

REACTIONS OF SULFUR OXIDES
WITH PHOSPHATE ROCK

A THESIS

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by
Laurence William Ross

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Chairman 

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ABSTRACT

This investigation was undertaken in order to explore the possible advantages of contacting phosphate rock with sulfur trioxide or sulfur dioxide. The considerations which directly inspired the investigation include the following:

1. Present-day processes of rendering phosphates into useful form have notable disadvantages. For example, the triple superphosphate process is thermally inefficient, and has serious problems with corrosion and fumes.

2. Equilibrium calculations have shown that the direct production of gaseous P_4O_{10} from phosphate rock by means of sulfur oxide contact is thermodynamically feasible in good yield by several postulated reaction mechanisms.

3. The heat of reaction of such a direct P_4O_{10} process is exothermic at all temperatures for which data are available.

4. A literature survey of sulfur oxide processes has revealed that reaction with phosphate rock has been achieved to a high degree of P_2O_5 conversion (although the processes reported are very slow).

5. One literature reference points to production of free P_4O_{10} by contact of phosphates with liquid sulfur trioxide. Exploratory laboratory experiments with liquid sulfur trioxide and phosphate rock produced a visible quantity of white sublimed P_4O_{10} powder.

6. The use of a fluidized bed for the proposed process might make possible greatly increased rates, together with the advantages of control inherent to fluidized-bed operation.

In this investigation, stationary contact was performed with liquid and gaseous sulfur trioxide, and gaseous sulfur dioxide, for varying periods of time at various temperatures from 200° C to 500° C. Fluidized contact was performed with sulfur dioxide and sulfur trioxide (alone and with infusion of steam and air) for periods of time up to 30 minutes, mainly at temperatures around 325° C. Analytical methods conformed to the official methods of the Association of Official Agricultural Chemists and to conventional methods of wet analytical chemistry. X-ray diffraction was applied to a sample of the unreacted phosphate rock and to a sample of product from the fluidized reaction.

The results of the investigation indicate that the phosphorus in phosphate rock can be converted quantitatively to phosphorus pentoxide by contact of phosphate rock with liquid sulfur trioxide, but the phosphorus pentoxide is mainly in a highly polymeric form and only a small quantity of gaseous P_4O_{10} can be freed. The amount of gaseous P_4O_{10} seems limited by the nature of the phosphate rock, possibly its moisture content. Liquid sulfur trioxide is apparently capable of liberating all P_2O_5 in phosphate rock from association with Ca, forming $CaSO_4$, but the remaining Ca in the sample is not reacted. Gaseous contact is less effective, and in the fluidized bed the reaction proceeds to about two-thirds completion, and yields about 55 per cent of the P_2O_5 in an "available" form by AOAC definitions. Regrinding and recontacting of the product leads to increased conversion. The most effective gas mixture was a combination of SO_3 , air, and steam, with only a small amount of steam required to enhance the conversion significantly. Conversion is unaffected over a wide range of compositions. The conversion is very rapid, taking place completely

within five minutes. In absence of water in the fluidizing gas, conversion approaches an upper limit which is less than the conversion possible with mixed gas. Sulfur dioxide does not react with phosphate rock at significant rate under any of the conditions studied.

A series of extractant solutions was tested for effectiveness with exhaustively reacted (with liquid SO_3) and fluidized-contact samples. With both types of product, acid extractant solutions were most effective. The exhaustively reacted product, featuring highly polymerized P_2O_5 and polyphosphates, is capable of hydrolysis by very dilute acid solutions. The standard product of fluidized contact can be extracted by slightly acid solutions of salt (e.g., potassium sulfate) to about the extent of P_2O_5 conversion. Strong sulfuric acid solutions also extract about two-thirds of the P_2O_5 from this product.

The product of fluidized-bed reaction seems of potential industrial interest because of the rapid rate of conversion obtained, the moderate temperatures involved, the possibility of using dilute sulfur trioxide gas mixtures, and the utility of the fluidized bed for conducting the process. However, conversion of P_2O_5 in this process is still too low for industrial practicality, and either conversion must be raised or a suitable extractant found for the P_2O_5 values of this product. In addition, the product is possibly of more interest to overseas producers, in view of the declining demand for low-analysis phosphate products in this country.

CHAPTER I

INTRODUCTION

A. Current State of Phosphate Technology

1. Importance of Phosphates

Nitrogen, phosphorus and potassium are the elements most important to plant nutrition, and thus to the agriculture of the world. As new nations and awakening peoples struggle to enter the modern era, their first concern is to feed their multitudes. This will very likely mean a great surge in production of plant food materials and therefore inspire increasing study of methods whereby these materials can be produced most efficiently from locally available raw materials.

The present investigation is a study of a particular process for converting mineral phosphates into a form assimilable by plants. The investigation, because it embodies new ideas not previously known to have been studied, is heavily exploratory. For the same reason, the investigation is fundamental, and is perhaps not directly translatable into a process on the industrial scale.

It is hoped that the knowledge accumulated in this study may form a significant contribution to basic understanding of phosphate conversion into fertilizer.

2. Natural Phosphates

Mineral phosphates occur at major deposits at a number of locations in the world and are generally termed phosphate rock or phosphorites. McKelvey et al¹ have summarized the nature of this material:

