VAPOR PHASE HYDROLYSIS OF SILICON TETRAFLUORIDE

by

Robert N. Secord

S. B. Massachusetts Institute of Technology

1942

Submitted in Partial Fulfillment of the Requirements for
The Degree of Master of Science
At The
Massachusetts Institute of Technology

1947

Signature of Author

Certified by
Thesis Supervisor

Chairman Department Committee on Graduate Students
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
The author wishes to thank Professor D. B. Broughton of the Institute and Mr. R. E. Dobbin and Mr. G. E. Engelson of Godfrey S. Cabot, Inc. for their assistance and helpful suggestions in the preparation of this thesis.
TABLE OF CONTENTS

I Summary ............................................. 1

II Introduction
   A. Statement of the Problem ..................... 3
   B. Literature Survey .............................. 6

III Procedure ......................................... 8

IV Results ............................................ 11

V Discussion of Results ............................ 14

VI Conclusions ....................................... 17

VII Recommendations ............................... 18

APPENDIX

A. Details of Procedure ............................ 20

B. Summary of Data and Calculations ............. 25

C. Sample Calculations ............................. 35

D. Bibliography ...................................... 42

DIAGRAMS AND GRAPHS

Diagram I Diagram of Apparatus .................... 24

Graph I Correlation of \( \text{H}_2\text{O}/\text{SiF}_4 \) vs. Surface area. 13

Graph II Equilibrium Data .......................... 30

Graph III City Gas Orifice Calibration Curves .... 32

Graph IV \( \text{SiF}_4 \) Orifice Calibration Curve ....... 34
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 tetrafluoride. SiF$_4$ gas produced readily from CaF$_2$, H$_2$SO$_4$ and sand was collected by displacement over CCl$_4$ and analyzed 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$^\circ$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$^\circ$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$_2$O: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 m²/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. 30) 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 μm diameter with specific surface areas between 65-107 m²/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) \( \text{Na}_2\text{SiO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{SiO}_2 \)
(b) \( 3\text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2\text{SiF}_6 \)
(c) \( \text{H}_2\text{SiF}_6 + 6\text{NH}_4\text{OH} \rightarrow 6\text{NH}_4\text{F} + \text{SiO}_2 + 4\text{H}_2\text{O} \)
(d) \( 2\text{H}_2\text{O} + \text{Na}_2\text{SiF}_6 + 4\text{Na}_2\text{CO}_3 \rightarrow \text{SiO}_2 + 6\text{NaF} + 4\text{NaHCO}_3 \)
(e) \( \text{H}_2\text{SiF}_6 + 6\text{NH}_3 + 2\text{H}_2\text{O} \rightarrow 6\text{NH}_4\text{F} + \text{SiO}_2 \)
(f) Silica gel dried in presence of protective colloid (gelatin or gum arabic)
(g) Colloidal solutions of silica gel dehydrated and ground.

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 SiO₂ according to Subbotin and Lukyanovich (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 μ. 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 μ 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 μm), 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 $\text{SiF}_4$ with water vapor was passed through a quartz tube at white heat quartz crystals were collected as the results of the hydrolysis of the $\text{SiF}_4$. Further study of this reaction

$$\text{SiF}_4 (g) + 2\text{H}_2\text{O} (g) \rightarrow \text{SiO}_2 + 4\text{HF} (g)$$

by Guntz (9), Troost, and Hautefeuille (10), and Baur (11) showed that the vapor phase hydrolysis of $\text{SiF}_4$ was very incomplete at moderate temperatures. Baur computed constants for the reaction at 104°C and 270°C as follows:

$$K_p = \frac{P_{\text{SiF}_4} \cdot P_{\text{H}_2\text{O}}^2}{P_{\text{HF}}^4} = 5.28 \times 10^7 \text{ at } 104°C; 1.21 \times 10^6 \text{ at } 270°C$$

(See App. Pg. 29)

He also determined the $Q$ for the reaction as -3945 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

\[ \text{SiF}_4(g) + 2\text{H}_2\text{O}(g) \rightarrow \text{SiO}_2 + 4\text{HF}(g) \]

at the highest practicable temperature and with various ratios of H$_2$O/SiF$_4$. It should be pointed out at this point that the reaction

\[ 3\text{SiF}_4 + 2\text{H}_2\text{O} (1) \rightarrow 2\text{H}_2\text{SiF}_6 + \text{SiO}_2 (.x\text{H}_2\text{O}) \]

goes very readily in liquid water at room temperature but this method yields a gel 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$_2$O, 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$_2$SO$_4$ according to the following equation:

\[ \text{SiO}_2 + 2\text{CaF}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{CaSO}_4 + \text{SiF}_4 + 2\text{H}_2\text{O} \]
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.

