilateral triangles set with the bases upwards, at 2" centres, each course being at right angles to the one above it. In the turbulent conditions of a Venturi Scrubber or Eductor Scrubber there will be but little chance for droplets to become coated.

b) Experimentally, the absorption of silicon tetrafluoride in a wetted wall column has the advantage that the area of the surface exposed is definite and can easily be measured.

Fig. 6 is a photograph of a general arrangement of the apparatus used.

Fig. 6.

The general flowsheet is given in Fig. 7.

Fig. 7.

The glass column itself was 2.46 cm diam. and 100 cm. long; important features were gas-calming sections at top and bottom to ensure steady conditions, and an accurately-ground weir at the top to cause the water to flow down inside the wall in an even film.

Metered quantities of dry air and silicon tetrafluoride were mixed and introduced at the base of the column, and the acid effluent was collected for analysis.

The effects of varying the three rates of flow were determined in the following ranges:

Water rate : 0.332 to 0.768 $\text{cm}^3/(\text{sec})(\text{cm. of periphery weir})$
Air rate : 166 to 2740 $\text{cm}^3/\text{sec.}$
 SiF_4 rate : 1.6 to 40.6 $\text{cm}^3/\text{sec.}$

The absorption rate was calculated as gm. mol. $\text{SiF}_4/(\text{sec})(\text{cm}^2)$. In the first series of experiments, the air rate and water rate were held constant, and the silicon tetrafluoride rate to the column was varied. Results obtained in this way were plotted in terms of normality of effluent (or absorption rate) against SiF_4 flow rate, and gave a straight line which passed through the origin.

The air flow rate was then altered to a second fixed value, keeping the water flow rate as before, and varying the silicon tetrafluoride flow rate. It was found that points thus obtained lay on a straight line with approximately the same slope as the previous one.

Two conclusions can be drawn from these results:

- i. At constant air and water flow rates, and over the experimental range of SiF_4 concentration, the silicon tetrafluoride absorbed is a constant fraction of that entering the apparatus.
- ii. The fraction of the SiF_4 absorbed depends only slightly on the rate of air flow.

In determining equilibrium partial pressures in the system fluosilicic acid - water, it was found that the partial pressure of silicon tetrafluoride over solutions of less than 35% w/w H_2SiF_6 was negligible at room temperature, so that there was no back pressure of SiF_4 in the wetted-wall column in any of the experiments.

The outlet partial pressure of silicon tetrafluoride was calculated from the liquor analyses, liquid rate down the column, and the air flow; as shown later, some fluosilicic acid is carried unabsorbed from the exit of the apparatus, making direct measurement very difficult.

The overall transfer coefficient,

$$K_G = (\text{gm. mol})/(\text{sec})(\text{cm}^2)(\text{atm. partial press. diff.})$$

was calculated for each run, using the arithmetic mean of the terminal partial differences, which in this case was not very different from the log mean.

By choosing experiments in which air velocity was constant, water flow rate was varied over the range 0.332 - 0.750 $\text{cm}^3/(\text{sec})(\text{cm})$, and SiF_4 flow was varied, the variation of the overall transfer coefficient with the water flow rate was found. On plotting the values, it was found that the overall transfer coefficient, K_G , did not vary much with the water rate. This observation means that the transfer rate is determined mainly by the gas film resistance or rate of chemical reaction or a combination of both.

The effect of variation of the gas velocity on K_G was then investigated in a further series of experiments. When K_G was plotted against v , a slightly curved line resulted; on plotting $1/K_G$ against $1/v^{0.8}$ however a straight line was obtained which almost passed through the origin.

Fig. 8.

It is suggested that reaction between SiF_4 and water occurs to some extent in the vapour phase, probably near to the water surface, as postulated by Denbigh and Prince (14) for the absorption of nitrogen peroxide in water. This brings the relation between K_G and gas velocity into line with the treatment by Chambers and Sherwood (15) of experimental values obtained in their work on the absorption of nitrogen peroxide in water.

