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

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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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APPROVED BY: _R.C. Quittenton_

F. Geldman

W J Ballard

296565

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 $500^{\circ}C$. 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.

ACKNOWLEDGEMENTS

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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,

$$Ca_{10}(PO4)_6F_2 + 7H_2SO_4 + 3H_2O =$$

$$3CaH_4(PO4)_2H_2O + 7CaSO_4 + 2HF \qquad (1)$$
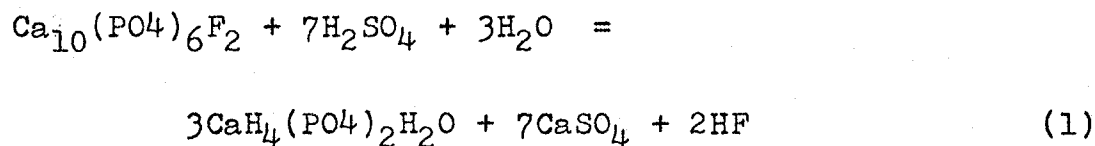
One objective of this investigation is to see if enough moles of fluorspar (CaF_2) can be added to fluorapatite to add enough fluorine to liberate phosphorus as a phosphorus oxyfluoride. A possible reaction could be,

$$Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18SO_2 + 9O_2 =$$

$$6POF_3 + 18CaSO_4 \qquad (2)$$
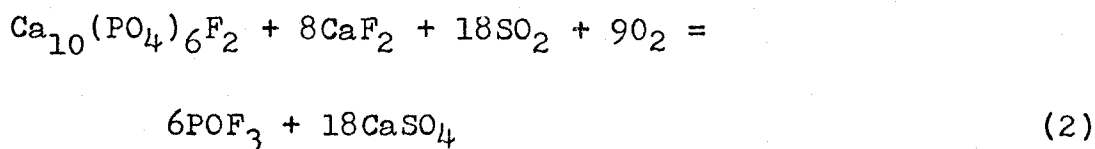
The contacting of phosphate rock directly with $SO_2 - O_2 - H_2O$ will also be studied according to the reaction,

$$Ca_{10}(PO4)_6F_2 + SO_2 + \tfrac{1}{2}O_2 + H_2O =$$

$$3Ca_3(PO4)_2 + CaSO_4 + 2HF \qquad (3)$$
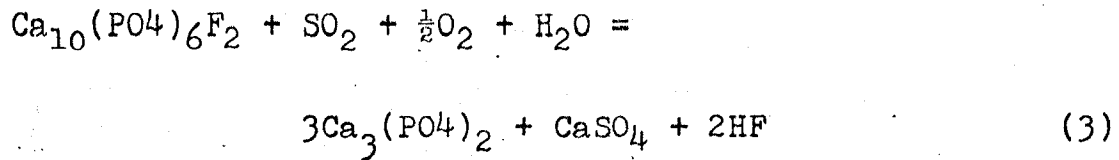
Equation (2) represents a more potentially attractive phosphate process since the fluorine (in CaF_2) is used to carry off the phosphorus as an oxyfluoride.

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 $Ca_{10}(PO4)_6F_2$ can be split up with SO_2 instead of H_2SO_4. However, even if H_2SO_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,

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF \qquad (4)$$
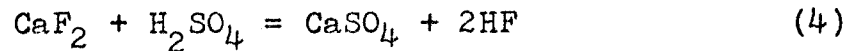
The object here, is to develop a fluo-solids process for the liberation of HF gas from CaF_2 by reaction with SO_2 as follows,

$$CaF_2 + SO_2 + \tfrac{1}{2}O_2 + H_2O = CaSO_4 + 2HF \qquad (5)$$
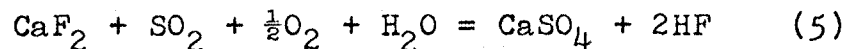
The present-day processes just described (equations 1, 4) are thermally inefficient and present serious problems with corrosion, fumes, and mechanical difficulties.

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.

II LITERATURE SURVEY

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 SO_2 and oxygen at $800^\circ C$, obtaining calcium sulphate and calcium pyrophosphate:

$$Ca_3(PO_4)_2 + SO_2 + \tfrac{1}{2}O_2 = CaSO_4 + Ca_2P_2O_7 \qquad (6)$$
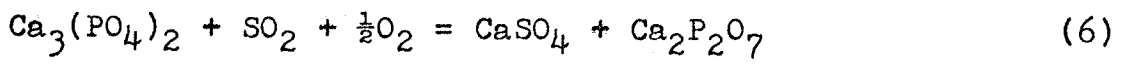
Water was not used as a reactant, and the fate of the fluorine in the phosphorite is not mentioned.

In 1930, Briner and Monnier[4] studied the reaction of pure calcium phosphate with SO_2. The optimum temperature was about $350^\circ C$ with the reaction being:

$$2Ca_3(PO_4)_2 + 3SO_2 = 2CaSO_4 + 2Ca_2P_2O_7 + S \qquad (7)$$
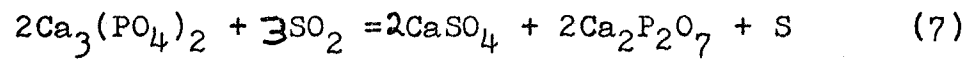
Hughes and Cameron[5] in 1931 reported on an intensive study made of the reaction of phosphate rock with SO_2 and SO_3. Their more important results may be summarized as follows:

i) Phosphate rock can be converted at temperatures of 350 to $450^\circ C$ at high pressures and long contact times by 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 $600^{\circ}C$, 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[6] for the defluorination of phosphate rock. The patent claims a process in which mixtures of $Ca_3(PO4)_2$ and $CaSO_4$ are prepared by reaction of SO_2 and O_2 at temperatures greater than $500^{\circ}C$, the gas containing 1 part by volume H_2O vapour per volume of SO_2. The reaction claimed is:

$$Ca_{10}(PO4)_6F_2 + SO_2 + \tfrac{1}{2}O_2 + H_2O =$$

$$3Ca_3(PO_4)_2 + CaSO_4 + 2HF \qquad (8)$$
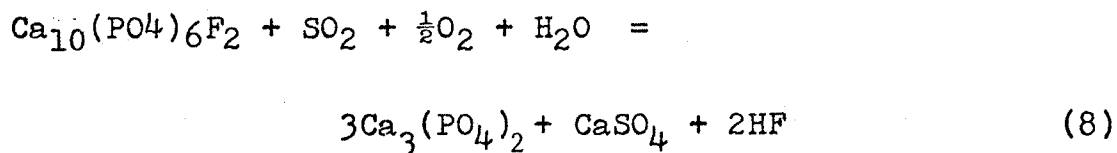
The elimination of the fluorine begins at about 500° and proceeds at a considerable rate at 600 to 700°.