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{HF}$$

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.

$$\text{NaF} + \text{HF} \rightarrow \text{NaHF}_2$$
$$2\text{NaF} + \text{SiF}_4 \rightarrow \text{Na}_2\text{SiF}_6$$

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°K.
The reaction is as follows:

\[ \text{SiF}_4(g) + 2\text{H}_2\text{O}(g) \rightarrow \text{SiO}_2 + 4\text{HF}(g) \]

The product was collected by impingement on the bottom of a large porcelain evaporating dish which was filled with hot water. Various ratios of \( \text{H}_2\text{O}/\text{SiF}_4 \) were used to vary the surface area of the product produced.

The analysis of the \( \text{SiF}_4 \) 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. \( \text{HF}/\text{liter} \) can be calculated or determined by difference.
IV RESULTS

The SiO₂ produced by the vapor phase hydrolysis of SiF₄ is a very fluffy powder with an apparent density of about .04 gms/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 H₂O/SiF₄ ratios show areas between 170-297 m²/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:

<table>
<thead>
<tr>
<th>Run</th>
<th>H₂O/SiF₄ ratio</th>
<th>H₂O Rate mol/s/min</th>
<th>SiF₄ Rate mol/s/min</th>
<th>Surface area m²/gm</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>9D</td>
<td>3.0</td>
<td>.0260</td>
<td>.0086</td>
<td>297</td>
<td>29.9</td>
</tr>
<tr>
<td>9A</td>
<td>3.9</td>
<td>.0234</td>
<td>.00602</td>
<td>198</td>
<td>42.7</td>
</tr>
<tr>
<td>9B</td>
<td>6.9</td>
<td>.0260</td>
<td>.00376</td>
<td>178</td>
<td>51.0</td>
</tr>
<tr>
<td>9E</td>
<td>17.3</td>
<td>.0538</td>
<td>.00312</td>
<td>170</td>
<td>44.7</td>
</tr>
</tbody>
</table>

(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 m²/gm. The average particle diameter determined from the photograph was less than 250 Å, giving a calculated surface area for spherical particles of greater than 109 m²/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:

<table>
<thead>
<tr>
<th>H₂O mols/min</th>
<th>SiF₄ mols/min</th>
<th>(HF)₁ mols/min</th>
<th>H₂O/SiF₄</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0744</td>
<td>.00637</td>
<td>.0173</td>
<td>11.6</td>
<td>43.7</td>
</tr>
</tbody>
</table>

*see footnote pg. 2
V DISCUSSION OF RESULTS

The vapor phase hydrolysis of SiF₄ 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 m²/gm by N₂ adsorption vs. 109 m²/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 H₂O 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 SiF₄ rate and the surface area but the resulting curve is not as good as that made from the plot of H₂O/SiF₄ vs. surface area which shows a very smooth curve with the highest area determined from the product made at the lowest H₂O/SiF₄ ratio. Although the four areas determined are not sufficient evidence to make a positive prediction of the trend of the particle size with the H₂O/SiF₄ 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 SiF₄ 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 H₂O/SiF₄ 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 SiF₄ 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 m² and smaller.

(3) The smaller the H₂O/SiF₄ 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 A

Details of Procedure

1. Preparation of SiF₄ (see diagram I pg. 24)(ref. 13)

On a laboratory scale it has been necessary to use approximately double the quantities of initial materials, SiO₂, H₂SO₄ and CaF₂, 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 SiF₄ with high percentage yields than was available. In general, a molal ratio of H₂SO₄: SiO₂: CaF₂ has been 3.5:6:2 using approximately 2 moles of CaF₂ for each run and collecting about one half mol of SiF₄ 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. H₂SO₄ (Dupont), technical CaF₂ (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 CCl₄.