Early in the series of experiments it was observed that a white deposit of "silica" had collected in the upper calming section of the apparatus. Analysis of samples of the white deposit showed it to be strongly acid, e.g. 27 - 31% w/w H_2SiF_6 . The concentration of the acid collected in this way appeared to be almost independent of the inlet partial pressure of the silicon tetrafluoride,

for example	SiF_4	=	0.95 mm Hg.	Acid =	30.0%w/w H_2SiF_6
			7.02 mm Hg.		32.1%w/w H_2SiF_6
			6.16 mm Hg.		35.2%w/w H_2SiF_6

This is in agreement with work already described, in which it was found that the strength of acid prepared from silicon tetrafluoride-air mixtures in this range of partial pressures should be 32-39% w/w (assuming equilibrium conditions).

When low air rates were used, mist particles could be seen in motion in the column itself. Certain experiments were obviously in the streamline range of flow, since the white particles could be plainly seen moving in straight lines up the centre of the tube. The course of individual particles could be followed, and several of them were seen to be carried from the inlet to the outlet without being captured by the water film.

With higher rates of air flow, no mist was visible, but a small plug of glass wool, suspended in the centre of the column on one occasion, collected a considerable amount of acidic silica.

It is evident then that, under some circumstances, reaction takes place to some extent in the vapour phase between SiF_4 and water, resulting in the formation of an aerosol of silica saturated with concentrated fluosilicic acid. Where this occurs, the most difficult task of the scrubbing system is likely to be the trapping of the aerosol. The presence of such an aerosol would make it very difficult to obtain a truly representative sample of the gas leaving a wash-tower.

Another indication of the difficulties caused by silica was the observation in some experiments of the formation of a film in the lower part of the absorption apparatus. The water flowed between the film and the glass surface, so that the film must have formed a major hindrance to absorption.

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FIG. 1.

REACTION VESSEL AND ABSORPTION TRAIN.

