VAPOR PHASE HYDROLYSIS OF SILICON TETRAFLUORIDE

by

Robert N. Secord

S. B. Massachusetts Institute of Technology

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Signature of Author_____
Department of Chem. Eng. Jan. 17, 1947

Certified by_____
Thesis Supervisor

_____
Chairman Department Committee on
Graduate Students

17 Fayette Street
Cambridge, Mass.
January 17, 1947

Joseph S. Newell
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts

Dear Sir:

In accordance with the requirements of the faculty I
herewith respectfully submit this thesis entitled
"Vapor Phase Hydrolysis of Silicon Tetrafluoride" in
partial fulfillment of the requirements for the degree of
Master of Science in Chemical Engineering.

Yours Truly,

Robert N. Secord

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I SUMMARY

Since silica of colloidal dimensions (1 micron) has reinforcing properties similar to carbon black, it was the objective of this thesis to produce finely divided silica, non-gel in structure, which could be used as a compounding agent for rubber, plastics, paints and other similar materials.

The method chosen to produce silica with the desired properties was the vapor phase hydrolysis of silicon tetra-fluoride. SiF_4 gas produced readily from CaF_2, H_2SO_4 and sand was collected by displacement over CCl_4 and analysed for SiF_4, HF, and inerts. It was then passed through a gas flame to react with water vapor, a product of combustion of the gas, at flame temperature (1800°K computed) to give SiO_2. The product was collected on the bottom of a porcelain evaporating dish by impingement. To prevent the condensation of water vapor from the gas flame the dish was filled with water and allowed to heat up somewhat to maintain the bath temperature at around 80°C.

In the above manner the desired product was obtained with yields between 30 and 56% of theoretical. The silicas prepared are non-gel in structure and have surface areas ranging from 170-297 m^2/gm * as determined by low temperature nitrogen adsorption. Changing the $H_2O:SiF_4$ ratio produced variations in the surface area of the product with the runs made at the lowest ratio giving the highest areas (see graph pg. /3). Surface areas determined by electron microscope pictures using average observed diameters and assuming

*Surface areas were determined by a commercial laboratory.

spherical particles, are in agreement with those of the adsorption method verifying the existence of a non-gel structure.* These silicas compare favorably with the reinforcing carbon blacks which have surface areas between 65-107 m^2/gm.

In addition to carrying out the process as outlined above additional investigation was done in an attempt to determine the reason for the yields being only 30-50%. Calculated yields from equilibrium constants found in the literature (pg.36) indicate that 100% yields should be expected even with a large excess of HF present. A run was tried introducing a large excess of anhydrous HF but the result showed a yield of the same magnitude as others made without it, indicating that equilibrium was not the cause of low yields.

It has been shown by the results of this thesis that a non-gel type of silica with high surface area may be prepared from inexpensive raw materials. However, in this work sufficient quantities of silica for use in test compounding with rubber etc. were not prepared. Further experimentation is necessary to (1) test the product as a compounding agent, (2) attempt to close a material balance around the system to determine conclusively whether equilibrium or collection is the cause of the comparatively low yields obtained, (3) investigate the rate of the hydrolysis reaction at flame temperature.

*The E. M. picture referred to was taken of silica prepared by other investigators in an identical manner, as herein described. [24]

II INTRODUCTION

A. Statement of the Problem:

For many years carbon black has been used in compounding rubber to strengthen it physically. The exact mechanism of the strengthening of the matrix by compounding with fillers of this type is unknown, but the theory most widely accepted and best supported by the available research data is that the colloidal carbon particles bind the long chain molecules of the rubber together by a combination of van der Waals' and chemical forces. This explanation is supported by the facts that

(a) compounding does not change the chemical structure of the matrix,

(b) saturated polymers do not change appreciably in their physical properties through compounding, whereas unsaturated polymers are considerably strengthened. (1)

The primary factors affecting the reinforcing action of carbon black on natural and synthetic rubbers have been found to be

(a) amount of carbon black used

(b) dispersion

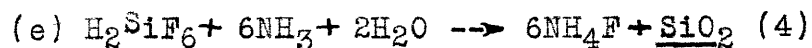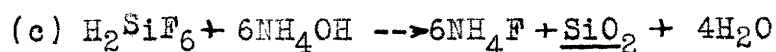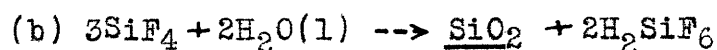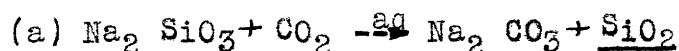(c) external surface of carbon black available (1)

All of the above factors are related directly or indirectly to the size of the carbon particles used. Further study of the effect of particle size on the reinforcing properties of carbon black (2) shows that although the fineness of division and surface area are primary factors in reinforcement of rubber, they are not the only ones since rubbers compounded with very

finely divided carbon black is weaker than that of other mixes with the exception of those using the very coarse particles. The best reinforcing blacks have particle sizes between 24 and 43 mμ diameter with specific surface areas between 65-107 m^2/gram.

In the search for other compounding agents for rubber, plastics, paints and other similar materials it was observed that colloidal silica imparted the same desirable properties to the compounded materials as carbon black, and in addition had the added advantage of having high dielectric strength and no color. The greatest drawbacks to the use of colloidal silica in this manner is the cost and difficulty of producing it in the desirable condition and somewhat lower reinforcement characteristics.

The previous methods suggested and attempted for the preparation of silica for compounding are many. Among the more recent ones are those based on the following reactions:

(a) $Na_2 SiO_3 + CO_2 \xrightarrow{aq} Na_2 CO_3 + \underline{SiO_2}$

(b) $3SiF_4 + 2H_2O(1) \dashrightarrow \underline{SiO_2} + 2H_2SiF_6$

(c) $H_2SiF_6 + 6NH_4OH \dashrightarrow 6NH_4F + \underline{SiO_2} + 4H_2O$

(d) $2H_2O + Na_2SiF_6 + 4Na_2CO_3 \rightarrow \underline{SiO_2} + 6NaF + 4NaHCO_3$ (3)

(e) $H_2SiF_6 + 6NH_3 + 2H_2O \rightarrow 6NH_4F + \underline{SiO_2}$ (4)

(f) Silica gel dried in presence of protective colloid (gelatin or gum arabic) (5)

(g) Colloidal solutions of silica gel dehydrated and ground. (6)

All of the above methods require extensive drying since they are carried out in water solutions. The formations of gels

instead of precipitates is an ever present nuisance from a manufacturing standpoint and the product obtained in a gel state is extremely difficult to dehydrate in such a way as to insure a uniform product of suitable dimensions.

One other process has been developed to produce finely divided silica, namely the combustion of organo-silicates. The silicas produced in this manner are non-gel in structure and have particle sizes of less than .1 μ (21) but the raw materials for manufacture in this manner are quite expensive.

The maximum tensile strength of rubber compounded from SiO_2 according to Subbotin and Lukyanchikov (6) is 121 kg/sq. cm. while carbon black compounds give tensile strengths up to 240 kg/sq. cm. with the least reinforcement obtained from carbon black being in the neighborhood of 210 kg/sq. cm. (1)

The smallest silica particles referred to in the literature have been .1 μ (21) whereas the carbon black used most successfully has been on the order of 50 mμ. It would seem that although in compounding with carbon black particle size and surface area are not the only factors controlling the reinforcing action of the filler, other factors do not have effect until the particle size is on the order of 50 mμ or about 1/2 as large as the smallest silica particles used so far.