The chemical reaction is as follows:

\[ 2\text{CaF}_2 + 2\text{H}_2\text{SO}_4 + \text{SiO}_2 \rightarrow 2\text{CaSO}_4 + 2\text{H}_2\text{O} + \text{SiF}_4 \]
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:

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 4\text{HF}$$

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°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 SiF₄ 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 CCl₄ 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 SiF₄ 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, CCl₄) 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 endpoint 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 SiF₄, 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.
<table>
<thead>
<tr>
<th>Run</th>
<th>SiO₂(1)</th>
<th>SiO₂(2)</th>
<th>Total P₃SiO₁₄</th>
<th>Total SiO₁₂</th>
<th>F₂O₅</th>
<th>H₂O</th>
<th>KOH (titreation)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.000</td>
<td>1.000</td>
<td>2.000</td>
<td>2.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.500</td>
<td>1.500</td>
<td>3.000</td>
<td>3.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.000</td>
<td>2.000</td>
<td>4.000</td>
<td>4.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.500</td>
<td>2.500</td>
<td>5.000</td>
<td>5.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.000</td>
<td>3.000</td>
<td>6.000</td>
<td>6.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
</tbody>
</table>

**APPENDIX 2**

**Summary of Data and Calculations**

- **Run Sample**
- **Volume gases in cc**
- **Fluoride gases in cc**
- **SiO₂(1)**
- **SiO₂(2)**
- **Total P₃SiO₁₄**
- **Total SiO₁₂**
- **F₂O₅**
- **H₂O**
- **KOH (titreation)**
- **Remarks**

**Table I**

- **Run 1**: Volume gases 1.000 cc, Fluoride gases 1.000 cc.
- **Run 2**: Volume gases 1.500 cc, Fluoride gases 1.500 cc.
- **Run 3**: Volume gases 2.000 cc, Fluoride gases 2.000 cc.
- **Run 4**: Volume gases 2.500 cc, Fluoride gases 2.500 cc.
- **Run 5**: Volume gases 3.000 cc, Fluoride gases 3.000 cc.

**Remarks**: Same as 5.
<table>
<thead>
<tr>
<th>Run</th>
<th>Date</th>
<th>T°C</th>
<th>P mm of Hg</th>
<th>4.2 cm H₂O</th>
<th>no man.</th>
<th>SiF₄ man. mm CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11/5</td>
<td>23</td>
<td>760</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11/7</td>
<td>22.5</td>
<td>758</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>11/15</td>
<td>23</td>
<td>767</td>
<td>4.2</td>
<td>no man.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>11/21</td>
<td>?</td>
<td>?</td>
<td>6.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>11/25</td>
<td>25</td>
<td>760</td>
<td>13.8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>11/26</td>
<td>22</td>
<td>760</td>
<td>7.0</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>11/27</td>
<td>24</td>
<td>762</td>
<td>9.3</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>8A</td>
<td>11/27</td>
<td>24</td>
<td>762</td>
<td>10.0</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>11/27</td>
<td>24</td>
<td>762</td>
<td>10.0</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>11/27</td>
<td>24</td>
<td>762</td>
<td>10.0</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>12/2</td>
<td>23</td>
<td>757</td>
<td>2.7</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>9A</td>
<td>12/3</td>
<td>25</td>
<td>772</td>
<td>2.0</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>12/3</td>
<td>25</td>
<td>772</td>
<td>2.3</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>12/3</td>
<td>25</td>
<td>772</td>
<td>6.9</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>12/3</td>
<td>25</td>
<td>772</td>
<td>2.3</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>12/4</td>
<td>25</td>
<td>768</td>
<td>6.9</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>10A</td>
<td>12/4</td>
<td>25</td>
<td>768</td>
<td>7.1</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>12/5</td>
<td>24</td>
<td>767</td>
<td>2.3</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>11A</td>
<td>12/6</td>
<td>25</td>
<td>771</td>
<td>2.4</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>12/6</td>
<td>25</td>
<td>771</td>
<td>11.7</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>12A</td>
<td>12/11</td>
<td>25</td>
<td>758</td>
<td>13.3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>12/12</td>
<td>24</td>
<td>763</td>
<td>13.1</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>12/12</td>
<td>25</td>
<td>763</td>
<td>13.3</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>14A</td>
<td>12/19</td>
<td>25</td>
<td>768</td>
<td>12.1</td>
<td>24 (with HF)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>12/20</td>
<td>24</td>
<td>774</td>
<td>10.6</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Filter</td>
<td>Temp</td>
<td>Pressure</td>
<td>Rate</td>
<td>Remarks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>----------</td>
<td>------</td>
<td>---------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>279</td>
<td>9.9</td>
<td>0.060</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>2.0</td>
<td>0.060</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>178</td>
<td>6.9</td>
<td>0.060</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>42.7</td>
<td>2.0</td>
<td>0.060</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Vacuum**