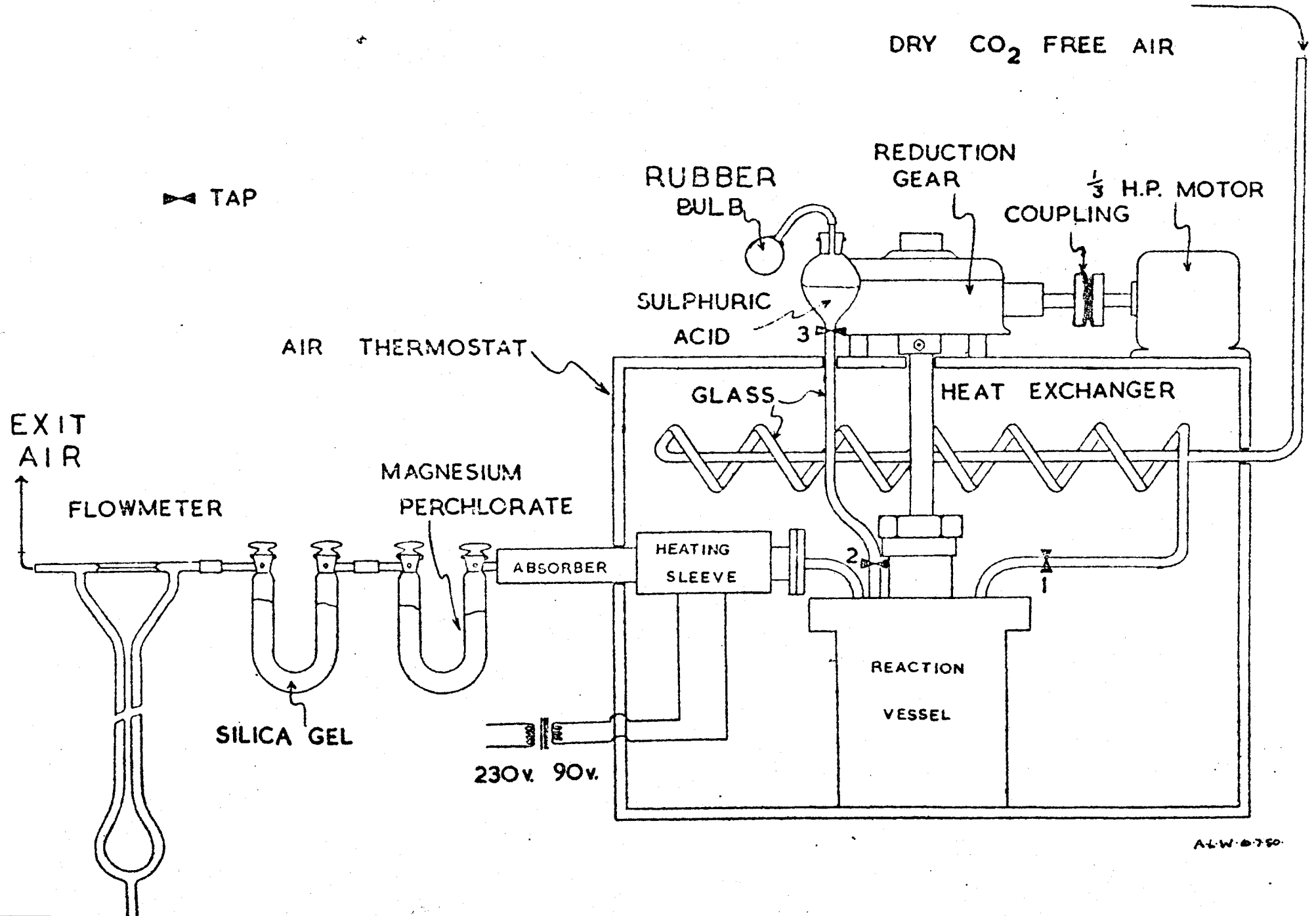


FIG. 2. REACTION VESSEL SCALE: FULL

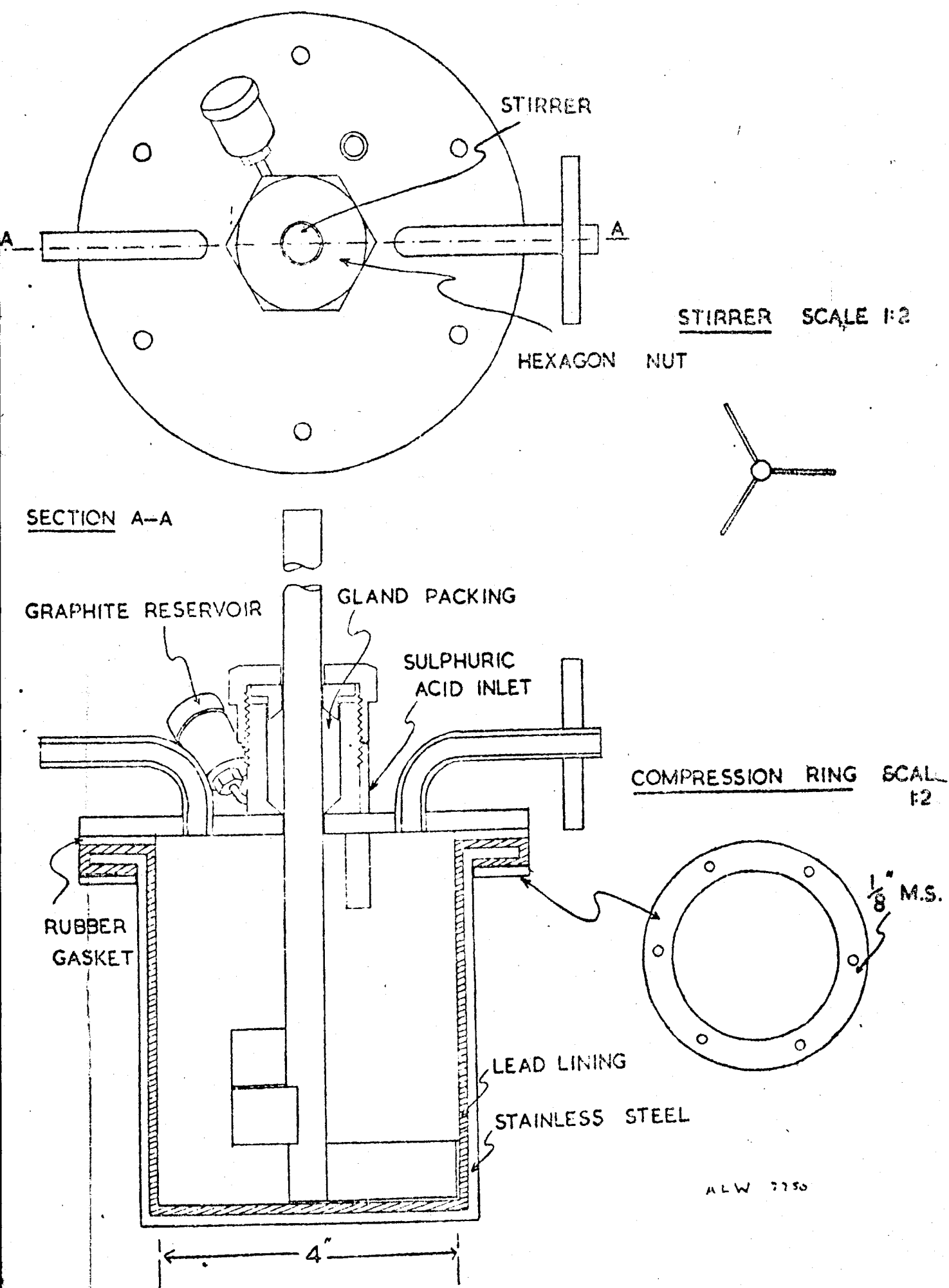