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% SO_2. 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 transformation of natural phosphorites by the action of a gaseous mixture of SO_2, air, and water. Samples were heated in an iron tube at 300 - 900° and air containing SO_2 1.7 - 1.9% and H_2O 0-7.29% was used. The duration of contact of gaseous and solid phases was 60-80 seconds. The products reported were $Ca_2P_2O_7$ and $CaSO_4$. The process was most effective in an iron tube or when Fe_2O_3 or V_2O_5 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 SO_2 and with SO_3 (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 SO_3, but that the reaction with SO_2 was very slow. The best conversion was with SO_3 at 325 $\pm$ 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, $CaSO_4$ forming entirely from calcium originally associated with phosphorus.

TABLE 2-1

Amount of Fluorine Driven Off From

Calcined Phosphate Rock[6]

Calcined Product After Treatment for 1 Hour	No Catalyst	1.9%FeSO$_4$	1.0%FeSO$_4$ +1.0%K$_2$SO$_4$	3.8%FeSO$_4$
% P$_2$O$_5$	32.2	31.0	30.2	30.0
% SO$_3$	9.4	11.7	17.2	18.6
% F	2.0	1.62	1.07	0.96
% of F Driven Off After				
15 mins.	17	25	28	29
1 hour	46	54	69	71

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_2O_5 were reported as:

$$3CaF_2 + 4P_2O_5 = 2POF_3 + 3C_a(PO_3)_2 \qquad (9)$$

$$6CaF_2 + 5P_2O_5 = 4POF_3 + 3Ca_2P_2O_7 \qquad (10)$$

$$3CaF_2 + 2P_2O_5 = 2POF_3 + Ca_3(PO_4)_2 \qquad (11)$$
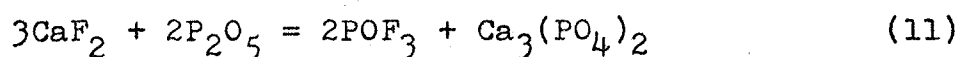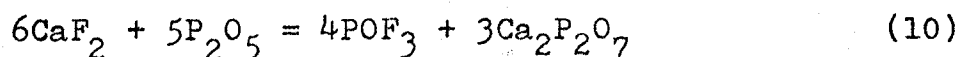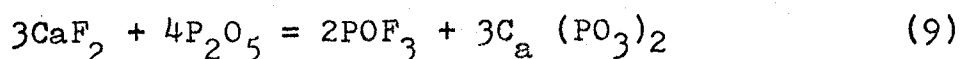
The temperature varied from 500 to $1000^{\circ}C$ and the weights of the volatile products obtained, corresponded closely to equation (9) on the basis of P_2O_5 added.

Mixtures of fluorapatite and P_2O_5 were heated to about 700°. 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 - $300^{\circ}C$ 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:

$$2NaCl + SO_2 + \tfrac{1}{2}O_2 + H_2O = Na_2SO_4 + 2HCl \qquad (12)$$
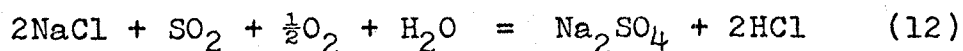
The reaction is exothermic, and sufficient heat is evolved to maintain the process once the reactants are brought

up to temperature. Operating temperatures may vary from $535^{\circ}C$ at the spent-salt end to $455^{\circ}C$ 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'fkovick 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 $500 - 550^{\circ}C$ the yield of sulphate is $95 - 96\%$, with the time requirement not longer than 1.5 hours.

In 1943, Vol'fkovick and Margolis[14] reported results of a study made of the catalysts tested for the reaction:

$$4KCl + 2SO_2 + O_2 + 2H_2O = 2K_2SO_4 + 4HCl \qquad (13)$$

The catalysts were Al_2O_3, CuO, $Co(NO_3)_2$, $CoSO_4$, Fe_2O_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, $Ca_{10}(PO_4)_6(F,Cl,OH)_2$ is the principal mineral in the phosphate rock deposits of the world[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[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 $(PO_4)^{3-}$ tetrahedra, ten Ca^{2+} ions, and two F-: $Ca_{10}(PO4)_6F_2$. Brasseur[17] in 1954, reported unit cell dimensions of fluorapatite as a = b = 9.364Å, and C = 6.88Å. Ross[8] concluded that the force field of a fluorine ion is largely occupied by calcium ions. The $(PO_4)^{3-}$ 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[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:

$$CaF_{2(s)} + SO_{2(g)} + \tfrac{1}{2}O_{2(g)} + H_2O_{(g)} = CaSO_{4(s)} + 2HF_{(g)} \quad (5)$$
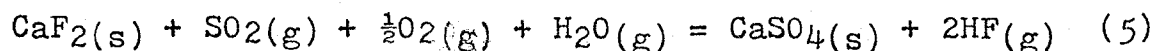
The heat of reaction (ΔH^o) at 1 atmosphere and 298^oK is calculated as follows:

$$\Delta H^o = \sum \Delta H^o_f \text{ (products)} - \sum \Delta H^o_f \text{ (reactants)}$$

$$= \left[(-342.6) + (-129.6)\right] - \left[(-292.0) + (-70.95) + (-57.8)\right]$$

and

$$\Delta H^o = -52.5 \text{ Kcals/mole.}$$

Similarly, the heat capacity equation (ΔC_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

$$\Delta C_{p_T} = -4.06 + 10.73 \times 10^{-3}T - .023 \times 10^5 T^{-2} \quad (14)$$

At constant pressure, the following relationship is true:

$$\left(\frac{\partial H}{\partial T}\right)_p = Cp$$

and

$$\Delta H_{T2} - \Delta H_{T1} = \int_{T_1}^{T_2} \Delta CpdT$$

or

$$\Delta H_{T2} = \Delta H_{T1} + \int_{T_1}^{T_2} \Delta CpdT$$

Here, if ΔH_{T1} is known, the relative value of ΔH_{T2} at any other temperature can be easily found. Therefore,

$$\Delta H298 - \Delta H_0^* = \int_0^{298} (- 4.06 + 10.73 \times 10^{-3}T - .023 \times 10^5 T^{-2}) \, dT.$$

ΔH_0^* does not signify the absolute value at $0^{\circ}K$, but is an arbitrary value at $0^{\circ}K$ devised for mathematical convenience [19]. Substituting $\Delta H298 = - 52,500$ 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:

$$\Delta H_T^0 = - 51,774 - 4.06T + 5.365 \times 10^{-3}T2 + .023 \times 10^5 T^{-1} \quad (15)$$

