A study of the reactions of fluorspar and phosphate rock with sulphur dioxide, air and water.

Ian Griff Sherbin
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A STUDY OF THE REACTIONS OF

FLUORSPAR AND PHOSPHATE ROCK

WITH SULPHUR DIOXIDE, AIR AND WATER

A THESIS

Submitted to the Faculty of Graduate Studies through the Department of Chemical Engineering in Partial Fulfilment of the Requirements for the Degree of Master of Applied Science at the University of Windsor

by

IAN GRIFF SHERBIN

Windsor, Ontario

1969
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ABSTRACT

A study was made of the reactions of phosphate rock (fluorapatite) and fluorspar (calcium fluoride) with sulphur dioxide, air and water.

From a consideration of the thermodynamics of various reactions, structure, and a literature survey, it was concluded that fluorspar could be defluorinated by reaction with sulphur dioxide, air, and water. Experimental results have shown that fluorspar can be defluorinated at temperatures greater than 500°C. The rate of defluorination was increased with the addition of a specific amount of catalyst.

It is recommended that further studies be made on the fluorspar reaction to determine the kinetics and optimum conditions of the reaction.

The reaction of phosphate rock with sulphur dioxide, air, and water was found to have been successfully carried out by previous investigators. The reaction of mixtures of phosphate rock and fluorspar did not give an indication of any feasible process at the present time.
I gratefully acknowledge the assistance rendered me by Dr. R. C. Quittenton, my advisor. The assistance of Mr. Wolfgang Eberhart, glassblower, and Mr. George Ryan, department technician, is greatly appreciated. I would also like to extend my gratitude to the National Research Council of Canada for their financial assistance during this study.
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Amount of Fluorine Driven off from Calcined Phosphate Rock

Thermodynamic Reaction Calculations

$\text{CaF}_2 - \text{SO}_2 - \text{O}_2 - \text{H}_2\text{O}$

$\text{NaCl} - \text{SO}_2 - \text{O}_2 - \text{H}_2\text{O}$

$\text{SO}_2 - \text{O}_2$

$\text{CaF}_2 - \text{SO}_3 - \text{H}_2\text{O}$

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 - \text{SO}_2 - \text{O}_2 - \text{H}_2\text{O}$

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 - \text{SO}_2 - \text{O}_2 - \text{H}_2\text{O}$

$\text{Ca}_3(\text{PO}_4)_2 - \text{SO}_3$

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 - \text{CaF}_2 - \text{H}_2\text{SO}_4$

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 - \text{CaF}_2 - \text{SO}_2 - \text{O}_2$

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 - \text{CaF}_2 - \text{SO}_2 - \text{O}_2$

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 - \text{CaF}_2 - \text{SO}_3$
I. INTRODUCTION

This thesis is a study of the reactions and thermodynamics involved in the contacting of phosphate rock (fluorapatite) and fluorspar (calcium fluoride) with sulphur dioxide, air and water. "It is hoped that out of this study would come either clear directions for experimental attack by subsequent workers, or a definite indication that the project should be abandoned". (1)

A. The Phosphate Rock Process

The acidulation of phosphate rock with sulphuric acid to produce superphosphate has been in use for nearly a century for making phosphate available for fertilizer purposes. The reaction (2) has long been given as,

$$\text{Ca}_{10} (\text{PO}_4)_6 \text{F}_2 + 7\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O} =$$

$$3\text{CaH}_4(\text{PO}_4)_2\text{H}_2\text{O} + 7\text{CaSO}_4 + 2\text{HF} \quad (1)$$

One objective of this investigation is to see if enough moles of fluorspar (CaF$_2$) can be added to fluorapatite to add enough fluorine to liberate phosphorus as a phosphorus oxyfluoride. A possible reaction could be,

$$\text{Ca}_{10} (\text{PO}_4)_6 \text{F}_2 + 8\text{CaF}_2 + 18\text{SO}_2 + 9\text{O}_2 =$$

$$6\text{POF}_3 + 18\text{CaSO}_4 \quad (2)$$

The contacting of phosphate rock directly with SO$_2$ - O$_2$ - H$_2$O will also be studied according to the reaction,
\[
\text{Ca}_{10}\text{(PO}_4\text{)}_6\text{F}_2 + \text{SO}_2 + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O} = \\
3\text{Ca}_3\text{(PO}_4\text{)}_2 + \text{CaSO}_4 + 2\text{HF}
\] 

Equation (2) represents a more potentially attractive phosphate process since the fluorine (in CaF\(_2\)) is used to carry off the phosphorus as an oxyfluoride.

If such a solid-gas reaction were possible, then a fluo-solids process could possibly be used. The success of the reaction then will depend on whether or not the CaF\(_2\) and Ca\(_{10}\)(PO\(_4\))\(_6\)F\(_2\) can be split up with SO\(_2\) instead of H\(_2\)SO\(_4\). However, even if H\(_2\)SO\(_4\) is used, this still would be a more attractive process since it would be possible to obtain a Ca free phosphate, (equation 2).

B. The Fluorspar Process

Fluorspar (calcium fluoride) is used today as a major source of hydrogen fluoride (HF). The reaction can be shown as,

\[
\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}
\] 

(4)

The object here, is to develop a fluo-solids process for the liberation of HF gas from CaF\(_2\) by reaction with SO\(_2\) as follows,

\[
\text{CaF}_2 + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{HF}
\] 

(5)

The present-day processes just described (equations 1, 4) are thermally inefficient and present serious problems with corrosion, fumes, and mechanical difficulties.
A fluo-solids system basically involves the suspension of solid particles in an upward rising stream of gas. The result is an agitated or fluidized bed. Because of the intense gas-solid contact, chemical reaction rates are generally faster, and transfer of heat from solids to solids to gases is extremely rapid.
A. Phosphate Rock Reactions

The earliest reported process for contacting sulphur dioxide with phosphate rock is that of Giana(3). The author claims a process for the contacting of phosphorite with \( \text{SO}_2 \) and oxygen at \( 800^\circ\text{C} \), obtaining calcium sulphate and calcium pyrophosphate:

\[
\text{Ca}_3(\text{PO}_4)_2 + \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{CaSO}_4 + \text{Ca}_2\text{P}_2\text{O}_7
\]  

(6)

Water was not used as a reactant, and the fate of the fluorine in the phosphorite is not mentioned.