<table>
<thead>
<tr>
<th>Temperature &amp; Pressure</th>
<th>Rate</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Insert the liquid phase hydrolysis only**

**Results of Runs**

**Table III**
<table>
<thead>
<tr>
<th>HP added</th>
<th>27.2</th>
<th>47.2</th>
<th>72</th>
<th>28.2</th>
<th>49.7</th>
<th>72</th>
<th>00637 11.6 8.4</th>
<th>77 14.6 8.4</th>
</tr>
</thead>
</table>

**Surface Impregnation on Cool**

*Free HP collection and remarks

**% Xtraal vol. H2O & H2 gas rate, stn. per min.**

Results of Runs

(cont.)
TABLE IV
CALCULATED EQUILIBRIUM RELATIONS
FROM LITERATURE DATA

<table>
<thead>
<tr>
<th>Ryss' Data (12)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T , ^\circ K$</td>
<td>$1000/T$</td>
<td>$K_p$ (amorph)</td>
</tr>
<tr>
<td>377</td>
<td>2.65</td>
<td>$10^{12}$</td>
</tr>
<tr>
<td>543</td>
<td>1.84</td>
<td>$10^7$</td>
</tr>
<tr>
<td>773</td>
<td>1.29</td>
<td>$4 \cdot 10^3$</td>
</tr>
<tr>
<td>873</td>
<td>1.145</td>
<td>$5.26 \cdot 10^2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Baur's Data (11)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>377</td>
<td>2.65</td>
<td>$5.26 \cdot 10^7$</td>
</tr>
<tr>
<td>543</td>
<td>1.84</td>
<td>$1.21 \cdot 10^6$</td>
</tr>
</tbody>
</table>

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

\[ 5 \text{Fe}(s) + 2 \text{H}_2\text{O}(g) \rightarrow \text{Fe}_2\text{O}_3(s) + 4 \text{H}_2(g) \]
### TABLE V

GAS ORIFICE CALIBRATION DATA

<table>
<thead>
<tr>
<th>ΔH in cm of H₂O</th>
<th>Stat Av. mm of Hg</th>
<th>Vol. cc</th>
<th>Time sec.</th>
<th>v in cc/sec</th>
<th>ΔH/v</th>
<th>ρ_air</th>
<th>fν</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.8</td>
<td>12.7</td>
<td>4000</td>
<td>95.5</td>
<td>2520</td>
<td>00866</td>
<td>00140</td>
<td>3.52</td>
</tr>
<tr>
<td>16.1</td>
<td>10.1</td>
<td>4000</td>
<td>100</td>
<td>2180</td>
<td>00738</td>
<td>00156</td>
<td>2.97</td>
</tr>
<tr>
<td>9.3</td>
<td>5.1</td>
<td>4000</td>
<td>143</td>
<td>1680</td>
<td>00551</td>
<td>00128</td>
<td>2.15</td>
</tr>
<tr>
<td>4.2</td>
<td>1.0</td>
<td>2000</td>
<td>109</td>
<td>1100</td>
<td>00378</td>
<td>00122</td>
<td>1.55</td>
</tr>
<tr>
<td>1.9</td>
<td>-0.8</td>
<td>2000</td>
<td>177</td>
<td>680</td>
<td>00276</td>
<td>00119</td>
<td>0.852</td>
</tr>
<tr>
<td>1.1</td>
<td>-1.2</td>
<td>1000</td>
<td>123.5</td>
<td>48.6</td>
<td>00224</td>
<td>00118</td>
<td>0.573</td>
</tr>
</tbody>
</table>