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,

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \quad \text{and integrating}$$

$$\ln K = -\frac{\Delta H}{RT} + I \quad \text{(where I = constant of integration)}$$

Now, substituting ΔH_t^c:

$$\ln K = \int \left(\frac{-51,774}{RT^2} - \frac{4.06}{RT} + \frac{5.365 \times 10^{-3}}{R} + \frac{.023 \times 10^5}{RT^3} \right) dT + I$$

and

$$4.575 \log_{10} K = +\frac{51,774}{T} - 9.34 \log T + 5.365 \times 10^{-3} T - \frac{.0115 \times 10^5}{T^2} + IR \quad (16)$$

The value of IR can be found if $\log_{10} K$ is known at $298^{\circ}K$. This can be determined from the relationship:

$$\Delta F^{\circ} = -RT \ln K = -4.575 T \log_{10} K = \Delta H - T \Delta S \quad (17)$$

Now, $\Delta S^{\circ}298 = \sum S^{\circ} \text{ (products)} - \sum S^{\circ} \text{ (reactants)}$

$$= -41.95 \text{ Cals/deg-mole}$$

At $298^{\circ}K$:

$$-4.575 T \log_{10} K = \Delta H^{\circ}298 - T \Delta S^{\circ}298$$

$$= -52,500 - (298)(-41.95)$$

$$\text{Log}_{10} K298 = 29.34$$

Substituting this into equation (16) and solving gives IR = - 15.20. Hence, the equilibrium constant at any temperature can be found from the relationship:

$$4.575\log_{10}K_T = \frac{51,774}{T} - 9.341\log_{10}T + 5.365 \times 10^{-3}T$$

$$- \frac{1150}{T^2} - 15.2 \tag{18}$$

c. <u>Derivation of Free Energy Values</u>

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

$$\Delta F_T = -4.575T\log_{10}K_T \tag{19}$$

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

2. <u>Calculations for Postulated Reaction Mechanisms</u>

a. <u>Fluorspar Reactions</u>

The results of the thermodynamic calculations for the reaction:

$$CaF_{2(s)} + SO_{2(g)} + \tfrac{1}{2}O_2(g) + H_2O(g) = CaSO_4 + 2HF \tag{5}$$
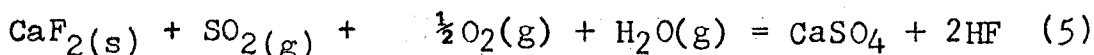
are presented in Table 3-1. The values obtained present an attractive picture up to temperatures where a good rate might be expected. The thermodynamics of the reaction:

$$2NaCl + SO_2 + \tfrac{1}{2}O_2 + H_2O = Na_2SO_4 + 2HCl \tag{12}$$
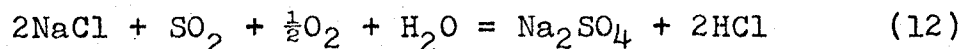
were also studied and the results tabulated in Table 3-2. It has been previously shown that the NaCl reaction could be carried out at temperatures in the range of 500-550°C with or without the use of a catalyst.

The thermodynamic calculations obtained for these two reactions are of the same magnitude, particularly

TABLE 3-1

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $CaF_2 + SO_2 + \frac{1}{2}O_2 + H_2O = CaSO_4 + 2HF$				
Temperature		$\triangle H$ Kcals/mole	$\triangle F$ Kcals/mole	$Log_{10}K$
^{o}K	^{o}C			
298	25	-52.50	-40.00	29.34
300	27	-52.50	-40.76	29.69
400	121	-52.53	-36.84	20.13
500	227	-52.46	-32.91	14.37
600	327	-52.28	-29.29	10.67
700	427	-51.98	-25.17	7.86
800	527	-51.59	-21.36	5.84
900	627	-51.08	-17.33	4.21
1000	727	-50.47	-13.92	3.04

TABLE 3-2

THERMODYNAMIC REACTION CALCULATIONS

| Reaction: $2NaCl + SO_2 + \frac{1}{2}O_2 + H_2O = Na_2SO_4 + 2HCl$				
Temperature		$\triangle H$ Kcals/mole	$\triangle F$ Kcals/mole	$Log_{10}K$
^{o}K	^{o}C			
298	25	-25.48	-19.72	14.47
300	27	-25.47	-19.69	14.35
400	127	-25.13	-17.81	9.73
500	227	-24.78	-16.21	7.09
600	327	-24.40	-14.32	5.22
700	427	-24.16	-12.84	4.01
800	527	-23.71	-11.26	3.08
900	627	-23.22	- 9.73	2.36
1000	727	-22.51	- 8.09	1.90

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,

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 \tag{20}$$

Duecker and West[20] reported that 80% conversions are possible using a vanadium catalyst and 8% SO_2 feed at $580^{\circ}C$ $(853^{\circ}K)$. 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:

$$CaF_2 + SO_3 + H_2O = CaSO_4 + 2HF \tag{21}$$
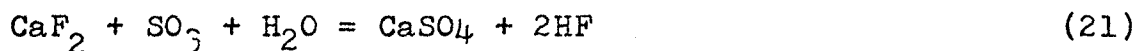
were studied and the results tabulated in Table 3-4 and Figures 3-1, 3-2 show the respective thermodynamic plots. The results are in favour of reaction (21) occurring with free energy and equilibrium values approximating those in the higher temperature range of the SO_2 reactions.
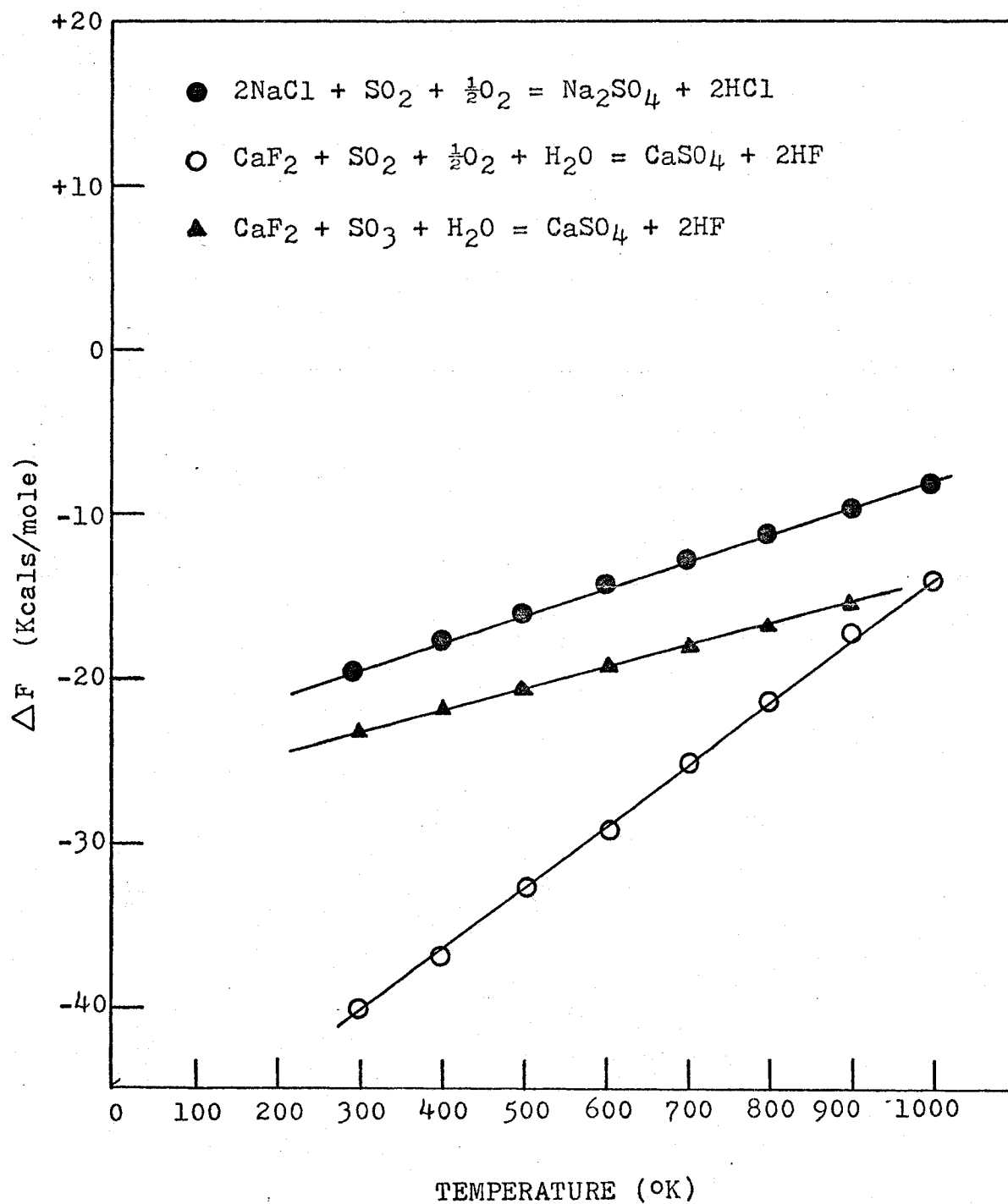
Scheel[6] in his studies on the elimination

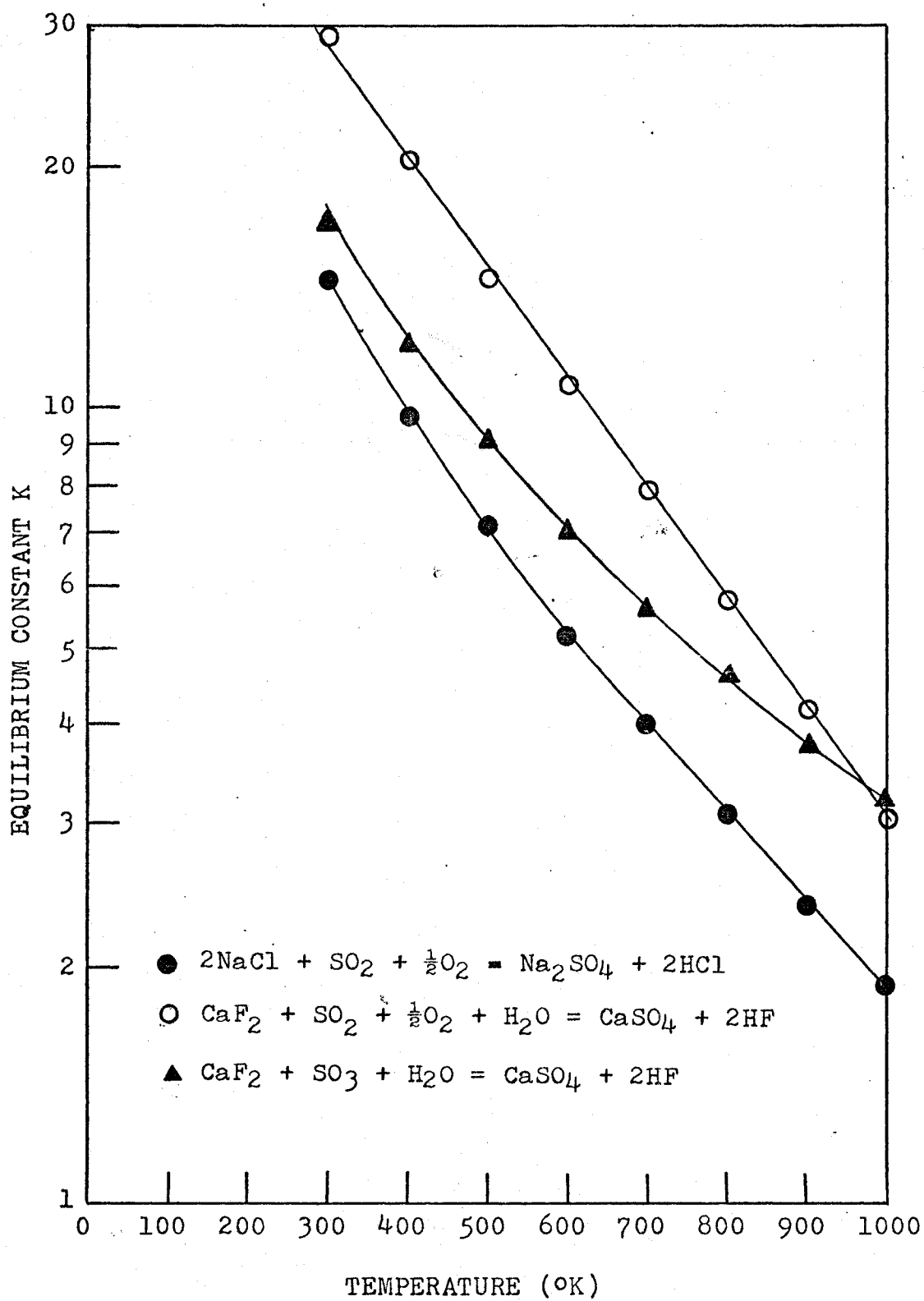Figure 3-1. The Free Energy of Reaction

Figure 3-2. Equilibrium Curves

TABLE 3-3

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $SO_2 + \frac{1}{2}O_2 = SO_3$				
Temperature		$\triangle H$ Kcal/mole	$\triangle F$ Kcal/mole	$Log_{10}K$
$^\circ K$	$^\circ C$			
298	25	-23.45	-16.72	12.27
300	27	-23.45	-16.68	12.16
400	127	-23.49	-14.42	7.88
500	227	-23.43	-12.14	5.31
600	327	-23.32	- 9.90	3.61
700	427	-23.17	- 7.68	2.40
800	527	-22.96	- 5.48	1.50
900	627	-22.72	- 3.32	.81
1000	727	-22.45	- 1.17	.26