Therefore, it was the purpose of this thesis to attempt to devise an inexpensive method to produce silica of a similar particle size as the carbon black referred to above

(50 mu), in such a manner as to eliminate the handling of gels and the necessity of drying the product. The vapor phase hydrolysis of silicon tetrafluoride was the method investigated.

B. Literature Survey

In 1849 A. Daubree (8) in his experiments, while trying to duplicate the geological processes of nature in forming minerals, found that when SiF_4 with water vapor was passed through a quartz tube at white heat quartz crystals were collected as the results of the hydrolysis of the SiF_4. Further study of this reaction

$$SiF_4 \text{ (g)} + 2H_2O \text{ (g)} \longrightarrow SiO_2 + 4HF \text{ (g)}$$
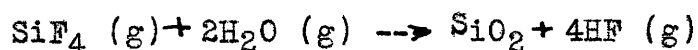
by Guntz (9), Troost, and Hautefeuille (10), and Baur (11) showed that the vapor phase hydrolysis of SiF_4 was very incomplete at moderate temperatures. Baur computed constants for the reaction at $104^{\circ}C$ and $270^{\circ}C$ as follows:

$$K_p = \frac{P_{SiF_4} \cdot P_{H_2O}^2}{P_{HF}^4} = 5.28 \cdot 10^7 \text{ at } 104^{\circ}C; \quad 1.21 \cdot 10^6 \text{ at } 270^{\circ}C$$

(See App. Pg. **29**)

He also determined the Q for the reaction as -8945 cal/gram mol.

Ryss (12) in a more complete investigation of the reaction determined constants at several temperatures. Plotting log K vs 1/T, (See App. Pg. **30**) a good straight line results, which seems to verify the accuracy of his technique. The Q calculated by Ryss was -27,740 cal/gram-mol for the reaction with amorphous silica and -22,540 cal/gram mol with quartz. Ryss' data was determined from theoretical considerations which

he did not verify experimentally. No data are available on
the rates of this reaction from any of the sources used.

III PROCEDURE

Objective

Considering the previous investigations of the equilibrium between SiF_4, water, and HF in the vapor phase it was decided that a process should be used which would carry out the reaction

$$SiF_4(g) + 2H_2O(g) \longrightarrow SiO_2 + 4HF(g)$$
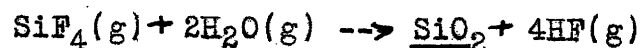
at the highest practicable temperature and with various ratios of H_2O/SiF_4. It should be pointed out at this point that the reaction

$$3SiF_4 + 2H_2O\ (1) \longrightarrow 2H_2SiF_6 + SiO_2\ (.xH_2O)$$

goes very readily in liquid water at room temperature but this method yields a <u>gel</u> and the maximum product produced is 1/3 of the total silica available.
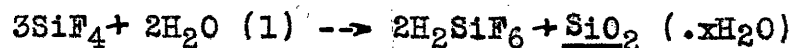
To meet the specifications set above two methods were suggested. (1) Hydrolysis in a flame rich in H_2O, and (2) hydrolysis in a furnace with steam introduced directly. Of the two methods the better one seemed to be the flame hydrolysis technique for two reasons: (1) higher reaction temperatures were available, and (2) the apparatus would be simpler to construct and the reaction more easily controlled.

General Procedure (13)

The apparatus was constructed from glass flasks etc. and rubber tubing. SiF_4 was produced readily by the reaction of CaF_2, SiO_2 (washed crucible sand), and H_2SO_4 according to the following equation:

$$SiO_2 + 2CaF_2 + 2H_2SO_4 \longrightarrow 2CaSO_4 + SiF_4 + 2H_2O$$
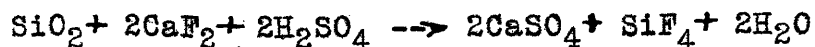
Moderate heating was necessary to keep the reaction going but care had to be taken against overheating in which case the reaction tended to become self sustaining and "run away." The SiF_4 produced by this reaction was not pure. Some air was entrained in the apparatus in spite of flushing, and HF was produced as an impurity by the reaction.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$
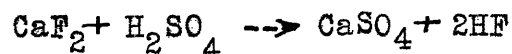
During the first part of the experimentation a trap of NaF dispersed on glass wool was used at room temperature to remove the HF produced from the product. This trap was discarded when an analysis of the trapped products showed that as much of the desired product was retained as the impurities. Thus, in this case, both of the following reactions seemed to go with equal ease at room temperature.

$$NaF + HF \longrightarrow NaHF_2$$

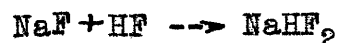$$2NaF + SiF_4 \longrightarrow Na_2SiF_6$$

The product gases were bubbled through concentrated sulfuric acid to insure the removal of water vapor and entrained liquid particles and then were stored in a large bottle over CCl_4. The displacement system may be readily seen by referring to Diagram I pg. (24).

After approximately 10 liters of SiF_4 were collected a sample was withdrawn and analysed (see below). The product gas after analysis was passed through a control manometer, mixed with city gas flowing at a known rate, and the mixture was fed to a bunsen burner where combustion and hydrolysis took place at a computed flame temperature of about $1800^\circ K$.

The reaction is as follows:

$$SiF_4(g) + 2H_2O(g) \longrightarrow \underline{SiO_2} + 4HF(g)$$
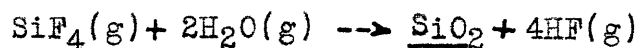
The product was collected by impingement on the bottom of a large porcelain evaporating dish which was filled with hot water. Various ratios of H_2O/SiF_4 were used to vary the surface area of the product produced.

The analysis of the SiF_4 was made by withdrawing a sample of the gas from the original reaction into a calibrated collection bottle and bubbling the sample through water. Inert gases were collected over water in a graduate. The silica precipitate from the liquid hydrolysis was filtered, washed with distilled water, dried, calcined and weighed. An aliquot portion of the filtrate was titrated with sodium hydroxide and evaporated to dryness. The resultant precipitate was washed, filtered, dried, calcined and weighed. Total silica, fluorides and inerts per liter, were determined in this manner. HF/liter can be calculated or determined by difference.

IV RESULTS

The SiO_2 produced by the vapor phase hydrolysis of SiF_4 is a very fluffy powder with an apparent density of about .04 grms/cc. It is highly electrostatic when brushed or scraped from a surface. A pinch of the silica rubbed between the fingers has no gritty feeling but does seem to dry the skin over which it is rubbed. A sample of this silica when mixed with approximately an equal weight of crude linseed oil gave a gel like material slightly increased in opacity which was probably due to air introduced during the mixing. This gel like mass did not dry in the open air after a period of a month.

Surface area determinations made on some of the products from runs using different H_2O/SiF_4 ratios show areas between 170-297 m^2/gm* which is well above those of carbon blacks used for compounding. The surface areas of the particles produced under varying conditions are contained in the following table:

Run	H_2O/SiF_4 ratio	H_2O Rate mols/min	SiF_4 Rate mols/min	Surface area m^2/gm *	% Yield
9D	3.0	.0260	.0086	297	29.9
9A	3.9	.0234	.00602	198	42.7
9B	6.9	.0260	.00376	178	51.0
9E	17.3	.0538	.00312	170	44.7

(graph pg. 13)

Determination of % moisture and hydrocarbon impurities show that less than 1% are present.

*see footnote pg. 1

Electron microscope photographs*(copies are not available at this time) have been taken of a sample whose total surface area was determined by low temperature nitrogen adsorption as 170 m^2/gm. The average particle diameter determined from the photograph was less than 250 A^0 giving a calculated surface area for spherical particles of greater than 109 m^2/gm which agrees within reasonable accuracy with that of the adsorption method.