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

### FOR CITY GAS

<table>
<thead>
<tr>
<th>Flow Assumed cc/min</th>
<th>ρ_gas 25°C</th>
<th>fν</th>
<th>ΔH/v from chart</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.000867</td>
<td>0.434</td>
<td>0.0019</td>
<td>0.95</td>
</tr>
<tr>
<td>1000</td>
<td>&quot;&quot;</td>
<td>0.867</td>
<td>0.0028</td>
<td>2.8</td>
</tr>
<tr>
<td>1500</td>
<td>&quot;&quot;</td>
<td>1.300</td>
<td>0.0038</td>
<td>5.7</td>
</tr>
<tr>
<td>2000</td>
<td>&quot;&quot;</td>
<td>1.735</td>
<td>0.0047</td>
<td>9.4</td>
</tr>
<tr>
<td>2500</td>
<td>&quot;&quot;</td>
<td>2.170</td>
<td>0.0057</td>
<td>14.3</td>
</tr>
<tr>
<td>3000</td>
<td>&quot;&quot;</td>
<td>2.602</td>
<td>0.0066</td>
<td>19.8</td>
</tr>
<tr>
<td>Run</td>
<td>Time Min</td>
<td>Volume in cc</td>
<td>$\Delta H$ mm of CC\textsubscript{4}</td>
<td>$v$ cc/min</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>--------------</td>
<td>-----------------</td>
<td>-----------</td>
</tr>
<tr>
<td>6B</td>
<td>5</td>
<td>800</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>6D</td>
<td>3</td>
<td>500</td>
<td>9</td>
<td>167</td>
</tr>
<tr>
<td>7B</td>
<td>4</td>
<td>600</td>
<td>12</td>
<td>150</td>
</tr>
<tr>
<td>8C</td>
<td>7</td>
<td>2100</td>
<td>20</td>
<td>300</td>
</tr>
<tr>
<td>9A</td>
<td>10</td>
<td>2000</td>
<td>11</td>
<td>200</td>
</tr>
<tr>
<td>B</td>
<td>16</td>
<td>2000</td>
<td>5.5</td>
<td>125</td>
</tr>
<tr>
<td>C</td>
<td>15</td>
<td>2000</td>
<td>5.5</td>
<td>133</td>
</tr>
<tr>
<td>D</td>
<td>7</td>
<td>2000</td>
<td>21</td>
<td>286</td>
</tr>
<tr>
<td>E</td>
<td>19</td>
<td>2000</td>
<td>3</td>
<td>105</td>
</tr>
<tr>
<td>10A</td>
<td>15</td>
<td>2000</td>
<td>6</td>
<td>133</td>
</tr>
<tr>
<td>B</td>
<td>25</td>
<td>4000</td>
<td>5.5</td>
<td>160</td>
</tr>
<tr>
<td>11B</td>
<td>22</td>
<td>2900</td>
<td>6</td>
<td>132</td>
</tr>
<tr>
<td>12A</td>
<td>13.5</td>
<td>2000</td>
<td>6</td>
<td>148</td>
</tr>
<tr>
<td>B</td>
<td>11</td>
<td>2000</td>
<td>7</td>
<td>182</td>
</tr>
<tr>
<td>13</td>
<td>13.5</td>
<td>2400</td>
<td>7</td>
<td>174</td>
</tr>
</tbody>
</table>
APPENDIX C

Sample Calculations

City Gas Analysis

Computation of H₂O Formed From Combustion

Gas Analysis Gr. 0.731 ref air BTU 528-535/cu. ft.

CO₂ 7.6%
H₂ 10.1
O₂ 0.6
CO 21.7
CH₄ 14.6%
H₂ 26.6
N₂ 18.8

Average analysis of city gas courtesy Cambridge Gas & Electric Company

Approximate analysis of illuminants C₂H₄/C₆H₆ = 3/1 (22)
therefore H₂O produced/100cc of gas is as follows:
from 14.6cc CH₄ 29.2
26.6cc H₂ 26.6
0.75·10.1cc C₂H₄ 15.0
0.25·10.1cc C₆H₆ 7.5

Total 78.3cc H₂O vapor/100cc of gas

22,400cc gas at STP will give 0.733gm mols of H₂O
Calculation of reactive gas analysis:

Example: run 9 1250cc sample $T = 25^\circ C$, $P = 772$ mm of Hg.