In 1930, Briner and Monnier(4) studied the reaction of pure calcium phosphate with \( \text{SO}_2 \). The optimum temperature was about \( 350^\circ\text{C} \) with the reaction being:

\[
2\text{Ca}_3(\text{PO}_4)_2 + 3\text{SO}_2 = 2\text{CaSO}_4 + 2\text{Ca}_2\text{P}_2\text{O}_7 + \text{S}
\]  

(7)

Hughes and Cameron(5) in 1931 reported on an intensive study made of the reaction of phosphate rock with \( \text{SO}_2 \) and \( \text{SO}_3 \). Their more important results may be summarized as follows:

1) Phosphate rock can be converted at temperatures of 350 to 450\(^\circ\text{C}\) at high pressures and long contact times by \( \text{SO}_2 \) and admixtures of water or air. Contact times of up to ten hours are generally required for good conversion. The fluorine in the phosphate rock was not considered.
ii) With contact times up to five hours and temperatures around 500 to 600°C, phosphate rock will react with $SO_3$.

iii) Increased conversions can be obtained by regrinding and retreating the reacted rock.

The results also showed that with $SO_2$ the conversions are smaller and contact times longer than those obtained with gaseous $SO_3 - H_2O$ systems.

In 1957, a patent was issued to Scheel for the defluorination of phosphate rock. The patent claims a process in which mixtures of $Ca_3(PO_4)_2$ and $CaSO_4$ are prepared by reaction of $SO_2$ and $O_2$ at temperatures greater than 500°C, the gas containing 1 part by volume $H_2O$ vapour per volume of $SO_2$. The reaction claimed is:

$$Ca_{10}(PO_4)_6F_2 + SO_2 + \frac{1}{2}O_2 + H_2O = 3Ca_3(PO_4)_2 + CaSO_4 + 2HF$$ (8)

The elimination of the fluorine begins at about 500°C and proceeds at a considerable rate at 600 to 700°C. The author found that the elimination of fluorine is greatly facilitated if small quantities of known catalyst are added to the crude phosphate. Scheel concludes that the catalyst accelerates the oxidation of $SO_2$ to $SO_3$. The process claimed is an exothermic one, and hence it requires only a small additional heat supply.

A typical run used ground pebble phosphate (33.5% $P_2O_5$, 1% $SO_3$, 3.72%F) granulated with the addition of a little
water or catalyst solution and calcined for one hour at a
temperature rising from 740 to 860° in a tube furnace in
a uniform current of roasting gases containing water vapour
and 6.6% SO₂. The quantities of fluorine driven off from
a 50 gram sample were determined after 15 minutes and one
hour. The results are tabulated in Table 2-1.

In 1962 Pompowski (7) reported a study on the trans­
formation of natural phosphorites by the action of a gaseous
mixture of SO₂, air, and water. Samples were heated in an
iron tube at 300 - 900° and air containing SO₂ 1.7 - 1.9%
and H₂O 0-7.29% was used. The duration of contact of gaseous
and solid phases was 60-80 seconds. The products reported
were Ca₂P₂O₇ and CaSO₄. The process was most effective in an
iron tube or when Fe₂O₃ or V₂O₅ was added as catalyst.

The first reported fluidized bed experiments with
phosphate rock were those reported by Ross (8) in 1967. Ross
studied the reaction of phosphate rock with SO₂ and with SO₃
(alone and with infusion of steam and air) at temperatures
around 325°C and for periods of time up to 30 minutes. It
was found that rapid conversion is possible with SO₃, but
that the reaction with SO₂ was very slow. The best conver­
sion was with SO₃ at 325 ± 5°C, along with admixtures of
air and steam. Ross also concluded that the Ca-F linkages
of the fluorapatite in the phosphate rock were undisturbed,
CaSO₄ forming entirely from calcium originally associated
with phosphorus.
<table>
<thead>
<tr>
<th>Calcined Product After Treatment for 1 Hour</th>
<th>No Catalyst</th>
<th>1.9%FeSO₄</th>
<th>1.0%FeSO₄ + 1.0%K₂SO₄</th>
<th>3.8%FeSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>% P₂O₅</td>
<td>32.2</td>
<td>31.0</td>
<td>30.2</td>
<td>30.0</td>
</tr>
<tr>
<td>% SΟ₃</td>
<td>9.4</td>
<td>11.7</td>
<td>17.2</td>
<td>18.6</td>
</tr>
<tr>
<td>% F</td>
<td>2.0</td>
<td>1.62</td>
<td>1.07</td>
<td>0.96</td>
</tr>
<tr>
<td>% of F Driven Off After</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 mins.</td>
<td>17</td>
<td>25</td>
<td>28</td>
<td>29</td>
</tr>
<tr>
<td>1 hour</td>
<td>46</td>
<td>54</td>
<td>69</td>
<td>71</td>
</tr>
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</table>
B. Calcium Fluoride Reactions

In 1941, Tarbutton et al.\(^{(9)}\) reported a study of the reactions of phosphorus pentoxide with calcium fluoride and fluorapatite. The possible reactions of CaF\(_2\) and P\(_2\)O\(_5\) were reported as:

\[
\begin{align*}
3\text{CaF}_2 + 4\text{P}_2\text{O}_5 &= 2\text{POF}_3 + 3\text{Ca}_2(\text{PO}_4)_2 \\
6\text{CaF}_2 + 5\text{P}_2\text{O}_5 &= 4\text{POF}_3 + 3\text{Ca}_2\text{P}_2\text{O}_7 \\
3\text{CaF}_2 + 2\text{P}_2\text{O}_5 &= 2\text{POF}_3 + \text{Ga}_3(\text{PO}_4)_2
\end{align*}
\]

(9) (10) (11)

The temperature varied from 500 to 1000°C and the weights of the volatile products obtained, corresponded closely to equation (9) on the basis of P\(_2\)O\(_5\) added.

Mixtures of fluorapatite and P\(_2\)O\(_5\) were heated to about 700°C. The results indicated that PF\(_3\) was formed.