FIG. 3 VARIATION OF FLUORINE EVOLUTION WITH ACID STRENGTH

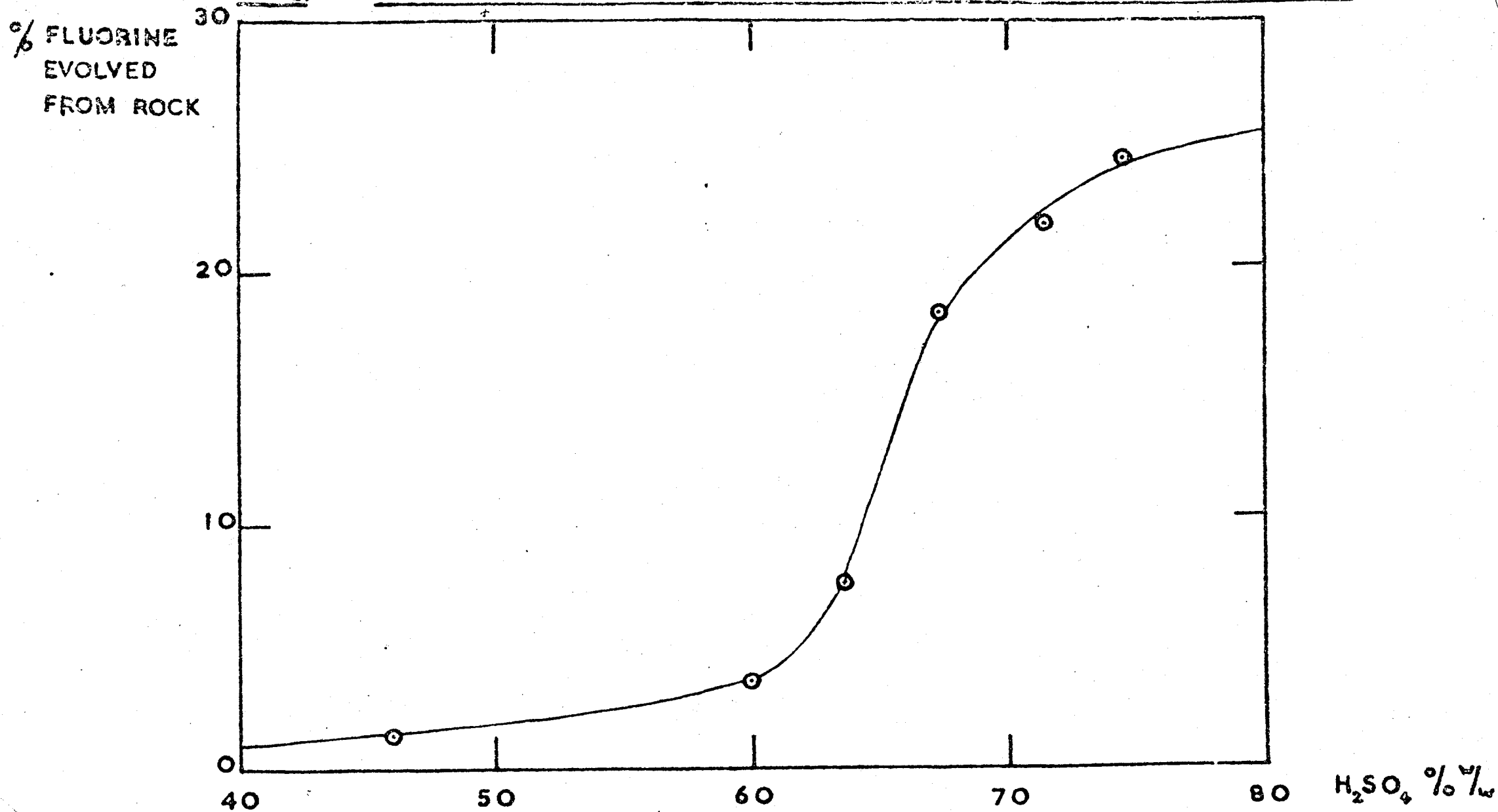