Volume of inerts = 210 cc

$SiO_2$ precipitated from hydrolysis = 0.4428 gms

$SiO_2$ precipitated from titration aliquot 100/440

$0.4095 \times 4.4 = 1.802$

Total $SiO_2 = 2.245$ or 0.0374 mols

Mols of gas

\[
\frac{1250 \times 273 \times 772}{22400 \times 298} = 0.0519 \text{ total mols}
\]

\%

\[
\frac{SiF_4}{0.0374/0.0519 \times 100} = 72\%
\]

\%

\[
\frac{\text{inerts}}{210/1250 \times 100} = 16.8\%
\]

\%

\[
\frac{(HF)}{x} = \text{by difference} = 11.2\%
\]

titration of 100cc portion of total filtrate with 0.993 N NaOH took 62.5 cc for a phenolphthalein end point.

\[
62.5 \times 0.993 \times 4.4 = 273 \text{ me/1250cc total fluoride.}
\]
Calculation of $H_2O/SiF_4$ Ratio

Run 9D       $T = 25^\circ C$       $P = 772$ mm of Hg.

Gas Rate:

Manometer $\Delta H = 2.0$ cm of $H_2O$
from graph pg. 32, $2.0$ cm. $= 800cc/min.$ gas

$\frac{800}{22,400} \times \frac{772}{760} \times \frac{273}{298} \times 0.783 = 0.0260$ mols/min. $H_2O$

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

$\frac{2000}{22,400} \times \frac{772}{760} \times \frac{273}{298} \times 0.72(\%SiF_4)/7 = 0.0086$ $SiF_4$
mols/min.

$H_2O/SiF_4 = \frac{0.0260}{0.0086} = 3.02$
Calculation of Flame Temperature and Yield

Run 9D  Basis 1 mol SiF₄

3.00 mols H₂O total/mol SiF₄ or 1.0 mols H₂O in residue
gas after hydrolysis.

Heat of combustion 531 BTU/cu. ft. = \[ \frac{531}{1.8} \times 28,317 \] cal/gram mol gas

since it takes \( \frac{1}{.783} \) cc of gas to give 1 cc of water vapor at
STP (see pg. 35) the \( \frac{1}{.783} \times 3 = 3.83 \) mols of gas to give 3 mols
of water vapor.

Ht. of combustion = 3.83 \times 106,000 = 407,000 cal/gm mol SiF₄

Gas Analysis Basis 100 mols of gas O₂ for complete combustion

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th></th>
<th>C₂H₄</th>
<th></th>
<th>C₆H₆</th>
<th></th>
<th>O₂</th>
<th></th>
<th>CO</th>
<th></th>
<th>CH₄</th>
<th></th>
<th>H₂</th>
<th></th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.6</td>
<td></td>
<td>7.5</td>
<td></td>
<td>2.5</td>
<td></td>
<td>.6</td>
<td></td>
<td>21.7</td>
<td></td>
<td>14.6</td>
<td></td>
<td>26.6</td>
<td></td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>99.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

air required \( \frac{95}{.21} = 453 \)

Basis 1 mol of SiF₄ combustion products CO₂ H₂O N₂

from CO₂ .291
C₂H₄ .575 .575
C₆H₆ .805 .402
CO .832
CH₄ .560 1.120
Combustion products (cont.) \( \text{CO}_2 \quad \text{H}_2\text{O} \quad \text{N}_2 \)

from \( \text{H}_2 \) \( 1.02 \)

\( \text{N}_2 \) from reaction gas \( .720 \)

\( \text{N}_2 \) from air \( 13.70 \)

Total \( 3.063 \quad 3.017 \quad 14.42 \)

Assuming complete hydrolysis

\[ \text{Ht. of reaction } \text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HF} - 22,500 \text{ cal.} \]

\[ 407,000 - 22,500 = \int_{291}^{T} \left[ 4(C_pHF) + 1.0(C_pH_2O) + 14.42(C_pN_2) + C_p\text{SiO}_2 + 3.06 \left(C_p\text{CO}_2\right) \right] dT \]

\[ C_p HF = 6.5 + .001T \]

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

\[ C_p\text{SiO}_2 = 1.2 \]

\[ C_p\text{CO}_2 = 10.4 + .00274T - 1.955 \cdot 10^5T^{-2} \]

\[ C_p N_2 = 6.5 + .001T \]