TABLE 3-4

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $CaF_2 + SO_3 + H_2O = CaSO_4 + 2HF$				
Temperature		$\triangle H$ Kcal/mole	$\triangle F$ Kcal/mole	$Log_{10}K$
$^\circ K$	$^\circ C$			
298	25	-27.80	-23.43	17.19
300	27	-27.80	-23.40	17.05
400	127	-27.80	-22.04	12.04
500	227	-27.77	-20.69	9.04
600	327	-27.69	-19.36	7.05
700	427	-27.56	-18.07	5.64
800	527	-27.36	-16.82	4.60
900	627	-27.09	-15.60	3.79
1000	727	-27.12	-14.42	3.16

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 SO_2 to 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:

$$Ca_{10}(PO_4)_6F_2 + SO_2 + \tfrac{1}{2}O_2 + H_2O =$$

$$3Ca_3(PO_4)_2 + CaSO_4 + 2HF \qquad (8)$$
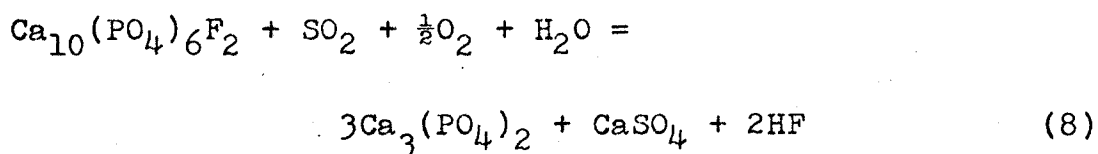
If the calcium fluoride constituent of the fluorapatite is reacting separately from the phosphate, the defluorination of the phosphate rock could be represented by the reaction:

$$CaF_2 + SO_2 + \tfrac{1}{2}O_2 + H_2O = CaSO_4 + 2HF \qquad (5)$$
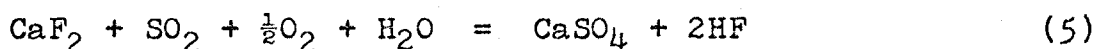
A survey of the literature on fluorspar reactions indicated that fluorspar reacted with various gaseous reagents only when temperatures were greater than $500^{\circ}C$. This would appear to be in contradiction with the results obtained from a study of the thermodynamics of the reactions considered.

Based on the above observations and the calculations of the CaF_2 and $NaCl$ reactions with $SO_2 - O_2 - H_2O$, 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_2O system. The reaction schemes postulated are:

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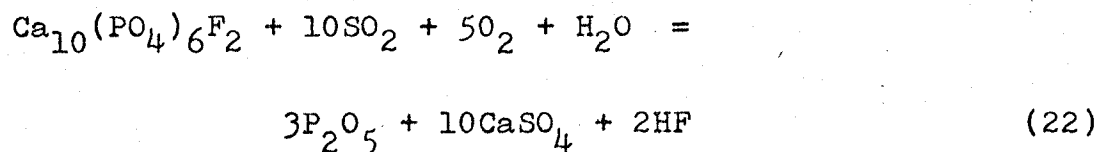
$$3Ca_3(PO_4)_2 + CaSO_4 + 2HF \qquad (3)$$

and

$$Ca_{10}(PO_4)_6F_2 + 10SO_2 + 5O_2 + H_2O =$$

$$3P_2O_5 + 10CaSO_4 + 2HF \qquad (22)$$
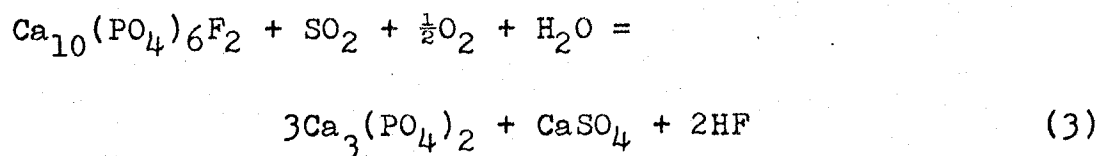
The results of the thermodynamic calculations are presented in Tables 3-5 and 3-6.

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 $327^{\circ}C$. Above this temperature level the results indicate non-spontaneous process occurring (i.e., positive $\triangle F$ and negative K values). Scheel[6], however, in his patent states that the elimination of fluorine begins at $500^{\circ}C$ and proceeds at a considerable rate at 600 to $700^{\circ}C$. 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 $850^{\circ}C$), the initially formed tricalcium phosphate was converted into calcium pyrophosphate. An alternative reaction then, could be as follows:

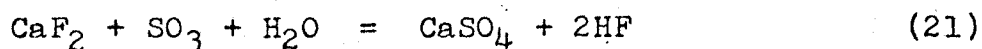$$CaF_2 + SO_3 + H_2O = CaSO_4 + 2HF \qquad (21)$$

TABLE 3-5

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $Ca_{10}(PO_4)_6F_2 + SO_2 + \frac{1}{2}O_2 + H_2O = 3Ca_3(PO_4)_2 + CaSO_4 + 2HF$				
Temperature		$\triangle H$ Kcals/mole	$\triangle F$ Kcals/mole	$Log_{10}K$
$^{\circ}K$	$^{\circ}C$			
298	25	-37.85	-27.99	20.53
300	27	-37.85	-27.89	20.32
400	127	-38.36	-22.34	12.21
500	227	-38.92	-15.58	6.81
600	327	-38.96	- 7.68	2.80
700	427	-38.24	+ 1.26	- .39
800	527	-36.84	+11.12	-3.04
900	627	-34.10	+21.79	-5.29
1000	727	-30.58	+33.24	-7.27

TABLE 3-6

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $Ca_{10}(PO_4)_6F_2 + 10SO_2 + 5O_2 + H_2O = 3P_2O_5 + 10CaSO_4 + 2HF$				
Temperature		$\triangle H$ Kcals/mole	$\triangle F$ Kcals/mole	$Log_{10}K$
$^{\circ}K$	$^{\circ}C$			
298	25	-589.1	-395.9	290.37
300	27	-589.0	-396.0	289.00
400	127	-588.6	-329.8	180.22
500	227	-586.6	-265.3	115.97
600	327	-582.2	-201.4	73.38
700	427	-575.1	-138.5	43.24
800	527	-565.1	- 76.8	20.97
900	627	-552.0	- 16.5	4.01
1000	727	-535.9	+ 42.3	-9.24

and

$$Ca_3(PO_4)_2 + SO_3 = Ca_2P_2O_7 + CaSO_4 \qquad (23)$$
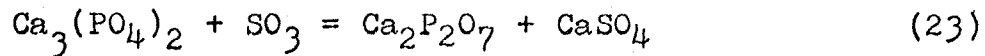
The previous discussion on the thermodynamic calculations for reaction (21) has shown that the reaction is feasible. Table 3-7 gives the thermodynamic calculations for reaction (23). The results are in favour of both reaction (21) and (23) occurring.