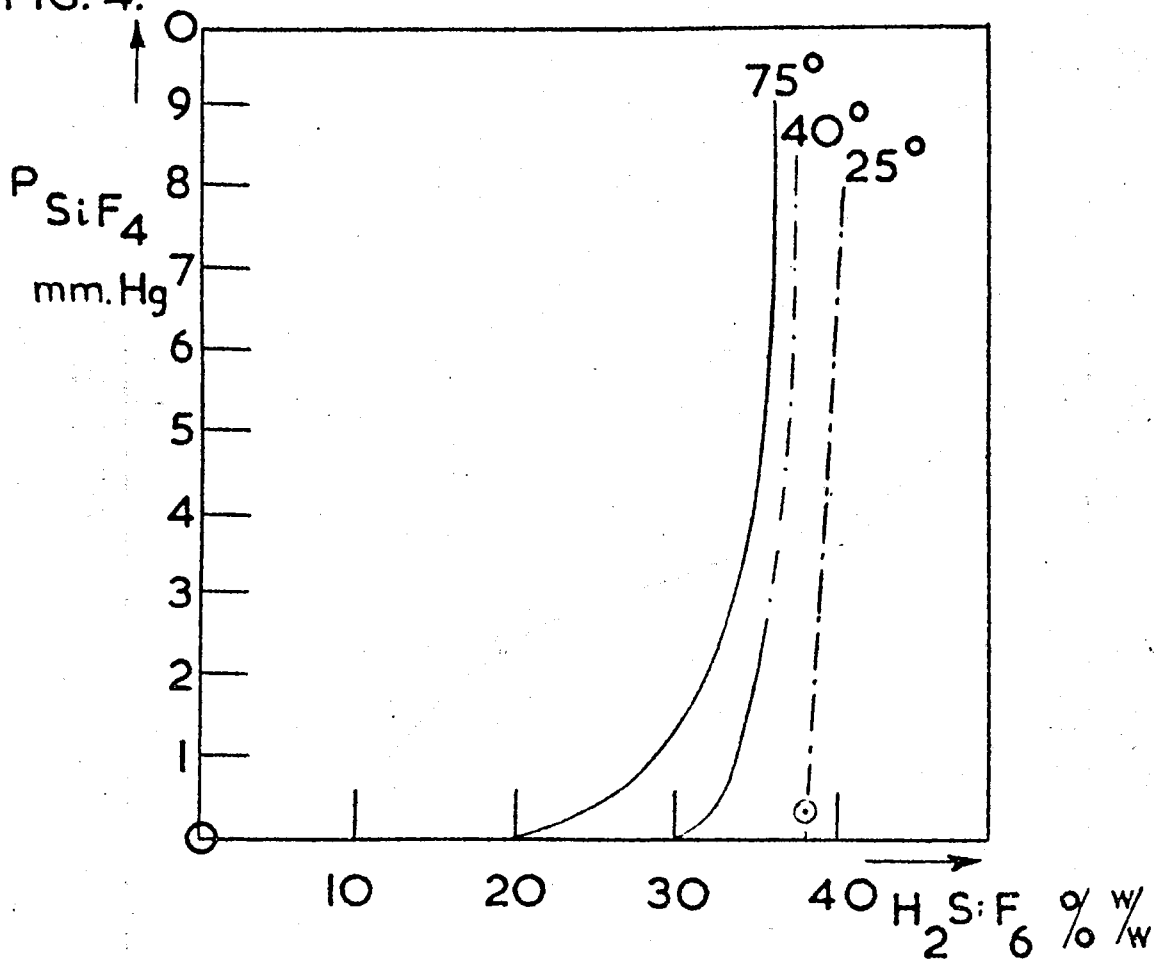
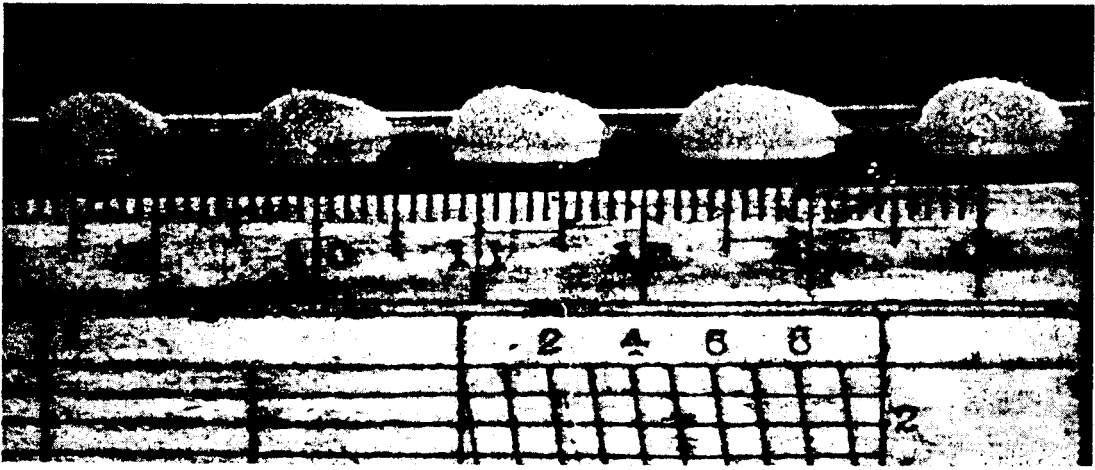