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

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

\[ = \left\{ \begin{array}{l}
161T + .0141T^2 + .447 \cdot 10^{-6}T^3 + 5.98 \cdot 10^5T^{-1} \\
291 
\end{array} \right\} \]

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

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

Solve for \( T \) by trial and error

\[ T = 1785^\circ C \quad 1000/T = .56 \text{ from graph pg. 30} \quad \log K_p = -1.05 \]

\[ K_p = .039 \]

\[ K_p = \frac{P_{\text{SiF}_4} \cdot P_{\text{H}_2\text{O}}^2}{P_{\text{HF}}^4} \]

The Equation being \( \text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{HF} + \text{SiO}_2 \)
Let $X$ = mols of $\text{SiF}_4$ reacted on the basis of 1 mol $\text{SiF}_4$ original

Total mols gas

\begin{align*}
\text{SiF}_4 & = 1 - x \\
\text{H}_2\text{O} & = 3 - 2x \\
\text{HF} & = 4x
\end{align*}

\[\text{total} = 4x\]

Partial pressure

\begin{align*}
\frac{1 - x}{4 + x} & \quad \frac{3 - 2x}{4 + x} \\
\frac{4x}{4 + x}
\end{align*}

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

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

\[x = 1\]

Therefore, the assumption of complete hydrolysis holds and the calculations are compatible.
Calculation of Run 14A

\[ T = 25^\circ C \quad P = 768 \text{ mm of Hg.} \]

Gas Rate: \(12.1 \text{ cm of H}_2\text{O} = 2280 \text{ cc/min.} \)

\[
\frac{2280}{22400} \times \frac{273}{298} \times \frac{768}{760} \times 0.783 = 0.0744 \text{ mols H}_2\text{O/min.}
\]

\(\text{SiF}_4\) Rate:

\(\text{SiF}_4\) only 4mm Volume 2000cc time 10 min.

\[
\frac{2000}{22400} \times \frac{273}{298} \times \frac{768}{760} \times 0.7710 = 0.00637 \text{ mols SiF}_4/\text{min.}
\]

HF Rate:

HF and \(\text{SiF}_4\) rate = 330cc/min. from chart pg. ( )

\(\text{SiF}_4\) rate = 200cc/min. therefore HF rate = 130cc/min.

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

therefore HF Rate = 390 cc/min. as \((\text{HF})_1^\text{1}\)

\[
390/22400 \times \frac{273}{298} \times \frac{768}{760} = 0.0161 \text{ mols/min.}
\]

Basis 1 min.

mols HF = 0.0161 added

\[
= 0.00121 \text{ from reaction gas HF}
\]

\[
\begin{array}{ccc}
\text{SiF}_4 & 0.00637 \\
\text{Inerts} & 0.00695 \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{total} & 0.02436 \\
\end{array}
\]
APPENDIX D

BIBLIOGRAPHY

1. Sze, M.C.; C. I. E. Journal 2, 95-104 (1944)
2. Parkinson, D.; Inst. of Rubber Industry Transactions,
   Vol. 19, P. 131, (1943-1944)
3. Fridberg, L. M.; Caoutchouc and Rubber. (U.S.S.R.),
   P. 82-83 (1939) A*
4. Sbornik Stalei; Gosudart Inst. Prikladnoi Khim,
   P. 56-73 (1939) A*
5. Behre, J; Ger. Patent No. 572,266, July 14, 1933 A*
6. Subbotin, S. A. and Lukyanchikov, A. N.; Lintet Kanchuk,
   1, 34-35; (1934) A*
7. F. K.; Gummi-Ztg 39, 2102-4, (1925)
9. Guntz, A.; Ann Chimie et des Physiques, Series VI 3,
   59 (1884)
10. Troost, L. and Hautefeuille P.; ibid, Series V, 7, 464 (1876)
12. Ryss, I.G.; Z. frizcheskoi Khammi (U.S.S.R.), 14, 571-81(1940)
   Soc. 61 2555-6 (1939)
17. Godfrey L. Cabot Inc.; Rubber Black Testing Procedure (1940)
18. Int. Critical Tables Vol. 7


   U. S. Pat. 2,399,687, 1946

   Pg. 2363 McGraw & Hill Book Co. (1941)

   46, 2183-91 (1924)


A* Abstract