Run 14 A was made using an excess of HF to determine its effect on the % yield recovered. The figures are as follows:

H_2O mols/min	SiF_4 mols/min	$(HF)_1$ mols/min	H_2O/SiF_4	% Yield
.0744	.00637	.0173	11.6	43.7

*see footnote pg. 2

Correlation Of Surface Area
with $H_2O : SiF_4$ Ratio
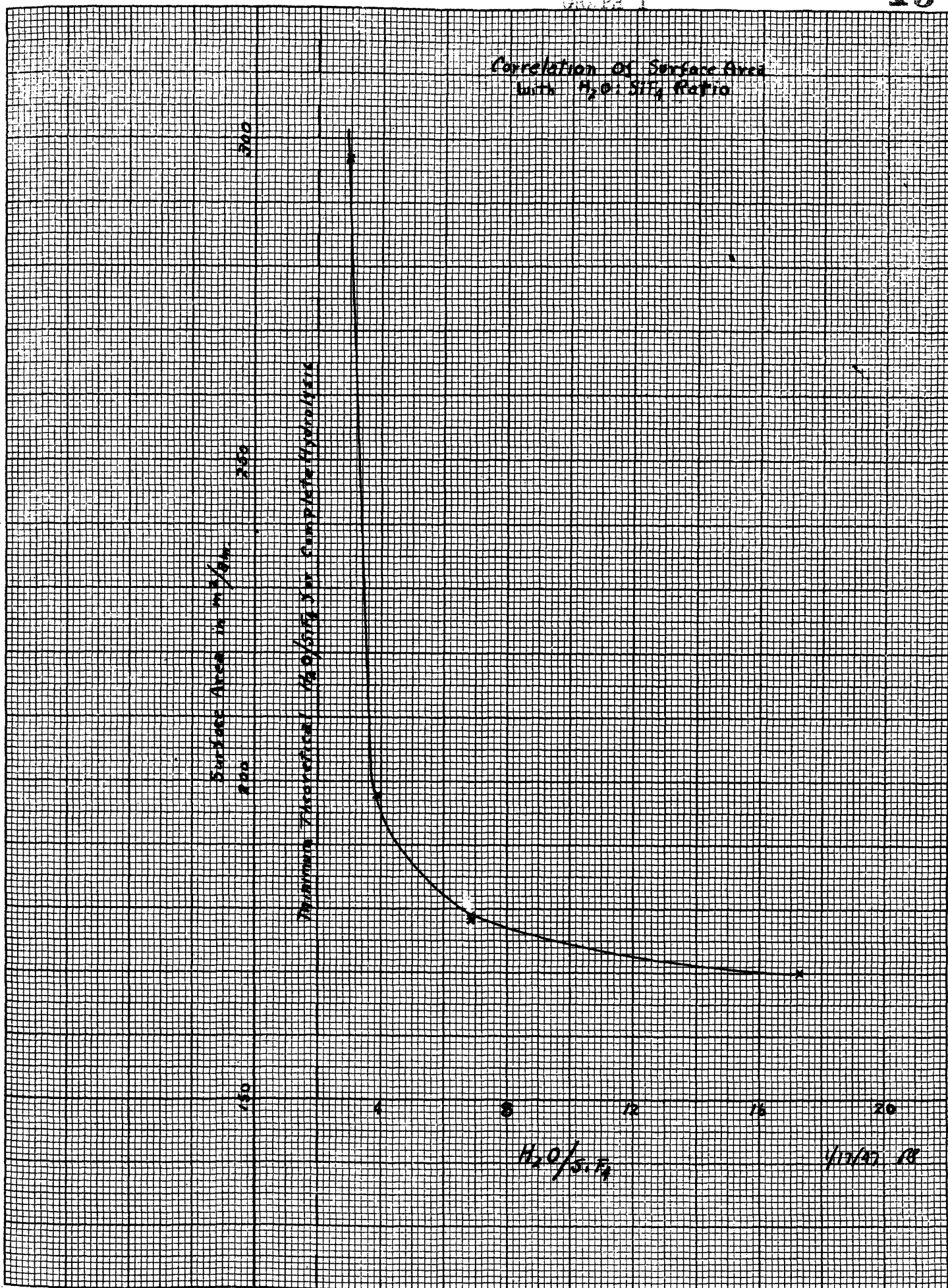
V DISCUSSION OF RESULTS

The vapor phase hydrolysis of SiF_4 has produced silicas of particle sizes comparable to those of the carbon blacks used for compounding with rubber. However, it has yet to be determined by further experimentation whether the reinforcing properties of this silica will be comparable to the blacks. As has been pointed out previously in the introduction very fine carbon blacks do not have the maximum reinforcing action as may be the case with this material.

The conclusion that the silica produced is non-gel in structure, as was desired, has been drawn from the fact that the area determined by the nitrogen adsorption technique which gives the total surface area of a particle, capillaries and all, is reasonably close to the area determined by the electron microscope i.e. 170 m^2/gm by N_2 adsorption vs. 109 m^2/gm by E. M. photograph.[*] Since the determination of surface area by E. M. photograph assumes smooth spherical particles the agreement between the two methods is sufficient evidence to justify the conviction that the particles are non-gel in structure.

Various attempts were made to correlate the change of the particle sizes of the products from different runs with the various changes of conditions used for each. Since the same H_2O rate was used in runs 9A and 9D with a large difference in the surface areas of the products resulting, it is apparent that no correlation between the two exists in this case, i.e. water rate and surface area. It is possible to

*see footnote pg. 2

graph a reasonable correlation between the SiF_4 rate and the surface area but the resulting curve is not as good as that made from the plot of H_2O/SiF_4 vs. surface area which shows a very smooth curve with the highest area determined from the product made at the lowest H_2O/SiF_4 ratio. Although the four areas determined are not sufficient evidence to make a positive prediction of the trend of the particle size with the H_2O/SiF_4 ratio they have shown sufficient correlation to have the fact pointed out.

Run 14A was made in an attempt to discover whether the equilibrium constants used were reliable since they were extrapolated from a curve made at much lower temperatures. The yield from this run (44%) was about the same as those recovered from other runs made without the excess HF. This indicates that the equilibrium conditions were not affecting the recovery at 50% yield. It is believed, however, that these results are inconclusive since the apparatus was glass and some of the tubing in the HF delivery system was badly etched indicating that additional SiF_4 was added to the stream which was not taken into account in the calculation of the % yield. There also does not appear to be any correlation between either of the gas rates or the H_2O/SiF_4 ratio and the % yield which would indicate that the equilibrium constant was not as computed. As a result of the data obtained from Run 14A and the lack of correlation of % yield to any of the data in the other runs it is concluded that a better collection system is needed, possibly

of the channel type used in the recovery of carbon black. However, further study of the equilibrium conditions by completing a material balance around the system and of the reaction rate at flame temperature may provide an explanation for the low yields obtained.

VI CONCLUSIONS

The following conclusions have been made from the results of this thesis:

(1) It is possible to produce finely divided silica which is non-gel in structure by the vapor phase hydrolysis of SiF_4 at flame temperature.

(2) The surface area of the silica produced is of the same order of magnitude as that of carbon blacks used for compounding with rubber etc. i.e. 25 mμ and smaller.

(3) The smaller the H_2O/SiF_4 ratio used for the process the higher the surface areas of the product.

(4) The method requires inexpensive and easily obtained raw materials.

(5) The general procedure for preparing silica by this method is simple and direct.