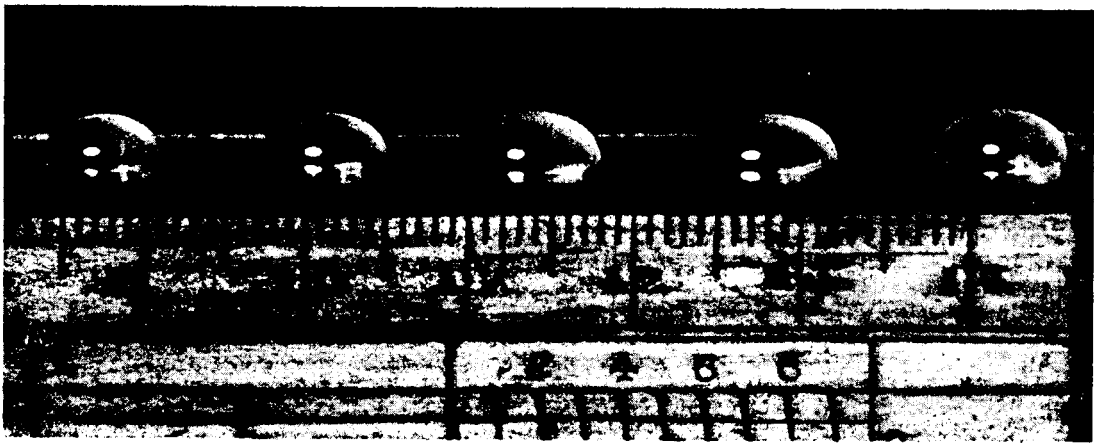
FIG. 4.