Muetterties and Coffman\(^{(10)}\) in 1958 reported a study in which pyrosulfuryl fluoride was formed when calcium fluoride reacted at 100 - 300°C with excess SO\(_3\) and then was treated with 60 - 98% sulphuric acid.

C. Miscellaneous Reactions

The Hargreaves Process\(^{(11)}\) was introduced in England in the late nineteenth century. The reactants are rock salt, SO\(_2\), air, and water vapour:

\[
2\text{NaCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HCl}
\]

(12)

The reaction is exothermic, and sufficient heat is evolved to maintain the process once the reactants are brought
up to temperature. Operating temperatures may vary from 535°C at the spent-salt end to 455°C at the raw salt end. Martin and Francis\(^{12}\) reported that the major disadvantage of the process was the length of time required for the complete conversion of the salt into sulphate.

Catalysts for the Hargreaves Process have since been found which make the process more economical. In 1942, Vol'f'kovivck and Margolis\(^{13}\) studying the process, found that the most effective catalyst was pyrite slag. Use of 1% by weight was found to be optimal. At optimal temperatures of 500 - 550°C the yield of sulphate is 95 - 96%, with the time requirement not longer than 1.5 hours.

In 1943, Vol'f'kovivck and Margolis\(^{14}\) reported results of a study made of the catalysts tested for the reaction:

\[
4\text{KCl} + 2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} = 2\text{K}_2\text{SO}_4 + 4\text{HCl} \tag{13}
\]

The catalysts were Al\(_2\)O\(_3\), CuO, Co(NO\(_3\))\(_2\), CoSO\(_4\), Fe\(_2\)O\(_3\) and various Fe-containing metallurgical by-products. The most effective catalysts were those containing Fe. Other factors aiding the conversion were fine grinding of the KCl, preliminary moistening of the KCl and proper design of the apparatus to ensure intimate contact between SO\(_2\) and KCl.
III THEORETICAL CONSIDERATIONS

A. Structure of Major Reactants

1. Phosphate Rock

The apatite group, $\text{Ca}_{10}(\text{PO}_4)_6(\text{F,Cl,OH})_2$ is the principal mineral in the phosphate rock deposits of the world\textsuperscript{(15)}. In the apatite group, the most common one found is fluorapatite. Calcium carbonate, silicon dioxide and many other minerals also occur in phosphate rock deposits. Kay et al\textsuperscript{(16)} reported a study on the structure of fluorapatite. The unit cell is considered to be the volume surrounded by a parallelogram with (F) at the apices, containing on the average six $(\text{PO}_4)^{3-}$ tetrahedra, ten Ca\textsuperscript{2+} ions, and two F\textsuperscript{-}: $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. Brasseur\textsuperscript{(17)} in 1954, reported unit cell dimensions of fluorapatite as $a = b = 9.364\,\text{Å}$, and $c = 6.88\,\text{Å}$. Ross\textsuperscript{(8)} concluded that the force field of a fluorine ion is largely occupied by calcium ions. The $(\text{PO}_4)^{3-}$ ions were considered to be somewhat independent of the fluorine ions, and influenced principally by calcium ions. It is reasonable then, to consider reaction mechanisms of fluorapatite as involving tricalcium phosphate and calcium fluoride.

2. Fluorspar

Calcium fluoride is an ionic compound with a cubic structure\textsuperscript{(18)}. The calcium ions lie on a face-centred cubic
lattice. Each fluorine is coordinated to 4 calcium ions, and each calcium to 8 fluorine atoms. Like phosphate rock deposits, calcium carbonate, silicon dioxide and many other minerals are found in calcium fluoride deposits.

B. Free Energy and Equilibrium Constant Analysis

1. Method of Calculation

The method of Biswas and Reginald (19) for calculating thermodynamic quantities was used in this thesis. A type calculation is presented here since all the thermodynamic results tabulated have been derived by this method.

a. Derivation of the Heat Content Equation

Consider the following reaction:

\[
\text{CaF}_2(s) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O}(g) = \text{CaSO}_4(s) + 2\text{HF}(g) \quad (5)
\]

The heat of reaction \( \Delta H^0 \) at 1 atmosphere and 298°K is calculated as follows:

\[
\Delta H^0 = \sum \Delta H^0_f \text{ (products)} - \sum \Delta H^0_f \text{ (reactants)}
\]
\[
= [(-342.6) + (-129.6)] - [(-292.0) + (-70.95)] + (-57.8)]
\]
and

\[
\Delta H^0 = -52.5 \text{ Kcals/mole.}
\]

Similarly, the heat capacity equation \( \Delta C_p \) as a function of temperature for reaction (5) is calculated:

\[
\Delta C_p = \sum C_p \text{ (products)} - \sum C_p \text{ (reactants)}
\]

and

\[
\Delta C_{p_T} = -4.06 + 10.73 \times 10^{-3}T - 0.023 \times 10^5T^{-2} \quad (14)
\]
At constant pressure, the following relationship is true:

\[
\left( \frac{\partial H}{\partial T} \right)_p = C_p
\]

and

\[
\Delta H_{T2} - \Delta H_{T1} = \int_{T_1}^{T_2} \Delta C_p dT
\]

or

\[
\Delta H_{T2} = \Delta H_{T1} + \int_{T_1}^{T_2} \Delta C_p dT
\]

Here, if \( \Delta H_{T1} \) is known, the relative value of \( \Delta H_{T2} \) at any other temperature can be easily found. Therefore,

\[
\Delta H_{298} - \Delta H^*_0 = \int_0^{298} (-4.06 + 10.73 \times 10^{-3}T - 0.23 x 10^{5T-2}) dT.
\]

\( \Delta H^*_0 \) does not signify the absolute value at 0°K, but is an arbitrary value at 0°K devised for mathematical convenience (19). Substituting \( \Delta H_{298} = -52,500 \) cals/mole and solving, we obtain \( \Delta H^*_0 = -51,774 \) cals/mole. The heat of reaction can now be found at any temperature for reaction (5) by solving the general heat content equation:

\[
\Delta H^*_0 = -51,774 - 4.06T + 5.365 \times 10^{-3}T^2 + 0.23 \times 10^{5T-1} (15)
\]