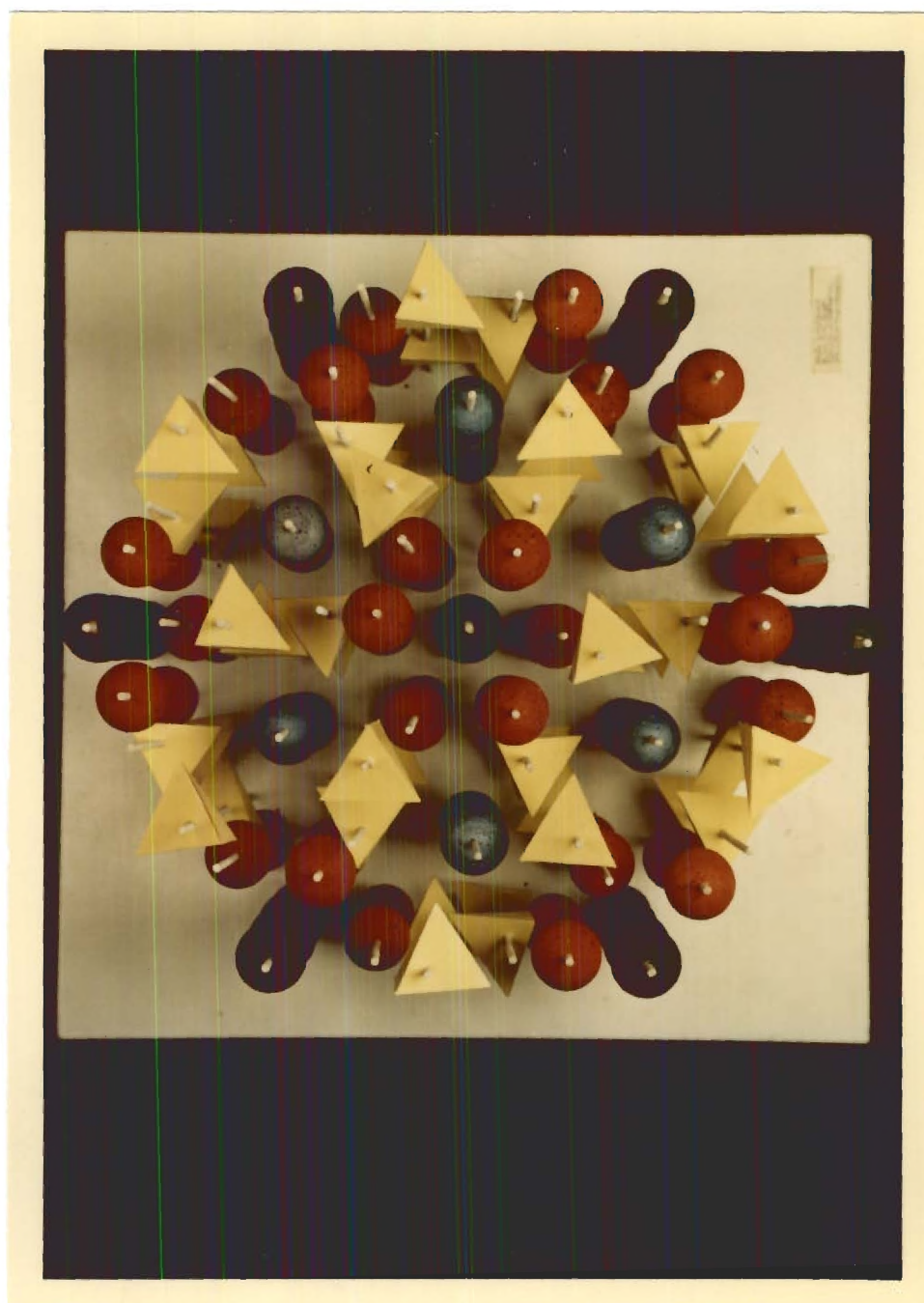
Phosphorus makes up about 0.2 per cent of the earth's crust--it is the eleventh most abundant element. It forms complex compounds with a wide variety of metals--more than 150 minerals are known that contain 1 per cent or more P_2O_5 . Most of the phosphorus in the earth's crust, however, is found in one mineral family, the apatite group, $Ca_{10}(PO_4, CO_3)_6 (F, Cl, OH)_2$. Because of its essential content of an anionic radical, the PO_4 tetrahedron, as well as of a simple anion, usually fluorine, and a simple cation, usually calcium, apatite serves as a host for a great many minor substitutions.

The apatite crystal structure has received detailed study in recent years; the crystallography laboratory of the Georgia Institute of Technology, directed by Dr. R. A. Young, has been active in this field, in both X-ray and neutron diffraction studies.^{2,3} Figure 1 is a photograph of the three-dimensional lattice structure of fluorapatite, which has been constructed by Dr. Young's group.

This model reveals several features worthy of mention with respect to the present study. The unit cell is considered to be the volume bounded by a parallelogram with F at the apices, containing on the average six $(PO_4)^{3-}$ tetrahedra, ten Ca^{2+} ions, and two F^- : $Ca_{10}(PO_4)_6F_2$. The unit cell has dimensions $a = b = 9.364 \text{ \AA}$.⁴ From the photograph it is evident that the force field of a fluorine ion is largely occupied by calcium ions. The $(PO_4)^{3-}$ ions are therefore somewhat independent of the fluorine ions, and influenced principally by calcium ions and neighboring $(PO_4)^{3-}$ ions.

Phosphate rock preserves the basic structure of fluorapatite, with a significant quantity of lattice inclusions and several per cent of other materials. Crystal size ranges from 0.02 to 1 micron.⁵ A typical Florida phosphate rock will have the following ranges of constituent materials⁶ (see also Table 1* for the phosphate rock used in the present

*All tables are found in Appendix A.



Red -- Calcium ions
Blue -- Calcium ions

Green -- Fluorine ions
Yellow -- PO_4 tetrahedra

Figure 1. Crystal Structure of Fluorapatite.
(Courtesy of Dr. R. A. Young.)

investigation) in weight per cent:

| | |
|--------------------------------|----------|
| CaO | 46-50 |
| P ₂ O ₅ | 30-36 |
| CO ₂ | 1.5-4.4 |
| F | 3.3-4 |
| Fe ₂ O ₃ | 0.7-2.6 |
| Al ₂ O ₃ | 0.7-1.1 |
| SiO ₂ | 7.3-9.8 |
| MgO | 0.04-0.5 |
| SO ₃ | 0.3-1.5 |
| H ₂ O | 7.3-2.6 |

Phosphate rock has been termed "carbonated fluorapatite."⁷ Indeed, phosphate rock is conjectured to owe its reactivity principally to its carbonate content, which is sufficient to generate foam on contact with sulfuric or phosphoric acid.

Although the apatite structure is capable of many substitutions, the manner in which this carbonate is incorporated in phosphate rock is unknown. Van Wazer⁸ discusses this problem at length. In brief, not only is there a problem of charge balance when a (CO₃)²⁻ ion replaces a (PO₄)³⁻ or F⁻ ion in the apatite lattice, but X-ray diffraction investigations have refuted the concept of lattice incorporation of (CO₃)²⁻. Calcium carbonate likewise cannot be detected as a separate phase. At present, the most tenable hypothesis is that carbonate ions are adsorbed on the surface of the crystallites.

The carbonate problem is presently a very active subject of investigation. Most recently, Elliott⁹ has employed polarized infrared spectroscopy in the study of the problem.

3. Phosphate Compounds Derivable from Fluorapatite

Calcium Phosphates. Phosphate rock is usable for direct fertilizer application only with very acid soils. Its water-soluble phosphate content is extremely low, and solubility in extractants that simulate the decomposition which takes place in soil is likewise below ten per cent of the total phosphate present. The crystal structure of the phosphate rock, even when ground to -100 mesh, is responsible for this inertness. It is believed that fluorine is the principal link that contributes stability to the crystal structure.

Treatment of phosphate rock with sulfuric acid destroys the crystal structure and gives rise principally to monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, and smaller quantities of dicalcium phosphate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, plus other calcium phosphates to the extent of about one per cent of the total.¹⁰ The overall product of the reaction is the familiar "superphosphate" (see section B below).