VII RECOMMENDATIONS

On the basis of the results obtained it is believed that sufficient progress has been made to warrant further investigation of the actual properties which this silica will show when used as a compounding material.

There are still many questions to be answered on the chemical problem which have not been covered during the present thesis. Although attempts have been made to determine the cause of the low yields, they have been inconclusive. It is realized that a considerable portion of the yield is lost due to incomplete collection. A more efficient channel type system could be devised to rectify this difficulty to a great extent.

Closing a material balance around the system would also be a problem the solution of which might disclose the reason for the low yields. It is possible that the equilibrium constants used may not be accurate and hydrolysis may not be as complete as computed using literature data.

Several other salient points have not been investigated. The flame temperature should be measured directly instead of computed as has been done. Since no determination of the secondary air used was made during the experimentation, the assumption that only enough air entered to allow complete combustion is obviously incorrect. Too short a time of contact between the gases in the flame may be another cause of low yield, therefore, a study of the reaction rate at flame temperature might provide the answer to the problem.

APPENDIX

APPENDIX A

Details of Procedure

1. Preparation of SiF_4 (see diagram I pg. 24)(ref. 13)

On a laboratory scale it has been necessary to use approximately double the quantities of initial materials, SiO_2, H_2SO_4 and CaF_2, to prepare the desired amount of product. The reason has been that the reaction tends to become very slow during the latter portion and more time would have been taken in producing the SiF_4 with high percentage yields than was available. In general, a molal ratio of H_2SO_4: SiO_2: CaF_2 has been 3.5:6:2 using approximately 2^{gm} mols of CaF_2 for each run and collecting about one half mol of SiF_4 or about a 50% yield.

It was noted that the reaction etched the reaction flask to a considerable extent. Upon weighing a flask before and after one run it was discovered that over 75% of the silica came from it. This, however, may not have been the case for every run.

The chemicals used were C. P. H_2SO_4 (Dupont), technical CaF_2 (fluorspar), and washed crucible sand. Possibly some other type of silica should be used in the original mix rather than sand, i.e. glass scraps, silicic acid, or a silica gel.

The product gas was passed through a frittered bubble plate immersed in concentrated sulfuric acid to remove the entrained liquid particles and water vapor. The gas was collected by displacement over CCl_4.

The chemical reaction is as follows:

$$2CaF_2 + 2H_2SO_4 + SiO_2 \longrightarrow 2\underline{CaSO_4} + 2H_2O + \overline{SiF_4}$$
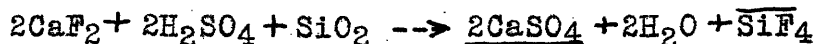
HF is also formed by this reaction, but attempts to remove it resulted in the removal of a large portion of SiF_4 so the impurity was allowed to remain in the product gas. The side reaction is:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 4HF$$
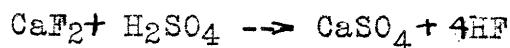
2. Hydrolysis of SiF_4 (see diagram I)

The SiF_4 gas produced above was passed through a piece of capillary tubing and the flow was controlled by a manometer across the tube measuring the pressure drop. During the first part of the experimentation a dry ice trap was used to freeze out the CCl_4 and the HF vapors, but this was discarded when it was found that these gases did not affect the product and in addition the trap caused a good deal of trouble when the inlet tube became clogged with frozen CCl_4.

City gas was passed through a calibrated orifice and the flow was measured by manometer deflection. The SiF_4 and gas streams were brought together and passed into the gas inlet of an ordinary bunsen burner. The air was adjusted to just give a blue flame.

A porcelain evaporating dish was placed so that the point of the flame just touched its surface and the product collected evenly on this surface. The water in the porcelain evaporating dish was preheated for about 15 minutes using the same gas flow that was used in the run. The water attained a temperature of about $80^{\circ}C$. The reason for maintaining a hot surface was to prevent condensation of water on the under side of the dish and subsequent liquid phase hydrolysis of the SiF_4.

The product was recovered by scraping it from the bottom of the dish onto a large piece of paper from which it could be transferred into a bottle or other suitable container for weighing.

3. Gas Analysis (See diagram I)

The product gases from the SiF_4 producer were analysed as follows:

a. 1250 cc were withdrawn into a calibrated gas collection bottle and the pressure was equalized by a ballast bottle to atmospheric pressure. The confining liquid was CCl_4 as in the collection system. The sample was then bubbled through a flask containing 400cc of distilled water. The delivery tube was immersed in a mercury seal to prevent the hydrolysis products of the SiF_4 from clogging the line. Gases not absorbed during this operation were measured by displacement of water from an inverted graduate. This determined the amount of inert gases (air, CCl_4) in the original product gas.

b. The products of hydrolysis were filtered and the precipitate was washed and the total filtrate was measured. The precipitated silica was dried, calcined, and weighed.

c. An aliquot portion of the filtrate was titrated with 1 normal NaOH while hot (80°C) to a phenolphthalein end point determining in this manner the total fluoride. The resultant solution when evaporated to dryness precipitated the silica formed during the titration. Water was added to the precipitate and the whole mixture was heated, filtered, and washed. The precipitate was then dried, calcined, and weighed. This portion of silica, allowing for the aliquot

taken, plus the precipitate from (b) above, determined the total silica.

d. The analysis determined SiF_4, total fluoride, and inerts. $(HF)_x$ may be calculated from this data or by difference.

e. All operations were carried out at room temperature unless otherwise stated.