This equation will be valid within the range of the heat capacity equation and below the temperature of any phase transformation that may occur.

b. Derivation of Equilibrium Constants

The Van't Hoff Isobar (19) is used as the
starting point here,

\[ \frac{\text{d} \ln K}{\text{d} T} = \frac{\Delta H}{RT^2} \] 

and integrating

\[ \ln K = - \frac{\Delta H}{RT} + I \] 

(where I = constant of integration)

Now, substituting \( \Delta H_t \):

\[ \ln K = \left( - \frac{51.774}{RT^2} - \frac{4.06}{RT} + 5.365 \times 10^{-3} + \frac{0.023 \times 10^5}{RT^3} \right) \text{d}T + I \]

and

\[ 4.575 \log_{10} K = \frac{51.774}{T} - 9.34 \log T + 5.365 \times 10^{-3} T - 0.0115 \times 10^5 + I \]  

(16)

The value of IR can be found if \( \log_{10} K \) is known at 298°K.

This can be determined from the relationship:

\[ \Delta P^0 = -RT \ln K = - 4.575 T \log_{10} K = \Delta H - T \Delta S \]  

(17)

Now,

\[ \Delta S^{298} = \sum S^0 \text{ (products)} - \sum S^0 \text{ (reactants)} \]

\[ = - 41.95 \text{ Cals/deg-mole} \]

At 298°K:

\[ - 4.575 T \log_{10} K = \Delta H^{298} - T \Delta S^{298} \]

\[ = - 52,500 - (298) (- 41.95) \]

\[ \log_{10} K^{298} = 29.34 \]

Substituting this into equation (16) and solving gives

IR = - 15.20. Hence, the equilibrium constant at any temperature can be found from the relationship:
\[ 4.575 \log_{10} K_T = \frac{51.774}{T} - 9.34 \log_{10} T + 5.365 \times 10^{-3} T \]

\[ - \frac{1150}{T^2} - 15.2 \] \hspace{1cm} (18)

**c. Derivation of Free Energy Values**

The free energy values at various temperatures can be calculated from the relationship:

\[ \Delta F_T = -4.575 \log_{10} K_T \] \hspace{1cm} (19)

Equations (15), (18), and (19) form the basis of the thermodynamic calculations presented in this report.

**2. Calculations for Postulated Reaction Mechanisms**

**a. Fluorspar Reactions**

The results of the thermodynamic calculations for the reaction:

\[ \text{CaF}_2(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O}(g) = \text{CaSO}_4 + 2\text{HF} \] \hspace{1cm} (5)

are presented in Table 3-1. The values obtained present an attractive picture up to temperatures where a good rate might be expected. The thermodynamics of the reaction:

\[ 2\text{NaCl} + \text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HCl} \] \hspace{1cm} (12)

were also studied and the results tabulated in Table 3-2. It has been previously shown that the NaCl reaction could be carried out at temperatures in the range of 500-550°C with or without the use of a catalyst.

The thermodynamic calculations obtained for these two reactions are of the same magnitude, particularly
### TABLE 3-1

**THERMODYNAMIC REACTION CALCULATIONS**

Reaction: \( \text{CaF}_2 + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{HF} \)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( ^\circ\text{K} )</th>
<th>( ^\circ\text{C} )</th>
<th>( \Delta H ) Kcals/mole</th>
<th>( \Delta F ) Kcals/mole</th>
<th>( \text{Log}_{10}K )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>25</td>
<td>-52.50</td>
<td>-40.00</td>
<td>29.34</td>
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</tr>
<tr>
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<td>27</td>
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<td>-40.76</td>
<td>29.69</td>
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</tr>
<tr>
<td>400</td>
<td>121</td>
<td>-52.53</td>
<td>-36.84</td>
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<td>227</td>
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<td>-32.91</td>
<td>14.37</td>
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<td>327</td>
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<td>-29.29</td>
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<tr>
<td>700</td>
<td>427</td>
<td>-51.98</td>
<td>-25.17</td>
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</tr>
<tr>
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<td>527</td>
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<td>-21.36</td>
<td>5.84</td>
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</tr>
<tr>
<td>900</td>
<td>627</td>
<td>-51.08</td>
<td>-17.33</td>
<td>4.27</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>727</td>
<td>-50.47</td>
<td>-13.32</td>
<td>3.44</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3-2

**THERMODYNAMIC REACTION CALCULATIONS**

Reaction: \( 2\text{NaCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HCl} \)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( ^\circ\text{K} )</th>
<th>( ^\circ\text{C} )</th>
<th>( \Delta H ) Kcals/mole</th>
<th>( \Delta F ) Kcals/mole</th>
<th>( \text{Log}_{10}K )</th>
</tr>
</thead>
<tbody>
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<td>298</td>
<td>25</td>
<td>-25.48</td>
<td>-19.72</td>
<td>14.47</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>27</td>
<td>-25.47</td>
<td>-19.69</td>
<td>14.35</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>127</td>
<td>-25.13</td>
<td>-17.81</td>
<td>9.73</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>227</td>
<td>-24.78</td>
<td>-16.21</td>
<td>7.09</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>327</td>
<td>-24.40</td>
<td>-14.32</td>
<td>5.22</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>427</td>
<td>-24.16</td>
<td>-12.84</td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>527</td>
<td>-23.71</td>
<td>-11.26</td>
<td>3.08</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>627</td>
<td>-23.22</td>
<td>-9.73</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>727</td>
<td>-22.51</td>
<td>-8.09</td>
<td>1.90</td>
<td></td>
</tr>
</tbody>
</table>
in the higher temperature ranges. In fact, the values obtained for the fluorspar reaction are better. A plot of the free energies and equilibrium constants (Figures 3-1 and 3-2) shows the close proximity of the two reactions to each other.

Of prime importance in the above, is the gaseous reaction,

\[ \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3 \]  

(20)

Duecker and West\(^{(20)}\) reported that 80% conversions are possible using a vanadium catalyst and 8% SO\(_2\) feed at 580°C (853°K). They further state that in contrast to the unfavorable effect of high temperatures on equilibrium, the velocity of the reaction increases rapidly with temperature. The thermodynamics of the reaction are presented in Table 3-3. It would appear then, that SO\(_3\) could be a major reactant instead of SO\(_2\) in the higher temperature ranges of the reaction.