Although none of the other calcium phosphates rivals monocalcium phosphate in water solubility, all the lower members of the $n\text{CaO} \cdot \text{P}_2\text{O}_5$ series have fertilizer value, at least theoretically. For example, calcium metaphosphate $\text{Ca}(\text{PO}_3)_2 = \text{CaO} \cdot \text{P}_2\text{O}_5$, is a very efficient plant food for certain applications and is higher in phosphorus percentage than superphosphate. Calcium acid phosphates analogous to monocalcium and dicalcium phosphates also exist for the higher members of the series, and the various phosphoric acids themselves (see below) also appear in fertilizers.

Even with water solubility essentially nil, some of these materials show crop effectiveness rivalling monocalcium phosphate. All of them are essentially completely soluble in neutral ammonium citrate (see Chapter

III). This has led investigators to equate water solubility in fertilizers with presence of monocalcium phosphate, and citrate solubility with the useful portion of the remainder, to which dicalcium phosphate is considered the largest contributor.

It is interesting, in anticipation of the investigation described below (Chapters IV, V, VI), to note that monocalcium phosphate decomposes completely by 320° C to acid pyrophosphate of variable composition.⁶ In fact, the decomposition begins at least by 200° C,¹¹ and perhaps by 150° C.¹² Beginning at about 225° C, calcium metaphosphate appears, and persists to about 400° C.¹³ As temperature is raised above 320° C or thereabouts, increasingly long-chained polyphosphates arise as water is lost, and these are increasingly less water-soluble as temperature is increased.

Phosphoric Acid and Polyphosphates. The mysteries of the phosphoric acids are now largely solved, as summarized by Van Wazer et al.¹⁴:

Until the last few years, misunderstanding as to the nature of the various condensed phosphates and their acids was nearly universal. Most analytical papers, even including some of today's publications, follow the obsolete notation of Thomas Graham, in which all phosphates are considered to be either ortho- (H_3PO_4) , pyro- $(H_4P_2O_7)$, or meta- (HPO_3) phosphates. It is now unequivocally known that the materials that Thomas Graham classified in 1833 as metaphosphates or mixtures of meta- and pyrophosphates consist of three general types of condensed phosphates: a series of chain phosphates, which are called polyphosphates (general formula of the acids: $H_{n+2}P_nO_{3n+1}$) the ring phosphates for which the term metaphosphate should still be used (general formula of the acids: $H_m(PO_3)_m$) and highly branched structures called ultraphosphates. . . .

It should be noted that as n becomes very large, the polyphosphate formula approaches the empirical composition of the metaphosphate formula, and thus the long-chain phosphates were formerly erroneously classified as "metaphosphates." For n equalling 1, 2, 3, and 4, the polyphosphate formula gives, respectively, the orthophosphate (H_3PO_4), the pyrophosphate

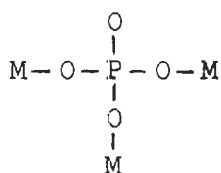
($\text{H}_4\text{P}_2\text{O}_7$), the triphosphate--often called tripolyphosphate--($\text{H}_5\text{P}_3\text{O}_{10}$), and the tetraphosphate ($\text{H}_6\text{P}_4\text{O}_{13}$). Thus the orthophosphate is the monomer of the polyphosphate series, and the pyrophosphate is the dimer of the series, or the first truly chain phosphate.

Some of the structures which these polymeric forms assume are shown in Figure 2.^{15,16}

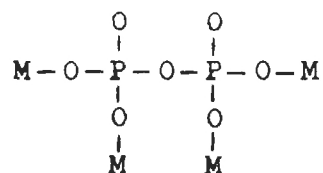
Orthophosphoric acid, H_3PO_4 , is never found in pure monomeric form. In laboratory solutions, commonly 85 per cent H_3PO_4 , the orthophosphate that will precipitate directly with ammonium molybdate is only about 8 per cent, according to tests performed by this author. Higher Phosphoric acids, so-called "superphosphoric" acids, which are finding increasing use in the fertilizer industry, may thus be expected to consist almost entirely of mixed phosphoric acid polymers whose molecular weight increases with the percentage of P_2O_5 . It is not surprising to discover that a point is reached where the polymer is insoluble in water, and ultimately even in strong acid or alkali solution.

In the present investigation, high polymers of phosphoric acid, some of them insoluble even in hot caustic solution, have been produced by dehydration of phosphoric acid. The implications of these polymers for the process developed in the investigation are discussed in Chapter V.

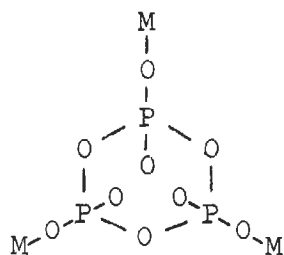
Phosphorus Pentoxide. Complete dehydration of phosphoric acids logically would lead to formation of phosphorus oxide, with the empirical formula P_2O_5 . Several forms of this oxide are known. The simplest form is the dimer, P_4O_{10} , characteristic of the vapor state and also of the solid hexagonal crystalline form (H-form):^{17,18}



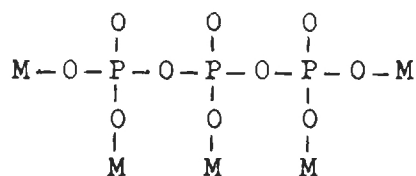
Orthophosphate



Pyrophosphate

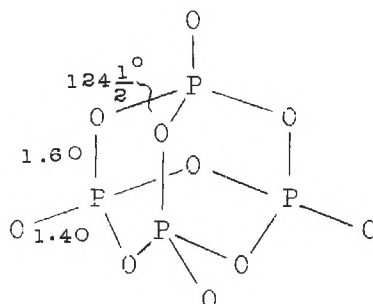


Trimetaphosphate



Tripolyphosphate

Figure 2. Structures of Lower Polyphosphates.
 (Van Wazer, J. R., Phosphorus and Its Compounds.
 Vol. I. New York: Interscience Publishers (1958),
 pp. 423-31; Morin, C., Bull. Soc. Chim. France
1961, 1718.)