The reaction of equation (22) is also possible. Ross[8] 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 $SO_2 - O_2' - H_2O$ system should follow the equations of (21)and (23):

$$CaF_2 + SO_3 + H_2O = CaSO_4 + 2HF \qquad (21)$$

and

$$Ca_3(PO_4)_2 + SO_3 = Ca_2P_2O_7 + CaSO_4 \qquad (23)$$
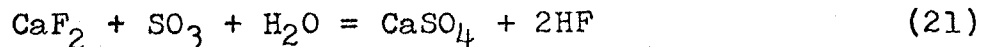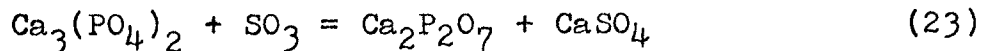
c. Mixtures of Phosphate Rock and Fluorspar

A third part of the investigation undertaken

TABLE 3-7

FREE ENERGY AND EQUILIBRIUM CONSTANT VALUES[8] FOR THE REACTION

$$Ca_3(PO_4)_2 + SO_3 = Ca_2P_2O_7 + CaSO_4$$
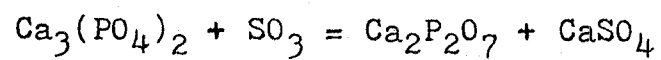
Temperature		$\triangle F$	$Log_{10}K$
°K	°C	Kcal/mole	
298	25	-100.0	73.35
300	27	- 99.0	72.12
400	127	- 94.5	51.64
500	227	- 88.1	38.51
600	327	- 78.8	28.71
700	427	- 68.5	21.39
800	527	- 56.0	15.30
900	627	- 40.5	9.84
1000	727	- 22.8	4.98

in this thesis was to see if enough moles of CaF_2 could
be added to $Ca_{10}(PO_4)_6F_2$ to add enough fluorine to liberate
POF_3 or PF_3 type products. The possible reactions are
as follows:

$$Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18H_2SO_4 =$$

$$18CaSO_4 + 6POF_3 + 18H_2O \qquad (24),$$

$$Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18SO_2 + 6O_2 =$$

$$6PF_3 + 18CaSO_4 \qquad (25),$$

$$Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18SO_2 + 9O_2 =$$

$$6POF_3 + 18CaSO_4 \qquad (26),$$

and

$$Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18SO_3 = 6POF_3 + 18CaSO_4 \qquad (27)$$
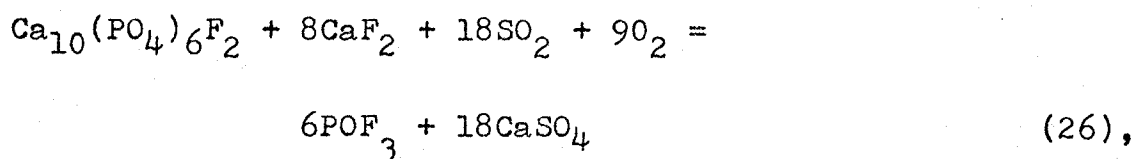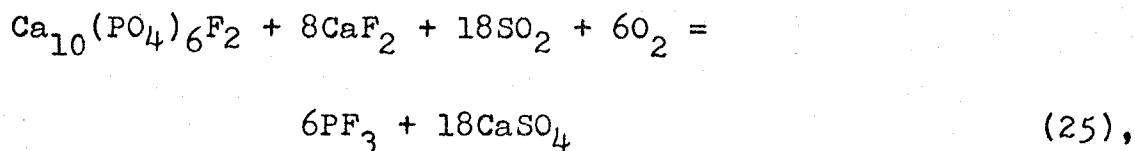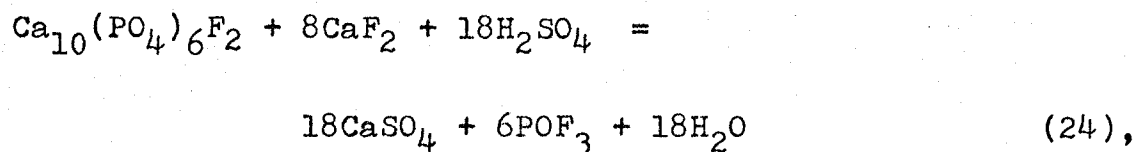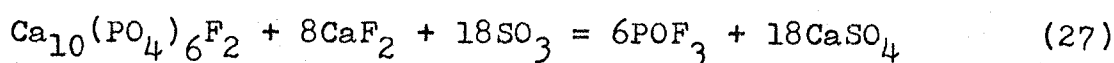
The thermodynamic results for these four reactions
are presented in Tables 3-8 to 3-11. The sulphuric acid
reaction (Table 3-8) is the most unfavourable one,
requiring very high energy requirements to overcome the
thermodynamic barrier present. Of the remaining three
reactions, equation (27) represents the most favourable
reaction in the thermodynamic approach. The reaction, however,
though favoured at low temperatures is not a spontaneous one
around $550^\circ C$.