The thermodynamics of the reaction:

\[ \text{CaF}_2 + \text{SO}_3 + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{HF} \]  

(21)

were studied and the results tabulated in Table 3-4 and Figures 3-1, 3-2 show the respective thermodynamic plots. The results are in favour of reaction (21) occurring with free energy and equilibrium values approximating those in the higher temperature range of the SO\(_2\) reactions.

Scheel\(^{(6)}\) in his studies on the elimination
Figure 3-1o  The Free Energy of Reaction

\begin{align*}
\text{●} \quad 2\text{NaCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 &= \text{Na}_2\text{SO}_4 + 2\text{HCl} \\
\text{○} \quad \text{CaF}_2 + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} &= \text{CaSO}_4 + 2\text{HF} \\
\triangle \quad \text{CaF}_2 + \text{SO}_3 + \text{H}_2\text{O} &= \text{CaSO}_4 + 2\text{HF}
\end{align*}
Figure 3-2. Equilibrium Curves

- $2\text{NaCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Na}_2\text{SO}_4 + 2\text{HCl}$
- $\text{CaF}_2 + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 + 2\text{HF}$
- $\text{CaF}_2 + \text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 + 2\text{HF}$
### TABLE 3-3

**THERMODYNAMIC REACTION CALCULATIONS**

Reaction: \( \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3 \)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \Delta H ) Kcal/mole</th>
<th>( \Delta F ) Kcal/mole</th>
<th>( \log_{10} K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298果 25</td>
<td>-23.45</td>
<td>-16.72</td>
<td>12.27</td>
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<tr>
<td>300果 27</td>
<td>-23.45</td>
<td>-16.68</td>
<td>12.16</td>
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<tr>
<td>400果 127</td>
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<td>-14.42</td>
<td>7.88</td>
</tr>
<tr>
<td>500果 227</td>
<td>-23.43</td>
<td>-12.14</td>
<td>5.31</td>
</tr>
<tr>
<td>600果 327</td>
<td>-23.32</td>
<td>-9.90</td>
<td>3.61</td>
</tr>
<tr>
<td>700果 427</td>
<td>-23.17</td>
<td>-7.68</td>
<td>2.40</td>
</tr>
<tr>
<td>800果 527</td>
<td>-22.96</td>
<td>-5.48</td>
<td>1.50</td>
</tr>
<tr>
<td>900果 627</td>
<td>-22.72</td>
<td>-3.32</td>
<td>.81</td>
</tr>
<tr>
<td>1000果 727</td>
<td>-22.45</td>
<td>-1.17</td>
<td>.26</td>
</tr>
</tbody>
</table>

### TABLE 3-4

**THERMODYNAMIC REACTION CALCULATIONS**

Reaction: \( \text{CaF}_2 + \text{SO}_3 + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{HF} \)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \Delta H ) Kcal/mole</th>
<th>( \Delta F ) Kcal/mole</th>
<th>( \log_{10} K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298果 25</td>
<td>-27.80</td>
<td>-23.43</td>
<td>17.19</td>
</tr>
<tr>
<td>300果 27</td>
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<td>17.05</td>
</tr>
<tr>
<td>400果 127</td>
<td>-27.80</td>
<td>-22.04</td>
<td>12.04</td>
</tr>
<tr>
<td>500果 227</td>
<td>-27.77</td>
<td>-20.69</td>
<td>9.04</td>
</tr>
<tr>
<td>600果 327</td>
<td>-27.69</td>
<td>-19.36</td>
<td>7.05</td>
</tr>
<tr>
<td>700果 427</td>
<td>-27.56</td>
<td>-18.07</td>
<td>5.64</td>
</tr>
<tr>
<td>800果 527</td>
<td>-27.36</td>
<td>-16.82</td>
<td>4.60</td>
</tr>
<tr>
<td>900果 627</td>
<td>-27.09</td>
<td>-15.60</td>
<td>3.79</td>
</tr>
<tr>
<td>1000果 727</td>
<td>-27.12</td>
<td>-14.42</td>
<td>3.16</td>
</tr>
</tbody>
</table>

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of fluorine from phosphate rock found that the elimination was greatly facilitated when small quantities of catalyst were present. He concluded that the catalyst accelerated the oxidation of \( \text{SO}_2 \) to \( \text{SO}_3 \). It has been pointed out that Ross\(^{(8)}\) considered the reaction of fluorapatite as involving tricalcium phosphate and calcium fluoride. Scheel reported the defluorination of phosphate rock by the reaction:

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + \text{SO}_2 + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O} = 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaSO}_4 + 2\text{HF} \tag{8}
\]

If the calcium fluoride constituent of the fluorapatite is reacting separately from the phosphate, the defluorination of the phosphate rock could be represented by the reaction:

\[
\text{CaF}_2 + \text{SO}_2 + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{HF} \tag{5}
\]

A survey of the literature on fluorspar reactions indicated that fluorspar reacted with various gaseous reagents only when temperatures were greater than \( 500^\circ\text{C} \). This would appear to be in contradiction with the results obtained from a study of the thermodynamics of the reactions considered.

Based on the above observations and the calculations of the \( \text{CaF}_2 \) and \( \text{NaCl} \) reactions with \( \text{SO}_2 - \text{O}_2 - \text{H}_2\text{O} \), it appears that the fluorspar reaction of equation (5) will work. The optimum temperature of reaction will have to be found through experiments.

**b. Phosphate Rock Reactions**

Two reactions can be studied for
the contacting of phosphate rock or more specifically, fluorapatite, with the SO$_2$ - O$_2$ - H$_2$O system. The reaction schemes postulated are:

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \\
3\text{Ca}_3(\text{PO}_4)_2 + \text{CaSO}_4 + 2\text{HF}
\]

and

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 10\text{SO}_2 + 5\text{O}_2 + \text{H}_2\text{O} = \\
3\text{P}_2\text{O}_5 + 10\text{CaSO}_4 + 2\text{HF}
\]

The results of the thermodynamic calculations are presented in Tables 3-5 and 3-6.