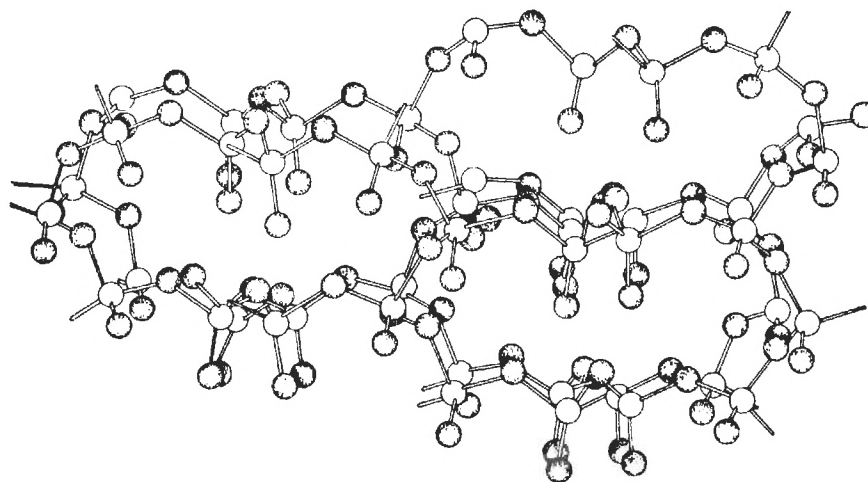


There are two other well-characterized infinite-sheet solid forms, both orthorhombic, illustrated in Figure 3. The so-called O-form at the top is metastable, while the O'-form at the bottom is stable and can be formed from the H-form by heating 24 hours at 450° C.

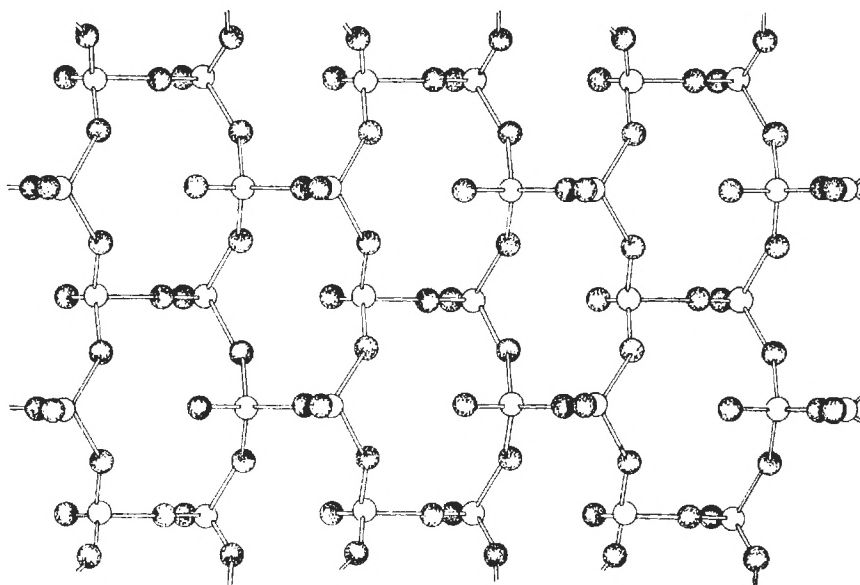
In addition to these forms, there are at least two other solid forms which are not as well defined: a powdery amorphous form usually admixed with some H-form, and a glassy or vitreous form. There are also two liquid forms.¹⁷

The H-form of the solid sublimates at about 360° C at one atmosphere; the orthorhombic forms melt near 600° C and the resulting liquid boils at about 610° C and one atmosphere.¹⁹

"Available" $P_{25}O_5$. Water solubility is not the sole criterion of a phosphate's ability to be absorbed by crops. It has long been recognized that many compounds of poor or even zero water solubility are excellent sources of fertilizer phosphate. Searching for a test that would correlate well with the actual degree of effectiveness, investigators came upon the citrates and adopted citric acid and ammonium citrate solutions as extractants believed to exert an action comparable to decomposition mechanisms found in soils. Citric acid (2%) is used to test basic phosphate slags; neutral ammonium citrate is the standard in the United States and a few other countries; and alkaline ammonium citrate (Petermann reagent) is the most widely used in Europe. The total



The O-form



The O'-form

Figure 3. Infinite Sheet Structure of Polymeric P_2O_5 .
(Van Wazer, J. R., Phosphorus and Its Compounds. Vol. I.
New York: Interscience Publishers (1958) p. 271. By
permission.)

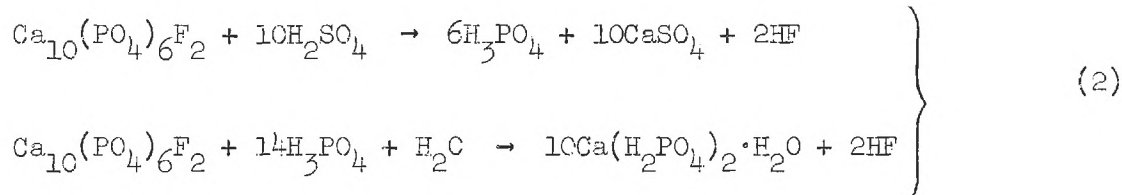
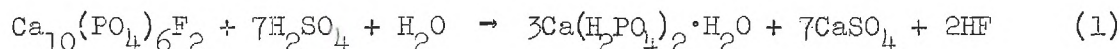
extractable P_2O_5 content of a fertilizer extracted by water and citrate, in succession, is termed "available phosphoric acid" or "available P_2O_5 ."

However, as Brabson and Burch²⁰ have pointed out, "Neutral ammonium citrate is so powerful an extractant that it dissolves most phosphates that occur in fertilizers, including precipitated apatites, regardless of their agronomic effectiveness." It has finally become clear that the alkaline citrate method provides much better discrimination between effective and ineffective sources of phosphate.^{21,22} Brabson and Burch have recently attempted to standardize the procedure.²³

B. Processes for Producing Phosphate Fertilizers

1. Normal Superphosphate

Normal superphosphate is the common designation of the product of the reaction in which sulfuric acid is reacted with ground phosphate rock. The reaction is thought to consist of about 70 per cent conversion of rock by sulfuric acid, and 30 per cent conversion of rock by phosphoric acid, as follows:²⁴



The assignment of the fluorapatite formula to phosphate rock is representative only of the majority constituent. Likewise HF is probably not found among the products, but reacts with the silicates present. The

resulting mixture contains 16 to 21 per cent P_2O_5 ,* about 80 per cent of it water soluble, 15 per cent citrate soluble, and 5 per cent insoluble. Sauchelli⁶ and Hatfield²⁴ have published extensive reviews of the process.

2. Triple Superphosphate

Triple superphosphate is the product of the reaction between phosphate rock and phosphoric acid, yielding monocalcium phosphate according to equation (2) above. Triple superphosphate contains 43 to 48 per cent P_2O_5 , with solubility distribution about the same as in normal superphosphate. Phosphoric acid for this process is largely provided by the "wet process" in which phosphate rock is reacted with 70 per cent sulfuric acid. Minor quantities of phosphoric acid are provided from the "furnace process" (see below).

In recent years triple superphosphate has steadily supplanted normal superphosphate for fertilizer use, and at present triple superphosphate is the largest source of fertilizer phosphate. Hatfield²⁵ has published the most recent review of the process.

3. Miscellaneous Phosphate Fertilizers

Monocalcium phosphate dominates the phosphate fertilizer use pattern by reason of its high water solubility. Other phosphates accordingly find more limited application.