DIAGRAM I

SiO₂ Production + Collection

SiF₄ Production + Collection

Compressed Air or atmosphere

Hot H₂O

SiO₂ Collection

Bunsen Burner

SiF₄ Control Manometer

gas Control Manometer

ballast

CCl₄

collection bottle

SiF₄

H₂SO₄

drier

gas Sampler

H₂O

H₂

hydrolysis flask

CCl₄

displacement Bottle

H₂

Saftey Manometer

CaF₂, H₂SO₄, SiO₂ Reaction flask
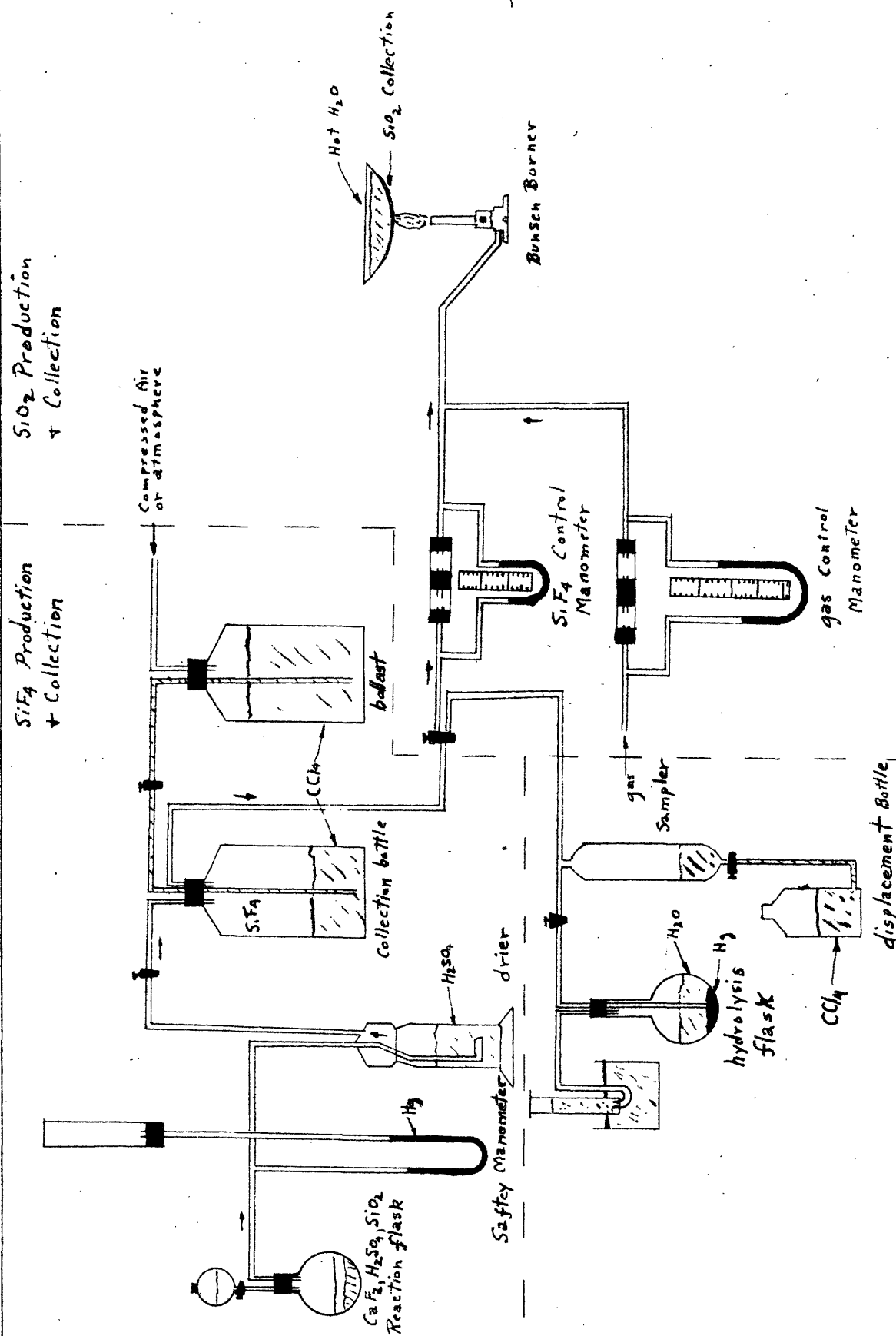
Sampling

Diagram #1
Vapor Phase Hydrolysis of SiF₄
1/17/42

TABLE I

Summary of Data and Calculations
Reaction Gas Analysis

Run	Sample volume in cc	Inert gases in cc	SiO₂(1) gms.	Total fluoride gms. in me	SiO₂(2) gms.	Total SiO₂ gms.	T °C	P mm Hg	%SiF₄	%HF	%Inerts	Remarks
1	14,750	6,780	5.63	475	29.0	34.6	23	760	12	42	46	KOH titration
2	10,900	3,080	3.00	1080	13.63	16.63	22	758	61.7	10.1	28.2	NaOH "
3	1,000	100	.345	666	1.260	1.605	25	767	58	32	10	"
4	1,250	50	.5664	166.8	1.806	2.473			75	21	4	"
5	1,250	150	.5144	158.5	1.765	2.279	25	760	68.2	19.8	12	"
6	same as 5											"
7	same as 5											"
8	1,250	150	.4185	229.8	1.6104	2.029	24	762	67	22.6	10.4	"
9	1,250	210	.4428	273	1.802	2.245	25	772	72	11.2	16.8	"
10	1,250	270	.3525	130.7	1.6305	1.982	25	768	72.2	6.2	21.6	"
11	1,250	160	.4340	151	1.720	2.154	25	771	67.2	20	12.8	"
12	1,250	415	.2124	100	1.210	1.422	25	756	50	16.2	33.8	"
13	1,250	650	.0987	91.3	1.395	1.494	25	763	48	0	52	"
14	1,250	105	.4854	150	1.880	2.365	25	763	77	14.6	8.4	"
14A	calculated						25	763	26.1	71.2	2.7	"

TABLE II

DATA FROM RUNS

Run	Date	T^oC	P mm of Hg	gas man. cm H_2O	SiF_4 man. mm CCl_4
1	11/ 5	23	760		
2	11/ 7	22.5	758		
3	11/15	23	767	4.2	no man.
4	11/21	?	?	6.9	"
5	11/25	25	760	13.8	8
6	11/26	22	760	7.0	10
7	11/27	24	762	9.3	12
8A	11/27	24	762	10.0	13
B	11/27	24	762	10.0	12
C	11/27	24	762	10.0	12
D	12/ 2	23	757	2.7	23
9A	12/ 3	25	772	2.0	11
B	12/ 3	25	772	2.3	5.5
C	12/ 3	25	772	6.9	5.5
D	12/ 3	25	772	2.3	21
E	12/ 4	25	768	6.9	3
10A	12/ 4	25	768	7.1	6
B	12/ 5	24	767	2.3	5.5
11A	12/ 6	25	771	2.4	8
B	12/ 6	25	771	11.7	6
12A	12/11	25	758	13.3	6
B	12/12	24	763	13.1	7
13	12/12	25	763	13.3	7
14A	12/19	25	768	12.1	24 (with HF)
B	12/20	24	774	10.6	10

TABLE III

RESULTS OF RUNS

Run	Analysis SiF₄	HF	Inerts	Gas Rate mols H₂O per min.	SiF₄ Rate mols per min.	H₂O/SiF₄	% Yield	Surface Area* m²/gm	Collection	Remarks
1	12	42	46	data unreliable liquid phase hydrolysis only						
2	62	10	28	"	"	"	"	"	vacuum	contaminated
3	58	32	10	.039	.00204	19.0	less 10%			
4	75.5	20.7	4	.0532	.00472	11.3	0			
5	68.2	19.8	12	.079	.0038	20.7	26.9	113	glass wool and vac.	"
6	68.2	19.8	12	.0556	.00517	10.4	26.4	144.5	glass wool filter	"
7	68.2	19.8	12	.0631	.0056	11.3	0		glass beads	"
8A	67	22.6	10.4	.0664	.0061	10.9	33		w/ glass wool	"
B				.0664	.0061	10.9	13.5		wire guaze filter	"
C				.0664	.0059	11.3	0		glass wool filter	
D				.0332	.00815	4.0	18.7		wire guaze filter	
9A	72	11.2	16.8	.0234	.00602	3.9	42.7		impingement	"
B				.0260	.00376	6.9	51	178		"
C				.0540	.0041	13.2	52			"
D				.0260	.0086	3.0	29.9	297		"

RESULTS OF RUNS
(cont.)