Reaction (3) was first proposed by Scheel$^6$ to explain the defluorination of phosphate rock. The thermodynamic results (Table 3-5) show that good equilibrium constants and free energy values are obtained up to 327°C. Above this temperature level the results indicate non-spontaneous process occurring (i.e., positive $\Delta$F and negative K values). Scheel$^6$, however, in his patent states that the elimination of fluorine begins at 500°C and proceeds at a considerable rate at 600 to 700°C. Based on the thermodynamic argument presented so far, the reaction of equation (3) would appear to be in question.

Scheel$^6$ also reported that on prolonged reaction at a lower temperature (500 to 850°C), the initially formed tricalcium phosphate was converted into calcium pyrophosphate. An alternative reaction then, could be as follows:

\[
\text{CaF}_2 + \text{SO}_3 + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{HF}
\]

(21)
### TABLE 3-5

**THERMODYNAMIC REACTION CALCULATIONS**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \Delta H ) Kcals/mole</th>
<th>( \Delta F ) Kcals/mole</th>
<th>( \log_{10} K )</th>
</tr>
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<tr>
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</tr>
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</tr>
<tr>
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<td>-38.36</td>
<td>-22.34</td>
<td>12.21</td>
</tr>
<tr>
<td>500 227</td>
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<td>-15.58</td>
<td>6.81</td>
</tr>
<tr>
<td>600 327</td>
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<td>-7.68</td>
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</tr>
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<td>-0.39</td>
</tr>
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<td>-3.04</td>
</tr>
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<td>+21.79</td>
<td>-5.29</td>
</tr>
<tr>
<td>1000 727</td>
<td>-30.58</td>
<td>+33.24</td>
<td>-7.27</td>
</tr>
</tbody>
</table>

### TABLE 3-6

**THERMODYNAMIC REACTION CALCULATIONS**

<table>
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<tr>
<th>Temperature</th>
<th>( \Delta H ) Kcals/mole</th>
<th>( \Delta F ) Kcals/mole</th>
<th>( \log_{10} K )</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>289.90</td>
</tr>
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<td>180.22</td>
</tr>
<tr>
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</tr>
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</tr>
<tr>
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<td>900 627</td>
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<td>-16.5</td>
<td>4.01</td>
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<tr>
<td>1000 727</td>
<td>-535.9</td>
<td>+42.3</td>
<td>-9.24</td>
</tr>
</tbody>
</table>
Ca₃(PO₄)₂ + SO₃ = Ca₂P₂O₇ + CaSO₄  \hspace{1cm} (23)

The previous discussion on the thermodynamic calculations for reaction (21) has shown that the reaction is feasible. Table 3-7 gives the thermodynamic calculations for reaction (23). The results are in favour of both reaction (21) and (23) occurring.

The reaction of equation (22) is also possible. Ross⁸ in his fluidized bed experiments with fluorapatite found evidence of phosphorus pentoxide formation in the temperature range studied, 325-340°C. No evidence of evolved fluorine was found. The results in Table 3-6 show very good free energy and equilibrium constant values up to 627°C. From here, the values taper off and at 727°C an unfavourable thermodynamic picture results.

The thermodynamic evaluation and the literature survey indicates that in a temperature range of 500 - 700°C the reaction of fluorapatite with the SO₂ - O₂ - H₂O system should follow the equations of (21) and (23);

\[
\begin{align*}
\text{CaF}_2 + \text{SO}_3 + \text{H}_2\text{O} &= \text{CaSO}_4 + 2\text{HF} \hspace{1cm} (21) \\
\text{Ca}_3(\text{PO}_4)_2 + \text{SO}_3 &= \text{Ca}_2\text{P}_2\text{O}_7 + \text{CaSO}_4 \hspace{1cm} (23)
\end{align*}
\]

C. Mixtures of Phosphate Rock and Fluorspar

A third part of the investigation undertaken
TABLE 3-7

FREE ENERGY AND EQUILIBRIUM CONSTANT VALUES (8) FOR THE REACTION

\[
\text{Ca}_3(\text{PO}_4)_2 + \text{SO}_3 = \text{Ca}_2\text{P}_2\text{O}_7 + \text{CaSO}_4
\]

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>°C</th>
<th>ΔF Kcal/mole</th>
<th>(\log_{10} K)</th>
</tr>
</thead>
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<td>73.35</td>
</tr>
<tr>
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<td>27</td>
<td>-99.0</td>
<td>72.12</td>
</tr>
<tr>
<td>400</td>
<td>127</td>
<td>-94.5</td>
<td>51.64</td>
</tr>
<tr>
<td>500</td>
<td>227</td>
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</tr>
<tr>
<td>900</td>
<td>627</td>
<td>-40.5</td>
<td>9.84</td>
</tr>
<tr>
<td>1000</td>
<td>727</td>
<td>-22.8</td>
<td>4.98</td>
</tr>
</tbody>
</table>

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in this thesis was to see if enough moles of CaF$_2$ could be added to Ca$_{10}$(PO$_4$)$_6$F$_2$ to add enough fluorine to liberate POF$_3$ or PF$_3$ type products. The possible reactions are as follows:

\[ \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 8\text{CaF}_2 + 18\text{H}_2\text{SO}_4 = 18\text{CaSO}_4 + 6\text{POF}_3 + 18\text{H}_2\text{O} \]  
\[ \text{(24)}, \]

\[ \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 8\text{CaF}_2 + 18\text{SO}_2 + 6\text{O}_2 = 6\text{PF}_3 + 18\text{CaSO}_4 \]  
\[ \text{(25)}, \]

\[ \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 8\text{CaF}_2 + 18\text{SO}_2 + 9\text{O}_2 = 6\text{POF}_3 + 18\text{CaSO}_4 \]  
\[ \text{(26)}, \]

and

\[ \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 8\text{CaF}_2 + 18\text{SO}_3 = 6\text{POF}_3 + 18\text{CaSO}_4 \]  
\[ \text{(27)} \]

The thermodynamic results for these four reactions are presented in Tables 3-8 to 3-11. The sulphuric acid reaction (Table 3-8) is the most unfavourable one, requiring very high energy requirements to overcome the thermodynamic barrier present. Of the remaining three reactions, equation (27) represents the most favourable reaction in the thermodynamic approach. The reaction, however, though favoured at low temperatures is not a spontaneous one around 550°C.