Phosphoric acid has the highest P_2O_5 percentage of any stable compound (72.4% for H_3PO_4) and, especially in view of the resounding success of direct ammonia application, has been considered for primary fertilizer

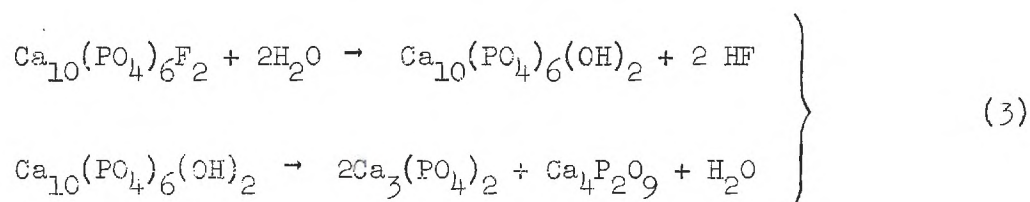
*The fertilizer industry commonly measures phosphorus content as P_2O_5 , even though phosphorus occurs mostly as $(PO_4)^{3-}$ in compounds, and as P_4O_{10} in free oxide form.

usage. The results have been disappointing, apparently because of excessive leaching.

Calcium metaphosphate is also appreciably higher in P_2O_5 (63.6 per cent) than triple superphosphate, but its high cost has held it back from universal acceptance. Although no longer produced commercially, calcium metaphosphate at one time captured a minor percentage of the market for high-analysis blending in fertilizers intended for acid soils. Calcium metaphosphate is produced by contacting phosphate rock with phosphorus oxide from burning of pure phosphorus, in a fixed bed.

Ammonium phosphates seem destined for increasing usage as the trend toward enriched fertilizers develops further. Diammonium phosphate already accounts for about one-third of all fertilizer P_2O_5 , and has a bright future because of its high nutrient content, ease of handling and ready solubility.

In the context of this investigation, the hydrothermal processes for producing phosphates should be considered, although the phosphates so produced are of very minor interest as fertilizers. In all hydrothermal processes the fundamental object is removal of fluorine.²⁶ However, not until the fluorine is about two-thirds removed is there an appreciable increase in citrate solubility of the phosphate.⁶ Water vapor is required, as well as an infusion of silica. The reaction apparently takes place in two steps:



Silica is required as a flux and also contributes to HF removal by formation of SiF_4 or fluorosilicates. There are numerous variations of this process in the literature, but all agree that 1400°C is about the minimum practical temperature.

Addition of alkali compounds has been used to produce fertilizers by high-temperature processes. Rhenania phosphate is the product of phosphate rock, soda ash, and silica at 1100°C ; another process uses sodium sulfate and carbon with the rock at 1330°C .²⁶ These processes are economically competitive with superphosphate only under specially advantageous conditions, and so are of minor interest.

The "electric furnace process" should be mentioned under the subject of high-temperature processes for producing phosphates. This process produces elemental phosphorus, which is burned to phosphorus oxide and absorbed in water to form phosphoric acid. The charge is a low-grade phosphate rock, which is made the conducting medium between electrodes and is smelted at about 1400°C in the presence of carbon (coke) as reducing agent. The phosphoric acid from this process is very pure "furnace grade" acid, and because of its high cost finds use in superphosphate fertilizers only when the market for other uses is saturated. However, it should be pointed out that liquid fertilizers require furnace acid and constitute a growing market for it.

C. Proposed Process

1. Concept

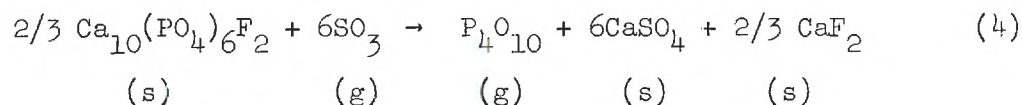
The ideal phosphate fertilizer is one that contains the maximum of water-soluble P_2O_5 . At present, triple superphosphate is the standard source of P_2O_5 against which other processes must be compared. However,

the process for manufacturing triple superphosphate is greatly complicated by the role played by water.

Water enters the process stream at two points: (1) in the contact sulfuric acid plant as absorbent for sulfur trioxide; and (2) in the wash water supplied to the calcium sulfate filters downstream of the reactor train. This water must subsequently be removed at two points in the process, namely, in the evaporators that concentrate the phosphoric acid and in the triple superphosphate dryers.

The water also introduces severe corrosion problems when it is used to dilute sulfuric acid for reaction, since the dilute acid is much more corrosive than the concentrated. A fume problem is caused by this dilution step, since air is blown through the hot liquid in order to provide cooling and agitation. The resulting mist is very difficult to filter and is a corrosion and pollution hazard due to its content of mineral acids and fluorine compounds.

What is the result if the superphosphate processes are conducted with the water removed? The reactants then become phosphate rock and sulfur trioxide. Among the several possible reaction mechanisms (see Section 3 below), the most attractive is direct production of phosphorus oxide:



If conditions could be found for which this reaction is realized in reasonable yield, the advantages would be immense. From the structural viewpoint, it must be admitted, there is little reason to suppose that

the apatite lattice can be broken down in this fashion. However, as will be discussed below, the literature contains one report of phosphate decomposition by sulfur trioxide to yield phosphorus oxide, and preliminary laboratory results have been encouraging. Perhaps a wide range of experimental conditions would reveal a range of feasible operation for the process.

Even if free phosphorus oxide cannot be produced, it may be possible to produce other phosphate compounds of fertilizer value. Consideration of the structure of fluorapatite indicates that calcium pyrophosphate, the next lowest member of the Ca-P-O family to the tricalcium phosphate configuration, is the most likely initial product. Subsequent products would logically consist of calcium associated with increasingly long chains of PO_4 tetrahedra, each of which shares one oxygen with the tetrahedron on one side, and another oxygen with the tetrahedron on the other side.

The omission of water removes the liquid phase, and the reaction now becomes a gas-solid contact process, which is theoretically capable of being conducted in a fluidized bed. The advantages of fluidized-bed operation for close control of temperature and simplicity of operation are well known. Without a liquid phase, it is also possible that the severe corrosion problems of present-day phosphate plants could be eliminated, and inexpensive materials of construction used.

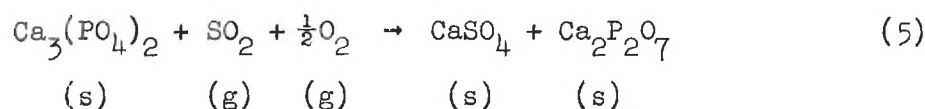
The concept contains so many advantageous possibilities that it has seemed worthwhile to undertake the investigation.