Run	Analysis SiF₄	HF	Inerts	Gas Rate mols H2O per min.	SiF4 Rate mols per min.	H2O/SiF4	% Yield	Surface Area* m²/gm	Collection Remarks
9E				.0538	.00512	17.3	44.7	170	Impingement
10A	72.2	6.2	21.6	.0545	.00352	15.5	56.7		Exptl. with collec-tion & % HF changes
B				.0260	.00473	5.5	35.1		
11A	67.2	20	12.8	.0273	.00478	5.7	32.5		impingement on hot surface
B				.0729	.0038	19.2	51		surface impingement on cool surface
12A	50	16.2	33.8	.078	.00285	27	49.7		attempt to prepare HF "
B				.077	.00353	21.8	38.2		"
13	48	-	52	.0771	.00348	22.2	31		
14A	26.1	71.2	2.7	.0744	.00637	11.6	43.7		anhydrous HF added
B	77	14.6	8.4				37.2		

* See footnote Pg. 1

TABLE IV

CALCULATED EQUILIBRIUM RELATIONS
FROM LITERATURE DATA

Ryss' Data (12)

T $^\circ$K	1000/T	K_p (amorph)	Log K_p
377	2.65	10^{12}	12.0
543	1.84	10^7	7.0
773	1.29	$4 \cdot 10^3$	3.60
873	1.145	$5.26 \cdot 10^2$	2.72

Baur's Data (11)

377	2.65	$5.26 \cdot 10^7$	7.72
543	1.84	$1.21 \cdot 10^6$	6.08

$$K_p = \frac{P_{SiF_4} \cdot P^2_{H_2O}}{P^4_{HF}}$$

GRAPH II

Plot of Equilibrium Data

$SiF_4(g) + 2H_2O(g) \rightleftharpoons SiO_2 + 4HF(g)$

$$K_p = \frac{P_{SiF_4} \cdot P_{H_2O}^2}{P_{HF}^4}$$

Log_{10} K_p

$\frac{1000}{T}$

1/10/41 RS
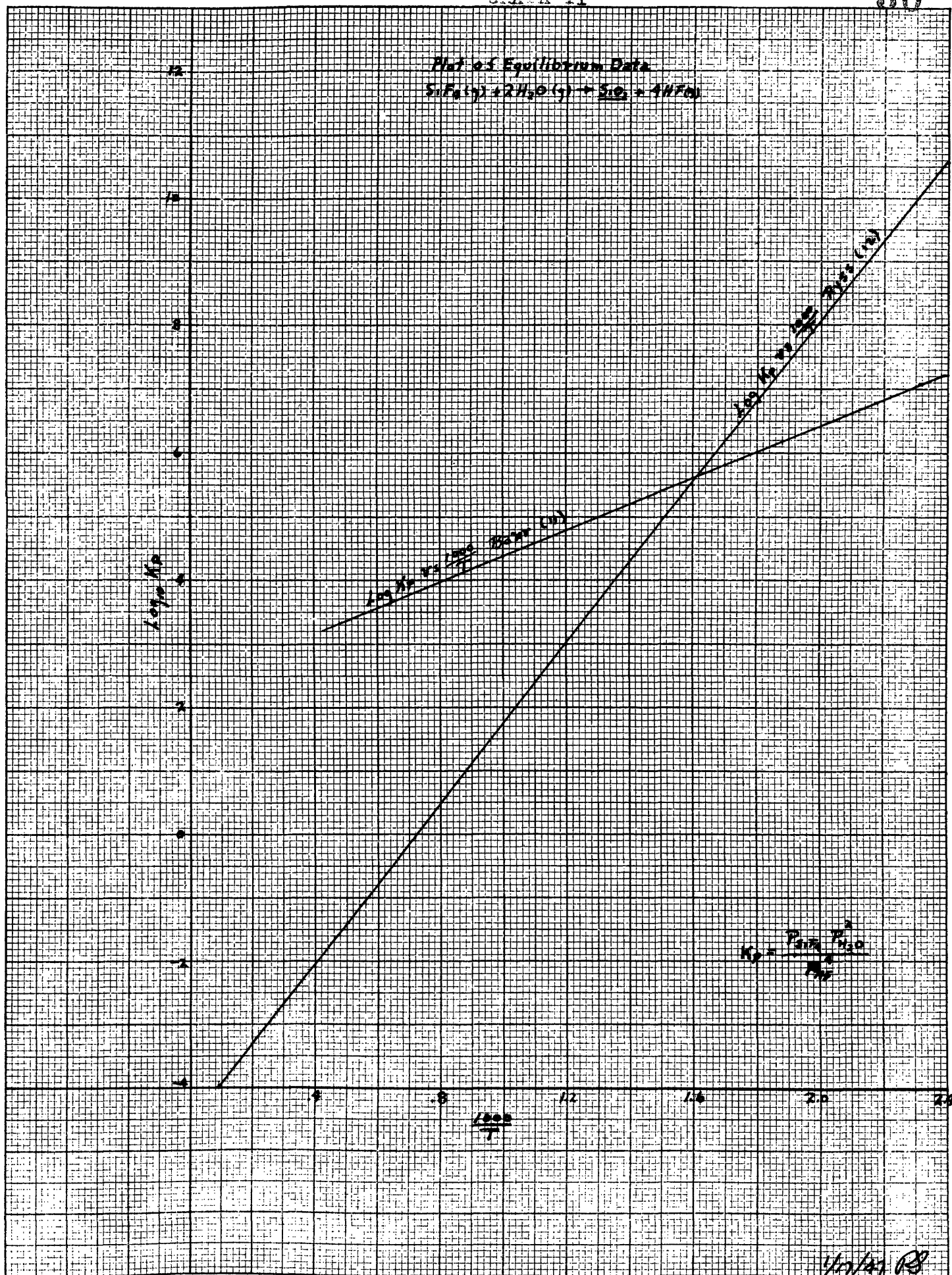
TABLE V

GAS ORIFICE CALIBRATION DATA

ΔH in cm of H2O	Stat Av. mm of Hg	Vol. cc	Time sec.	v in cc/min	ΔH/v	ρair	ρv
21.8	12.7	4000	95.5	2520	.00866	.00140	3.52
16.1	10.1	4000	100	2180	.00738	.00136	2.97
9.3	5.1	4000	143	1680	.00551	.00128	2.15
4.2	1.0	2000	109	1100	.00378	.00122	1.35
1.9	-.8	2000	177	680	.00276	.00119	.852
1.1	-1.2	1000	123.5	48.6	.00224	.00118	.573

gas used for calibration air.   T 21°C; P 758.5 mm of Hg.

FOR CITY GAS

Flow Assumed cc/min	ρgas 25°C	ρv	ΔH/v from chart	ΔH
500	.000867	.434	.0019	.95
1000	" " "	.867	.0028	2.8
1500	" " "	1.300	.0038	5.7
2000	" " "	1.735	.0047	9.4
2500	" " "	2.170	.0057	14.3
3000	" " "	2.602	.0066	19.8