We have already shown that Scheel[6] produced fluorine
from phosphate rock at temperatures greater than $500^\circ C$.
Ross[8] found no evidence of fluorine production in the temper-
ature range $325-350^\circ C$ but did obtain some conversion of
phosphate rock to P_2O_5. Tarbutton et al[9] were able to
react fluorspar with P_2O_5 according to the equation:

TABLE 3-8

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18H_2SO_4 = 18CaSO_4 + 6POF_3 + 18H_2O$				
Temperature		$\triangle H$ Kcal/mole	$\triangle F$ Kcal/mole	$Log_{10}K$
^oK	^oC			
298	25	126.00	194.54	-142.69
300	27	125.40	195.05	-142.10
400	127	97.14	222.57	-121.62
500	227	72.95	256.79	-112.26
600	327	52.52	295.39	-107.61
700	427	35.84	337.23	-105.30
800	527	22.88	381.17	-104.14
900	627	13.62	426.37	-103.54
1000	727	8.05	427.74	-103.33

TABLE 3-9

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18SO_2 + 6O_2 = 6PF_3 + 18CaSO_4$				
Temperature		$\triangle H$ Kcal/mole	$\triangle F$ Kcal/mole	$Log_{10}K$
^oK	^oC			
298	25	-653	-403.66	296
300	27	-654	-402.14	293
400	127	-655	-300.12	164
500	227	-656	-233.33	102
600	327	-653	-148.23	54
700	427	-649	- 64.05	20
800	527	-641	+ 18.30	- 5
900	627	-632	+ 98.82	-24
1000	727	-617	+183.00	-40

TABLE 3-10

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18SO_2 + 9O_2 = 6POF_3 + 18CaSO_4$				
Temperature		$\triangle H$	$\triangle F$	$Log_{10}K$
°K	°C	Kcal/mole	Kcal/mole	
298	25	-857.00	-570.50	418.46
300	27	-857.11	-568.31	414.07
400	127	-861.57	-970.96	257.36
500	227	-863.99	-373.19	163.14
600	327	-864.07	-275.03	100.19
700	427	-861.67	-177.03	55.28
800	527	-856.73	- 79.53	21.73
900	627	-849.02	+ 17.13	-19.03
1000	727	-839.09	+113.14	-24.73

TABLE 3-11

THERMODYNAMIC REACTION CALCULATIONS

Reaction: $Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18SO_3 = 6POF_3 + 18CaSO_4$				
Temperature		$\triangle H$	$\triangle F$	$Log_{10}K$
°K	°C	Kcal/mole	Kcal/mole	
298	25	-434.00	-269.00	+197.00
300	27	-434.08	-268.03	+195.29
400	127	-437.97	-212.11	115.91
500	227	-441.32	-155.24	67.87
600	327	-443.39	- 97.86	35.65
700	427	-443.84	- 40.20	12.55
800	527	-442.52	+ 17.36	- 4.74
900	627	-439.33	+ 74.61	-18.12
1000	727	-434.22	+131.53	-28.75

$$3CaF_2 + 4P_2O_5 = 2POF_3 + 3Ca(PO_3)_2 \qquad (9)$$
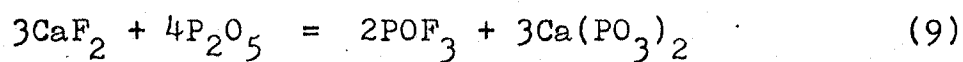
The temperature range at which their reactions were carried out was from 500 to $1000^{\circ}C$.

Considering an SO_3 reacting system, a possible alternative for the over-all reaction,

$$Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18SO_3 = 6POF_3 + 18CaSO_4 \qquad (27),$$

is as follows:

$$3Ca_3(PO_4)_2 + 9SO_3 = 3P_2O_5 + 9CaSO_4 \qquad (28),$$

and

$$3CaF_2 + 4P_2O_5 = 2POF_3 + 3Ca(PO_3)_2 \qquad (9).$$
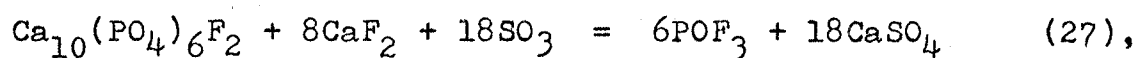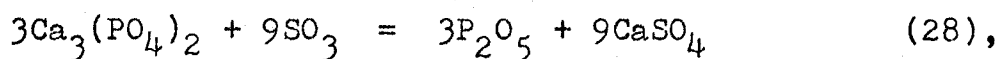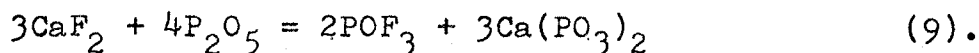
Reaction (28) using the method of Ross[8] would be carried out around $325-350^{\circ}C$ while reaction (9) would have to be carried out at $500-700^{\circ}C$.

IV EXPERIMENTAL PROCEDURE

The defluorination of fluorspar by the reaction of CaF_2 with SO_2 - O_2 - H_2O 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 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
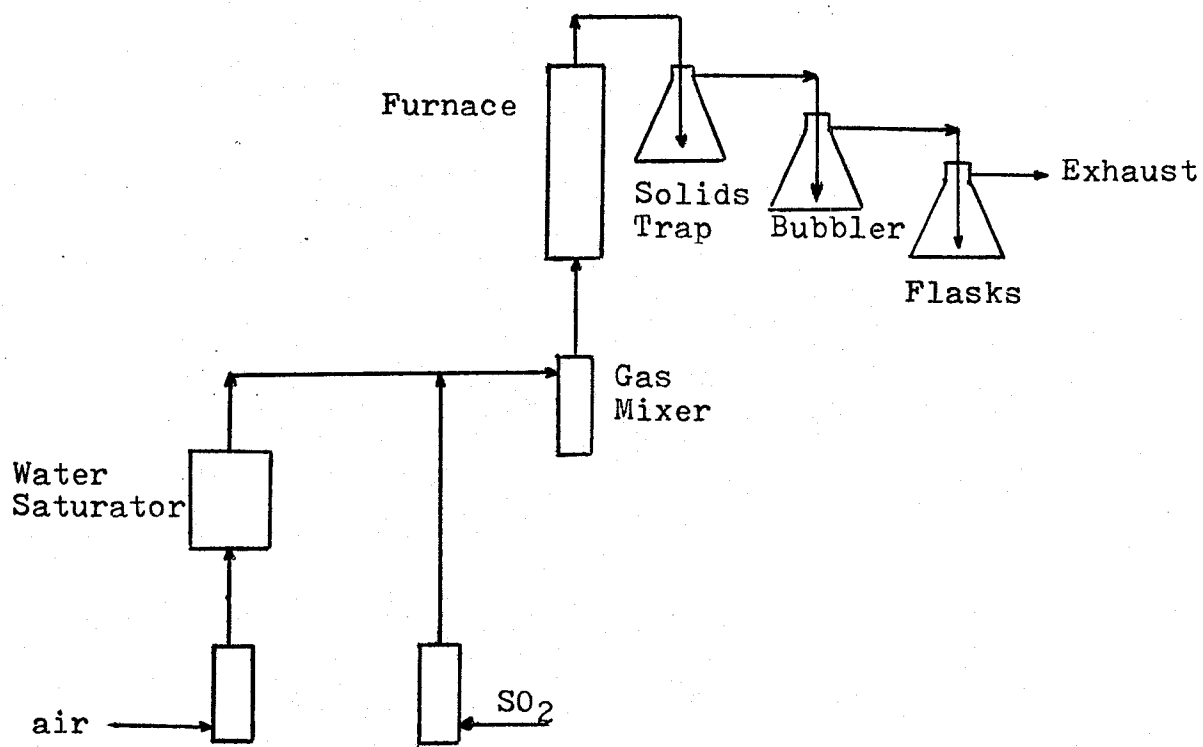
Figure 4-1. Reaction System Flow Sheet

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 CaF_2 was used with some runs also having 4% by weight ferric sulphate pre-mixed with the CaF_2. 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 CaF_2 being defluorinated.