2. Literature Review

The concept presented above is an old one. As soon as the

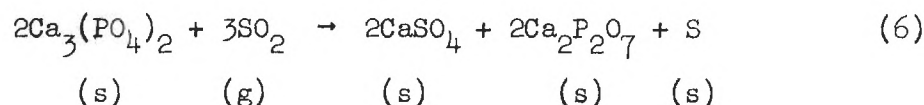
superphosphate process was proven, investigators began to explore use of sulfur oxides.

The earliest reported successful (not to say economic) process is that of Giana,²⁷ who contacted phosphorite with SO_2 and oxygen at 800°C , obtaining calcium sulfate and pyrophosphate:



The fate of the fluoride (or other apatitic constituents combined with phosphate) is not known.

In 1930 Briner and Monnier²⁸ reported a study in which pure calcium phosphate was converted to pyrophosphate as follows:



The optimum temperature was about 350°C .

In 1931 Hughes and Cameron²⁹ published an extensive investigation. Their results with phosphate rock may be summarized as follows:

(1) Phosphate rock can be converted to an available (citrate soluble) form to a maximum extent of about 90 per cent at temperatures around 500° or 600°C by five hours of contact with SO_3 . Water solubility of the product is low.

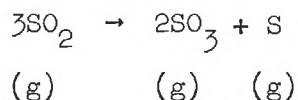
(2) Phosphate rock can be converted by SO_2 in a water-soluble form to a maximum extent of about two-thirds, at temperatures of 350° to 450°C depending on the pressure and the quantity of admixed H_2O or air. Contact times of about ten hours are required for conversion of about two-thirds of the P_2O_5 to water-soluble form.

(3) Regrinding and retreating the reacted rock results in increased conversion.

The results of this study are summarized in Figure 4, dealing with sulfur trioxide contact, and Figures 5 through 7 which concern sulfur dioxide alone and with various admixtures of air and water vapor. The most interesting feature of these curves is the tendency to increased conversions in the neighborhood of 400° C, shown most dramatically in the case of sulfur trioxide (Figure 4).

The distinct maximum revealed by Figure 4 suggests the onset of a new mechanism at about 400° C, followed by appearance of a competing mechanism which lowers the conversion from about 550° C onward. It is possible to guess that this second mechanism either involves the formation of higher polyphosphates, or else reflects the decomposition of SO_3 to SO_2 and O_2 . The initial rise in conversion, however, is harder to explain and is probably more complex, since there is no record of what compounds may be formed by the gas-solid reaction. It should be noted that Hughes and Cameron obtained sulfur trioxide from boiling pure sulfuric acid, and therefore the vapor mixture was certainly about half water (molar basis).

The sulfur dioxide experiments reported in the Hughes-Cameron study actually owe their conversion to sulfur trioxide, as the investigators themselves point out. Their evidence is formation of considerable sulfur and sulfides, pointing to decomposition of SO_2 according to the familiar mechanism



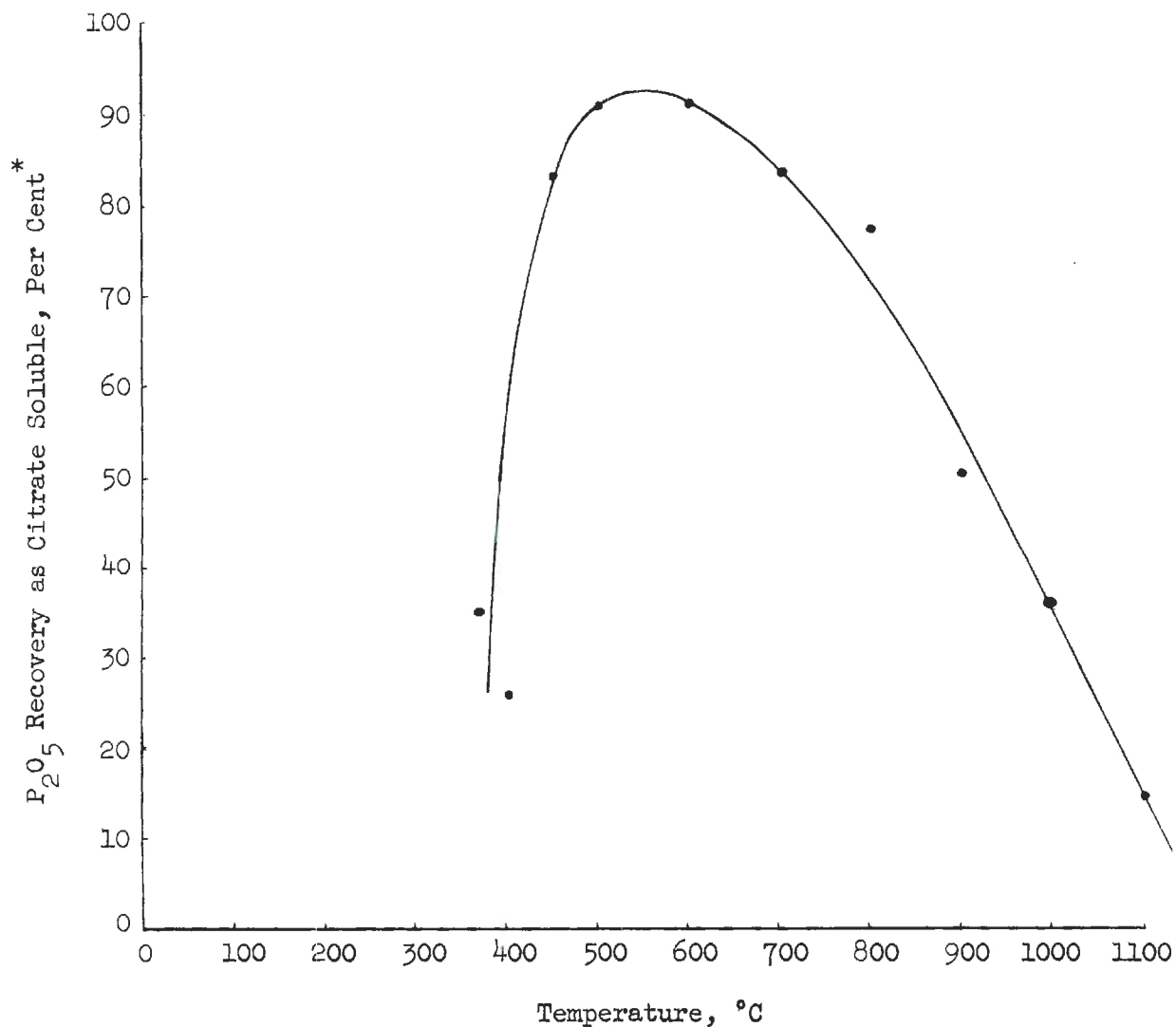


Figure 4. Recovery of Phosphate Values from Phosphate Rock by Contact with Sulfur Trioxide for Five Hours. (Hughes, A. E. and F. K. Cameron, Ind. Eng. Chem. 23, 1262-71 (1931)).