GRAPH III

Orifice Calibration Curves for City Gas at 5" c4
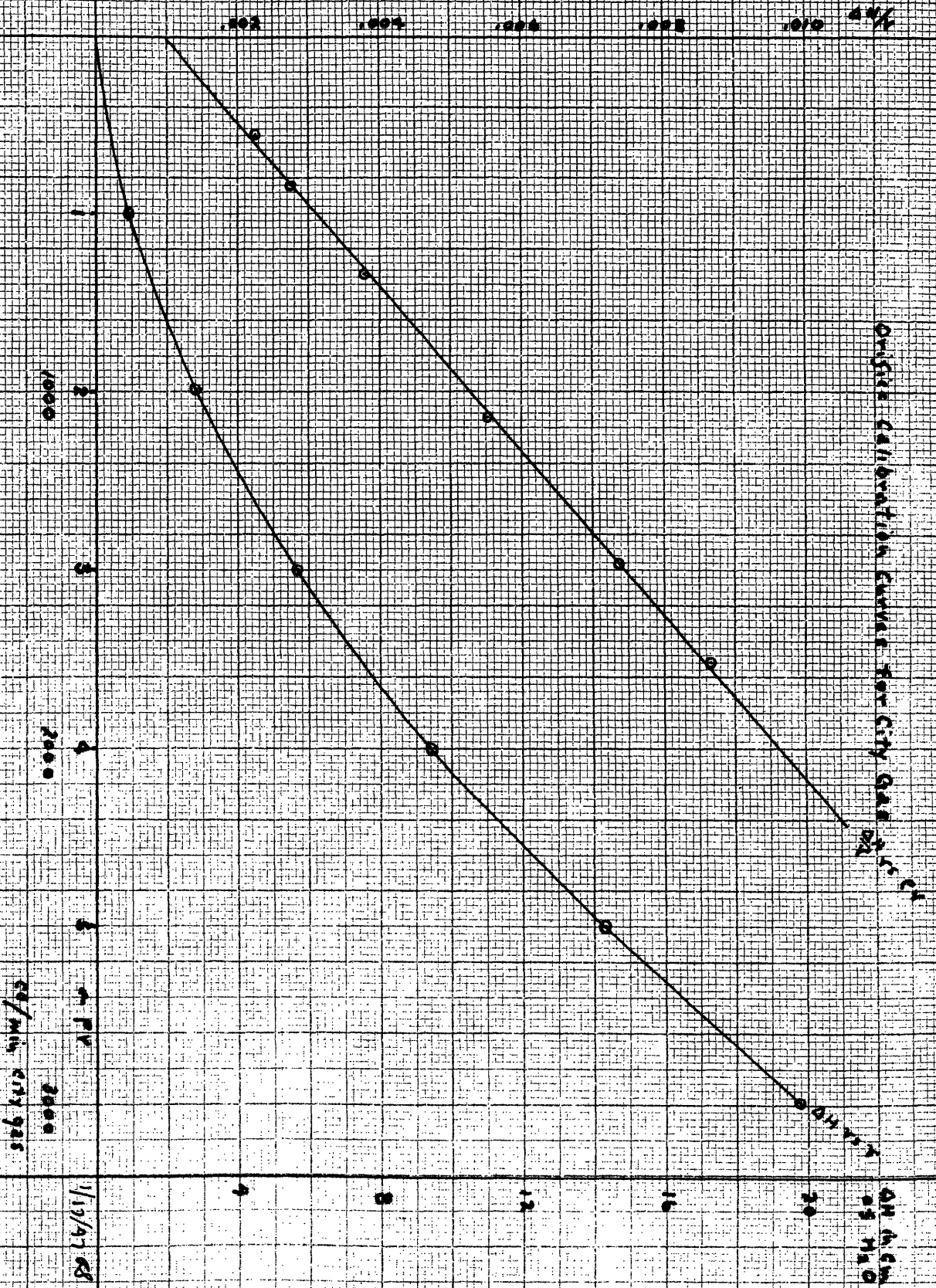
TABLE VI

SiF$_4$ ORIFICE CALIBRATION DATA

For Run Fourteen A

Run	Time Min	Volume in cc	ΔH mm of CCl$_4$	v cc/min
6B	5	800	10	300
6D	3	500	9	167
7B	4	600	12	150
8C	7	2100	20	300
9A	10	2000	11	200
B	16	2000	5.5	125
C	15	2000	5.5	133
D	7	2000	21	286
E	19	2000	3	105
10A	15	2000	6	133
B	25	4000	5.5	160
11B	22	2900	6	132
12A	13.5	2000	6	148
B	11	2000	7	182
13	13$\frac{3}{4}$	2400	7	174

GRAPH IV

SiF_4 on fine Calcination Curve

ΔH in mm of CO_2
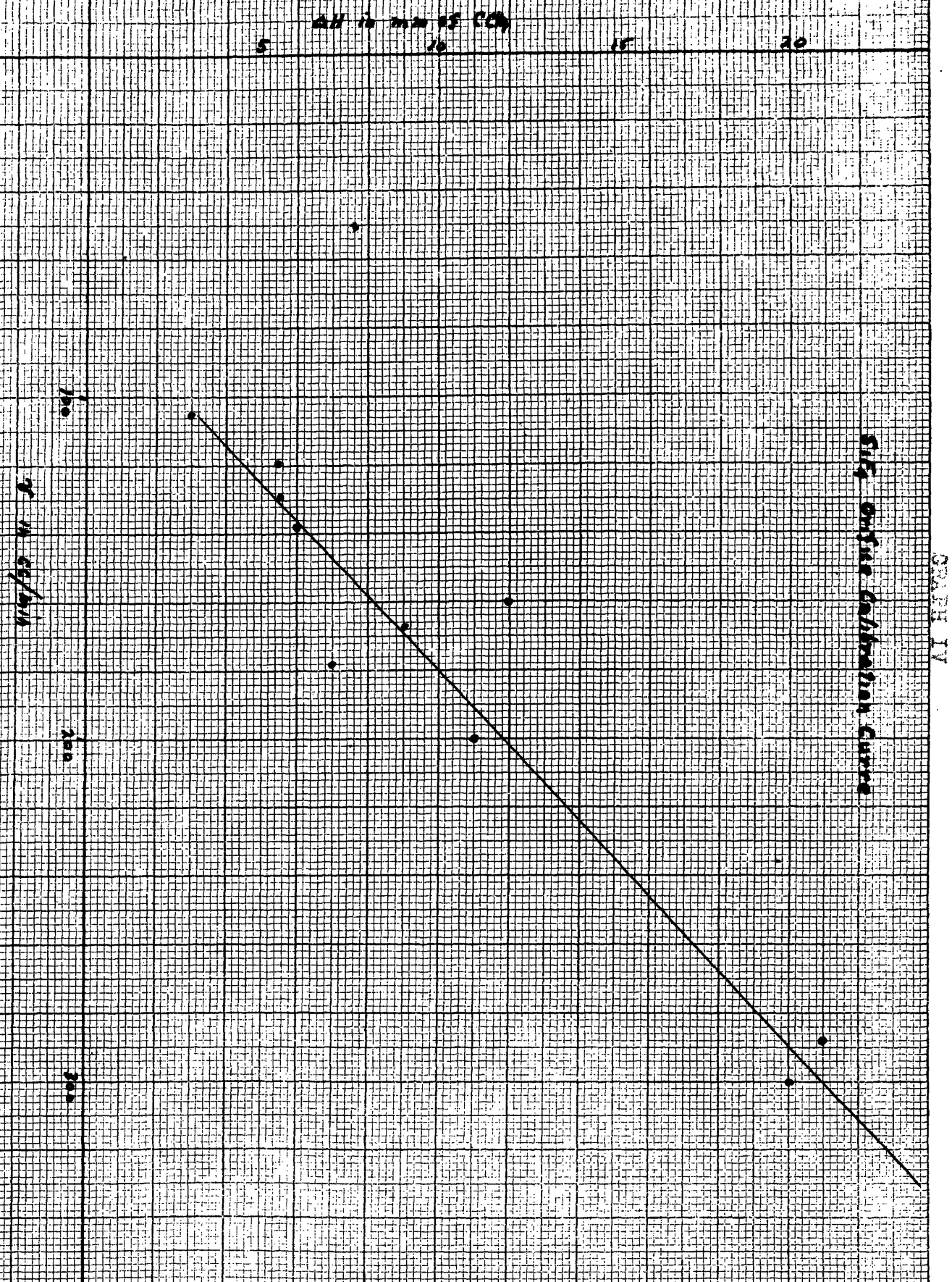
APPENDIX C

Sample Calculations

City Gas Analysis

Computation of H_2O Formed From Combustion

Gas Analysis   Gr. .731 ref air   BTU 528-535/cu. ft.