B. Fixed-Bed Experiments

Experimental runs at temperatures of 615, 630 and 650°C were attempted using 10 gram samples of CaF_2. 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 CaF_2 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 $FeSO_4$ was pre-mixed with 10 grams of CaF_2. An air flow rate of 700 ml./min. and an $SO_2:H_2O$ 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 Na_2CO_3 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 $650^{\circ}C$ in which no catalyst was used, the etching was only slight compared to the run at $615^{\circ}C$ in which a catalyst was employed.
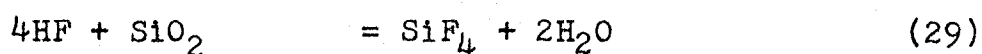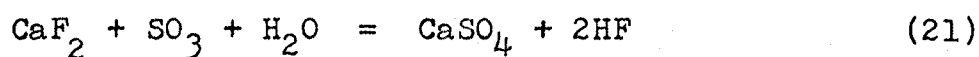
VI. CONCLUSIONS

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, ΔF 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 $500^\circ C$.

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 SO_2 is converted to SO_3. Tables 3-1 and 3-4 showed that on the basis of the thermodynamics both reactants were favourable.

The conclusion that CaF_2 was defluorinated is based on the etching of the glass reactor tube. The mechanism for this reaction would be as follows:
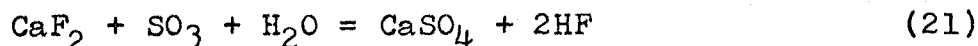
$$CaF_2 + SO_3 + H_2O = CaSO_4 + 2HF \qquad (21)$$

$$4HF + SiO_2 = SiF_4 + 2H_2O \qquad (29)$$

and in water,
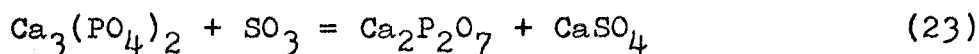
$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6 \qquad (30)$$

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 CaF_2. The upper limit of conversion could be controlled, however, by the formation of $CaSO_4$ 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 SO_2 instead of 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 $500^{\circ}C$) proceed by the mechanism:

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 \tag{20}$$

$$CaF_2 + SO_3 + H_2O = CaSO_4 + 2HF \tag{21}$$

and

$$Ca_3(PO_4)_2 + SO_3 = Ca_2P_2O_7 + CaSO_4 \tag{23}$$

At temperatures below $500^{\circ}C$ there was no evidence of CaF_2 reacting with SO_2 or SO_3. Ross[8], however, did show that $Ca_3(PO_4)_2$ will react with SO_2 or SO_3 below $500^{\circ}C$ to produce P_2O_5. A possible reaction could be:

$$Ca_3(PO_4)_2 + 3SO_3 = P_2O_5 + 3CaSO4 \tag{28}.$$
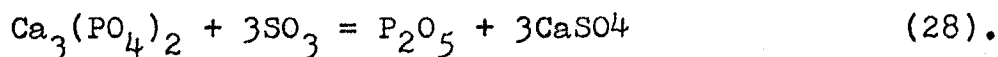
It has already been shown that P_2O_5 reacts with CaF_2 at temperatures greater than $500^{\circ}C$ according to the reaction:

$$3CaF_2 + 4P_2O_5 = 2POF_3 + 3Ca(PO_3)_2.$$
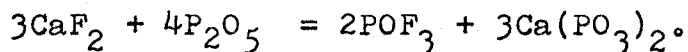
The formation of oxyfluorides is, therefore, possible, The problems of carrying out such a reaction scheme, however, would be many.

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 $600^\circ C$ 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 SO_2 - O_2 - H_2O 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 an 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 SO_2 to SO_3 should also be investigated.

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NOMENCLATURE

Symbol	Definition	Units
ΔH_F^O	Heat of Formation at 298°K	Kcals/Mole
ΔH_T	Heat of Reaction at Temperature T	Kcals/Mole
ΔC_{p_T}	Heat Capacity Equation at Temperature T (°K)	Cals/Deg-Mole
$Log_{10} K_T$	Equilibrium Constant at Temperature T (°K)	
ΔF_T	Free Energy Change at Temperature T (°K)	Kcals/Mole
ΔS^O	Entropy change at 298°K	Cals/Mole

APPENDIX I

THERMODYNAMIC CALCULATION DATA

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THERMODYNAMIC CALCULATION DATA

Compound	Chemical Formula	ΔH_f^o Kcals/Mole	ΔS^o Cal/Deg-Mole	$Cp = a + b \times 10^{-3}$ $+ C \times 10^5 T^{-2}$			Reference
				a	$b.10^3$	$C.10^{-5}$	
Fluorapatite	$Ca_{10}(PO_4)_6F_2$	-3267	185.50	226.04	28.88	-48.82	H 21 S_2Cp22
Calcium Fluoride	CaF_2	- 292	16.45	14.3	7.28	+00.47	23
Sulphur Dioxide	SO_2	-70.95	59.25	10.38	2.54	- 1.42	23
Oxygen	O_2	-	49.00	7.16	1.00	- 0.40	19
Water	H_2O	-57.8	45.10	7.17	2.56	+ 0.08	23
Calcium Sulphate	$CaSO_4$	-342.	25.5	18.52	21.97	- 1.568	23
Hydrogen Fluoride	HF	- 64.8	41.5	6.43	0.82	+ .26	23
Sulphur Trioxide	SO_3	- 94.4	61.2	13.7	6.42	- 3.12	23
Sodium Chloride	NaCl	- 98.6	17.4	10.98	3.90	-	23
Hydrogen Chloride	HCl	- 22.0	44.65	6.34	1.10	+ 0.26	23
Sodium Sulphate	Na_2SO_4	-333.5	35.73	29.06	19.34	-	23
Calcium Phosphate	$Ca_3(PO_4)_2$	-986.2	57.6	48.24	39.64	- 5.0	19
Phosphorus Trifluoride	PF_3	-226	64.12	17.56	1.97	- 4.57	23

VITA AUCTORIS

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