* These authors apparently define per cent recovery as the percentage of citrate-soluble P_2O_5 compared to the original total P_2O_5 in the sample.

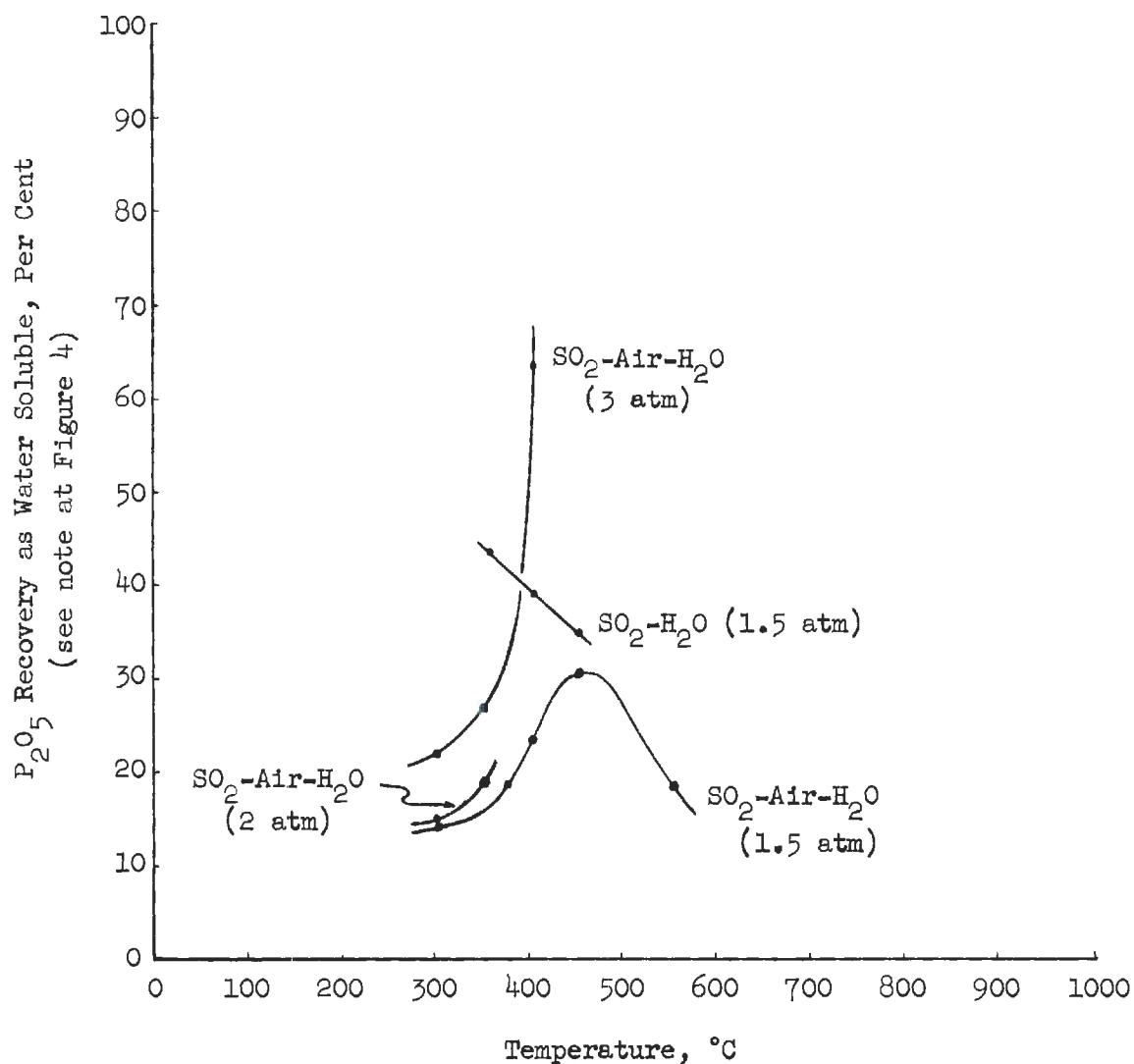


Figure 5. Recovery of Phosphate Values from Phosphate Rock by Contact with Sulfur Dioxide-Air-Water Mixtures, at Various Pressures, for Five Hours. (Hughes, A. E. and F. K. Cameron, Ind. Eng. Chem. 23, 1262-71 (1931)).