We have already shown that Scheel produced fluorine from phosphate rock at temperatures greater than 500°C. Ross found no evidence of fluorine production in the temperature range 325-350°C but did obtain some conversion of phosphate rock to P$_2$O$_5$. Tarbutton et al were able to react fluorspar with P$_2$O$_5$ according to the equation:
### TABLE 3-8

**THERMODYNAMIC REACTION CALCULATIONS**

Reaction:
\[ \text{Ca}_{10} \text{(PO}_4\text{)}_6 \text{F}_2 + 8 \text{CaF}_2 + 18 \text{H}_2\text{SO}_4 = 18 \text{CaSO}_4 + 6 \text{POF}_3 + 18 \text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>ΔH</th>
<th>ΔF</th>
<th>Log_{10}K</th>
</tr>
</thead>
<tbody>
<tr>
<td>°K</td>
<td>Kcal/mole</td>
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### TABLE 3-9

**THERMODYNAMIC REACTION CALCULATIONS**

Reaction:
\[ \text{Ca}_{10} \text{(PO}_4\text{)}_6 \text{F}_2 + 8 \text{CaF}_2 + 18 \text{SO}_2 + 6 \text{O}_2 = 6 \text{PF}_3 + 18 \text{CaSO}_4 \]

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TABLE 3-10

THERMODYNAMIC REACTION CALCULATIONS

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TABLE 3-11

THERMODYNAMIC REACTION CALCULATIONS

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$3\text{CaF}_2 + 4\text{P}_2\text{O}_5 = 2\text{POF}_3 + 3\text{Ca(PO}_3\text{)}_2 \quad (9)$

The temperature range at which their reactions were carried out was from 500 to 1000°C.

Considering an SO$_3$ reacting system, a possible alternative for the over-all reaction,

$$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 8\text{CaF}_2 + 18\text{SO}_3 = 6\text{POF}_3 + 18\text{CaSO}_4 \quad (27),$$

is as follows:

$$3\text{Ca}_3(\text{PO}_4)_2 + 9\text{SO}_3 = 3\text{P}_2\text{O}_5 + 9\text{CaSO}_4 \quad (28),$$

and

$$3\text{CaF}_2 + 4\text{P}_2\text{O}_5 = 2\text{POF}_3 + 3\text{Ca(PO}_3\text{)}_2 \quad (9).$$

Reaction (28) using the method of Ross$^8$ would be carried out around 325-350°C while reaction (9) would have to be carried out at 500-700°C.
IV EXPERIMENTAL PROCEDURE

The defluorination of fluorspar by the reaction of $\text{CaF}_2$ with $\text{SO}_2 - \text{O}_2 - \text{H}_2\text{O}$ was chosen in an attempt to test the thermodynamic arguments previously advanced. The gas-solid contact experiments were attempted in fluidized and fixed-bed systems.

A. Fluidized-Bed Experiments

Experiments were designed (Figure 4-1) in which 1 gram samples of pure calcium fluoride were to be fluidized in a 30 x $\frac{1}{2}$ inch glass tube. The tube was placed in a metallurgical combustion furnace and heating tapes placed around the upper and lower sections of the tube. Air was bubbled through water and then mixed with $\text{SO}_2$ gas in a cylinder packed with berl saddles. The sample was held inside the reactor tube by means of a stainless steel screen and glass pyrex wool. The off gases were passed into solutions of sodium carbonate. In some of the runs a catalyst was added to the sample. A temperature range of 280 to 400°C was selected for the various runs.

B. Fixed-Bed Experiments

A series of fixed bed experiments were performed using a high temperature, high silica content glass combustion tube 21 x $\frac{1}{2}$ inch. The reactor tube was placed horizontally...
Figure 4-1. Reaction System Flow Sheet
in the metallurgical combustion furnace and the experimental set-up used as in Figure 4-1. For all experimental runs a 10 gram sample of pure CaF₂ was used with some runs also having 4% by weight ferric sulphate pre-mixed with the CaF₂. The sample was distributed throughout the length of the reactor tube.

Temperature measurements in all cases were determined with chromel-alumel thermocouples connected through a selector switch to a Leeds and Northrup potentiometer. The furnace employed was a Hevi-Duty Single Tube, Type 70T, manufactured by the Hevi-Duty Electric Company. The calcium fluoride used in all experiments was of synthetic grade supplied by the Fisher Scientific Co. Ltd.
V RESULTS

A. Fluidized-Bed Experiments

Experimental runs at temperatures of 280, 300, 325, and 400°C, were tried for 30 and 60 minutes with one gram sample of pure calcium fluoride. In one run (400°C), 4% by weight ferric sulphate was added to the calcium fluoride. Fluidization proved to be very difficult to obtain uniformly in all experimental runs. At the end of each run, the sample showed evidence of caking. For the 300°C run, 25% fluidization was obtained using an air and sulphur dioxide flow of 4170 and 17.3 ml./min. respectively. The particle size of the calcium fluoride was 100 mesh for all the experiments. In all cases there was no evidence of CaF₂ being defluorinated.

B. Fixed-Bed Experiments

Experimental runs at temperatures of 615, 630 and 650°C were attempted using 10 gram samples of CaF₂. The runs were carried out for a duration of 60 minutes. In some of the runs 4% by weight ferric sulphate was first premixed with the sample.