CO_2 7.6%

Ill.10.1

O_2 .6

CO 21.7

CH_4 14.6%

H_2 26.6

N_2 18.8   Average analysis of city gas courtesy
Cambridge Gas & Electric Company

Approximate analysis of illuminants C_2H_4/C_6H_6 = 3/1 (22)

  therefore H_2O produced/100cc of gas is as follows:

from   14.6cc CH_4 29.2

          26.6cc H_2 26.6

  .75·10.1cc C_2H_4 15.0

  .25·10.1cc C_6H_6 7.5

          total   78.3cc H_2O vapor/100cc of gas

22,400cc gas at STP will give .783 gm mols of H_2O

Calculation of reactive gas analysis:

    Example: run 9 1250cc sample T = 25°C   P = 772 mm of Hg.

        Volume of inerts = 210cc

    SiO_2 precipitated from hydrolysis   .4428 gms

    SiO_2 precipitated from titration aliquot   100/440

                .4095 x 4.4 =   1.802

        Total SiO_2 =   2.245   or .0374 mols

mols of gas

    $$\frac{1250}{22400} \times \frac{273}{298} \times \frac{772}{760} = .0519 \text{ total mols}$$

    % SiF_4 =   .0374/.0519   x   100 = 72%

    % inerts = 210/1250   x   100   = 16.8%

    % $(HF)_x$ = by difference   = 11.2%

titration of 100cc portion of total filtrate with .993 N NaOH
took 62.5cc for a phenolphthalein end point.

    62.5 x .993 x 4.4 = 273 me/1250cc total fluoride.

Calculation of H_2O/SiF_4 Ratio

Run 9D   T = 25°C   P = 772 mm of Hg.

Gas Rate:

Manometer ΔH = 2.0 cm of H_2O

from graph pg. 32, 2.0 cm. = 800cc/min. gas

800/22,400 x 772/760 x 273/298 x .783 = .0260 mols/min. H_2O

SiF_4 Rate: time = 7 min.   volume = 2000 cc

2000/22,400 x 772/760 x 273/298 x .72(%SiF_4)/7 = .0086 SiF_4 mols/min.

H_2O/SiF_4 = .0260/.0086 = 3.02

Calculation of Flame Temperature and Yield

Run 9D   Basis 1 mol SiF_4

3.00 mols H_2O total/mol SiF_4 or 1.0 mols H_2O in residue
gas after hydrolysis.

Heat of combustion 531 BTU/cu. ft. $= \dfrac{531}{1.8} \dfrac{454}{28,317} 22,400 = 106,000 \quad \text{cal/gram mol gas}$

since it takes 1/.783 cc of gas to give 1cc of water vapor at
STP (see pg. **35**) the 1/.783 x 3 = 3.83 mols of gas to give 3 mols
of water vapor.

Ht. of combustion = 3.83 x 106,000 = 407,000 cal/gm mol SiF_4

Gas Analysis   Basis 100 mols of gas O_2 for complete combustion

	CO_2	7.6	0
ill	C_2H_4	7.5	23.5
	C_6H_6	2.5	18.75
	O_2	.6	-.6
	CO	21.7	10.85
	CH_4	14.6	29.2
	H_2	26.6	13.3
	N_2	18.8	0
		99.9	95.00

air required   95/.21 = 453

Basis 1 mol of SiF_4 combustion products CO_2 H_2O N_2

	CO_2	H_2O	N_2
from CO_2	.291		
C_2H_4	.575	.575	
C_6H_6	.805	.402	
CO	.832		
CH_4	.560	1.120	

Combustion products (cont.) CO_2 H_2O N_2

from	H_2		1.02	
	N_2 from reaction gas		.720	
	N_2 from air			13.70
	Total	3.063	3.017	14.42

Assuming complete hydrolysis

Ht. of reaction $SiF_4 + 2H_2O \longrightarrow SiO_2 + 4HF$ $-22,500$ cal.

$$407,000 - 22,500 = \int_{291}^{T} \left[4(C_pHF) + 1.0(C_pH_2O) + 14.42(C_pN_2) + C_pSiO_2 + 3.06 (C_pCO_2) \right] dT$$

$C_p \, HF = 6.5 + .001T$

$C_p \, H_2O = 8.22 + .0015T + 1.34 \cdot 10^{-6}T^2$

$C_pSiO_2 = 1.2$

$C_pCO_2 = 10.4 + .00274T - 1.955 \cdot 10^5 T^{-2}$

$C_pN_2 = 6.5 + .001T$ (18)

$$384,500 = \int_{291}^{T} \left[26 + .004T + 8.22 + .0015T + 1.34 \cdot 10^{-6}T^2 + 93.8 + .0144T + 1.2 + 31.8 + .0084T - 5.98 \cdot 10^5 T^{-2} \right] dT$$

$$384,500 = \int_{291}^{T} \left[161 + .0283T + 1.34 \cdot 10^{-6}T^2 - 5.98 \cdot 10^5 T^{-2} \right] dT$$

$$= \left| {}_{291}^{T} \; 161T + .0141T^2 + .447 \cdot 10^{-6}T^3 + 5.98 \cdot 10^5 T^{-1} \right|$$

$$384,500 - 46,900 - 1,200 - 10 - 2050 = 161T + .0141T^2 +$$
$$.447 \cdot 10^{-6}T^3 + 5.98 \cdot 10^5 T^{-1}$$

$$334,300 = 161T + .0141T^2 + .447 \cdot 10^{-6}T^3 + 5.98 \cdot 10^5 T^{-1}$$

solve for T by trial and error

T = $1785°K$ $1000/T = .56$ from graph pg. 30 $\log K_p = -1.05$

$K_p = .089$

$$K_p = \frac{P_{SiF_4} \cdot P^2_{H_2O}}{P^4_{HF}}$$

The Equation being $SiF_4 + 2H_2O \longrightarrow 4HF + SiO_2$

Let X = mols of SiF_4 reacted on the basis of 1 mol SiF_4 original

Total mols gas

		partial pressure
SiF_4	$= 1 - x$	$\dfrac{1 - x}{4 + x}$
H_2O	$= 3 - 2x$	$\dfrac{3 - 2x}{4 + x}$
HF	$= 4x$	$\dfrac{4x}{4 + x}$

total $= 4\ x$

$$K_p = .089 = \frac{\left(\dfrac{1-x}{4+x}\right)\cdot\left(\dfrac{3-2x}{4+x}\right)^2}{\left(\dfrac{4x}{4+x}\right)^4} = \frac{(1-x)(9-12x+4x^2)(4+x)}{4x^4}$$

expands to $-4x^4 + 43x^2 - 75x + 36 = .356x^4$

$$x = 1$$

Therefore, the assumption of complete hydrolysis holds and the calculations are compatable.

Calculation of Run 14A

$T = 25^{\circ}C$ $P = 768$ mm of Hg.

Gas Rate: 12.1 cm of $H_2O = 2280$cc/min.

$2280/22,400 \times 273/298 \times 768/760 \times .783 = .0744$ mols H_2O/min.

SiF_4 Rate:

SiF_4 only 4mm Volume 2000cc time 10 min.

$2000/22,400 \times 273/298 \times 768/760 \times .77/10 = .00637$ mols SiF_4/min.

HF Rate:

HF and SiF_4 rate $= 330$cc/min. from chart pg.( )

SiF_4 rate $= 200$cc/min. therefore HF rate $= 130$cc/min.

$(HF)_x$ at $24.5^{\circ}C = (HF)_3$ (ref 23)

therefore HF Rate $= 390$ cc/min. as $(HF)_1$

$390/22,400 \times 273/298 \times 768/760 = .0161$ mols/min.

Basis 1 min.

		%
mols HF $= .0161$ added		
$= \underline{.00121}$ from reaction gas HF		
.0173		71.2
SiF_4 .00637		26.1
Inerts .000695		2.7
total .02436		100.00

APPENDIX D

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A* Abstract