FORMATION OF SILICA FILM ROUND WATER DROPS



Water drops on greased microscope slide.



Drops after short exposure to SiF_4 - air mixture ; showing silica film round drop.



End drop cut surplus liquid removed by filter paper, showing hollow nature of drop.

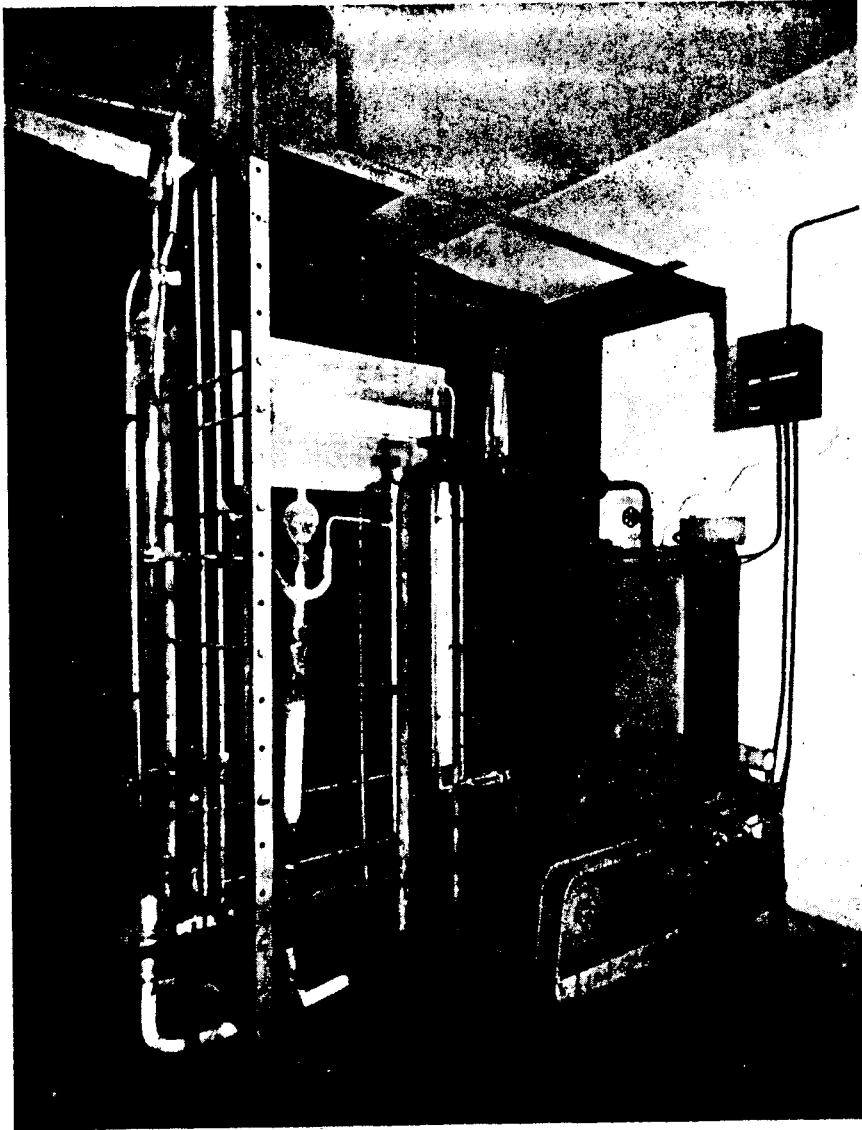


Fig. 6. General Arrangement of Apparatus used.

FIG. 7. FLOW DIAGRAM OF ABSORPTION APPARATUS.