All experimental runs showed evidence of CaF₂ being defluorinated. The evidence of fluorine production was the etching that occurred on the walls of the reactor and solids trap. The best result was for the 615°C run. Here, 4% by weight FeSO₄ was pre-mixed with 10 grams of CaF₂. An air flow rate of 700 ml./min. and an SO₂:H₂O ratio of 2:1 was employed. The duration of the run was 60 minutes.
The length of the reactor above the sample was etched as was the entire inside of the solids trap. In the first bubbler flask (containing 10 grams Na₂CO₃ in 400 ml. of water) a fine white precipitate was formed. The second bubbler showed no evidence of precipitate formation. For the runs at 630 and 650°C in which no catalyst was used, the etching was only slight compared to the run at 615°C in which a catalyst was employed.
VI. CONCLUSIONS

This thesis has dealt with possible reactions of fluorapatite and fluorspar. As a result of thermodynamic calculations, possible reactions were explored in terms of free energies, $\Delta F$ and equilibrium constants, $K_T$. The reactions were also explored in terms of structure. A literature survey was used to determine what reactions appeared the most favourable and what, if any, were the temperature requirements. It must be remembered that thermodynamic calculations give an insight on the driving forces and prediction of equilibrium states for chemical reactions. The calculated values will depend on the assumed reactions and thermodynamics by itself cannot verify this. However, the use of thermodynamic quantities together with structural considerations, and a literature survey provides an extremely good starting point in the study of possible chemical reactions. The explanation of what actually happens can at present, only be found through experimentation.

The combination of thermodynamic calculations, structure, and literature survey previously led to the conclusion that fluorspar could be defluorinated by reaction with $SO_2 - O_2 - H_2O$. The temperature range for the reaction was shown through calculations to be favourable from room temperature up to $1000^\circ K$. The literature survey and structural studies indicated probable reaction temperatures would have to be greater than $500^\circ C$. 

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The experimental results have shown that fluorspar can be defluorinated at temperatures greater than 500°C. The addition of ferric sulphate as a catalyst facilitates the reaction rate. This is probably due to the fact that SO₂ is converted to SO₃. Tables 3-1 and 3-4 showed that on the basis of the thermodynamics both reactants were favourable.

The conclusion that CaF₂ was defluorinated is based on the etching of the glass reactor tube. The mechanism for this reaction would be as follows:

\[
\text{CaF}_2 + \text{SO}_3 + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{HF} \tag{21}
\]

\[
4\text{HF} + \text{SiO}_2 = \text{SiF}_4 + 2\text{H}_2\text{O} \tag{29}
\]

and in water,

\[
3\text{SiF}_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2\text{SiF}_6 \tag{30}
\]

The fixed-bed experiments were carried out because of the problems incurred in the fluidized-bed experiments. Fluidized-bed experiments, however, would be the best approach since better gas-solid contact is maintained than in fixed-bed or rotary-bed experiments. The fluidized-bed then, should ensure good contact, and the high temperatures, good rates for the defluorination of CaF₂. The upper limit of conversion could be controlled, however, by the formation of CaSO₄ which could coat the fluorspar particles and hence impede their contact with the gas phase. The reaction of hydrogen fluoride (HF) with the silicon dioxide can be avoided if an iron or a stainless steel reactor tube is substituted for the glass reactor tube.
The use of \( \text{SO}_2 \) instead of \( \text{SO}_3 \) is preferred because of economics and its availability.

The experimental results support the conclusion that the reaction of fluorapatite should (at temperatures greater than 500°C) proceed by the mechanism:

\[
\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3 \quad (20)
\]

\[
\text{CaF}_2 + \text{SO}_3 + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{HF} \quad (21)
\]

and

\[
\text{Ca}_3(\text{PO}_4)_2 + \text{SO}_3 = \text{Ca}_2\text{P}_2\text{O}_7 + \text{CaSO}_4 \quad (23)
\]

At temperatures below 500°C there was no evidence of \( \text{CaF}_2 \) reacting with \( \text{SO}_2 \) or \( \text{SO}_3 \). Ross(8), however, did show that \( \text{Ca}_3(\text{PO}_4)_2 \) will react with \( \text{SO}_2 \) or \( \text{SO}_3 \) below 500°C to produce \( \text{P}_2\text{O}_5 \). A possible reaction could be:

\[
\text{Ca}_3(\text{PO}_4)_2 + 3\text{SO}_3 = \text{P}_2\text{O}_5 + 3\text{CaSO}_4 \quad (28)
\]

It has already been shown that \( \text{P}_2\text{O}_5 \) reacts with \( \text{CaF}_2 \) at temperatures greater than 500°C according to the reaction:

\[
3\text{CaF}_2 + 4\text{P}_2\text{O}_5 = 2\text{POF}_3 + 3\text{Ca}(\text{PO}_3)_2.
\]

The formation of oxyfluorides is, therefore, possible, the problems of carrying out such a reaction scheme, however, would be many.
Though the formation of oxyfluorides appears to be possible, the reaction of mixtures of phosphate rock and fluorspar to form oxyfluorides does not appear likely. The reasons for this are:

(1) Postulated reactions all show unfavourable thermodynamic values from 600°C on, the area of defluorination.

(2) The conclusion that CaF$_2$ and Ca$_3$(PO$_4$)$_2$ are reacting separately indicates that the P-O bonds are shielded from fluorine in fluorapatite.
VII. RECOMMENDATIONS

The theory and experimental work of this thesis have shown that the reaction of fluorspar with $\text{SO}_2 - \text{O}_2 - \text{H}_2\text{O}$ can be carried out. It is recommended that further investigations of this system be continued. Further experimental work should concentrate on the kinetics of the process to obtain information on optimum conditions. The optimum conditions will give an idea as to the economics of the process.

It is also recommended that a fluidized-bed investigation be carried out. Further work should make use of an iron or stainless-steel reactor tube. Commercial catalysts for converting $\text{SO}_2$ to $\text{SO}_3$ should also be investigated.
REFERENCES

1. Quittenton, R.C., personal communication, (June, 1968)
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<th>Definition</th>
<th>Units</th>
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<td>Kcals/Mole</td>
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<td>$\Delta H_T$</td>
<td>Heat of Reaction at Temperature T</td>
<td>Kcals/Mole</td>
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<td>$\Delta S^o$</td>
<td>Entropy change at 298°K</td>
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APPENDIX I

THERMODYNAMIC CALCULATION DATA
## APPENDIX I

### THERMODYNAMIC CALCULATION DATA

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<th>Compound</th>
<th>Chemical Formula</th>
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VITA AUCTORIS

1941 Born at Timmins, Ontario.

1960 Graduated from Schumacher High School, Schumacher, Ontario.

1963 Graduated from Ryerson Institute of Technology, Toronto, Ontario, with a Diploma in Chemical Technology.

1968 Graduated from the University of Windsor with the degree of B.A.Sc. in Chemical Engineering.

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