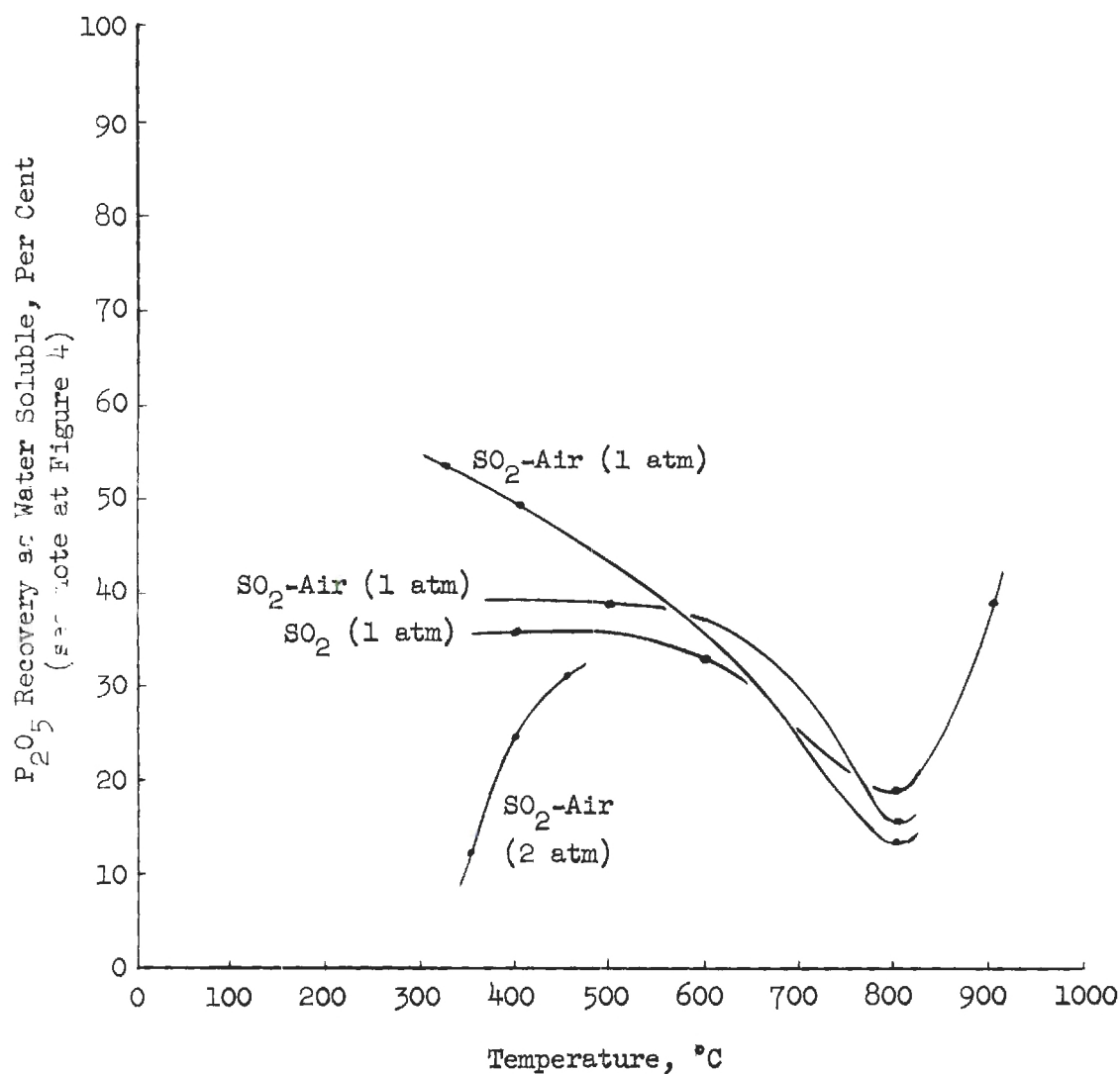


Figure 6. Recovery of Phosphate Values from Phosphate Rock by Contact with Sulfur Dioxide-Air Mixtures, at Various Pressures, for Five Hours. (Hughes, A. E. and F. K. Cameron, Ind. Eng. Chem. 23, 1262-71 (1931)).

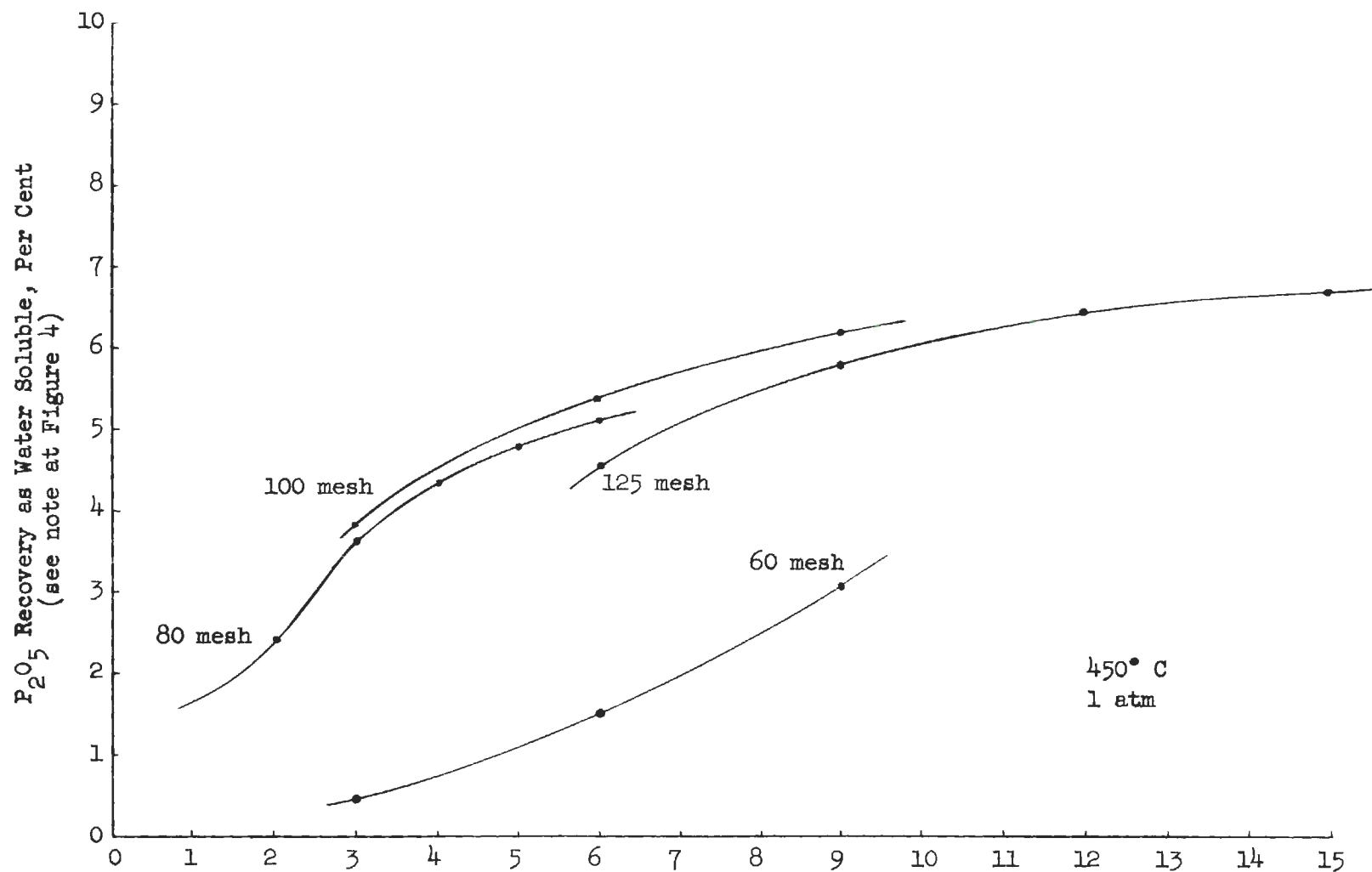
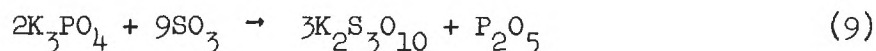
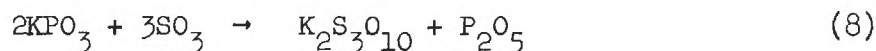
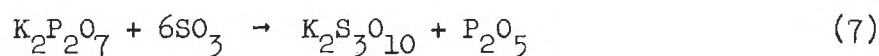


Figure 7. Recovery of Phosphate Values from Phosphate Rock by Contact with Sulfur Dioxide at $450^{\circ}C$ and 1 Atmosphere, at Various Particle-Size Distributions. (Hughes, A. E. and F. K. Cameron, Ind. Eng. Chem. 23, 1262-71 (1931)).

which is apparently catalyzed by phosphate rock. The conversions are smaller and contact times longer than those obtained with gaseous $\text{SO}_3\text{-H}_2\text{O}$, which suggests either that water is very important to the mechanism or that the catalysis of SO_2 to SO_3 and S is poor.

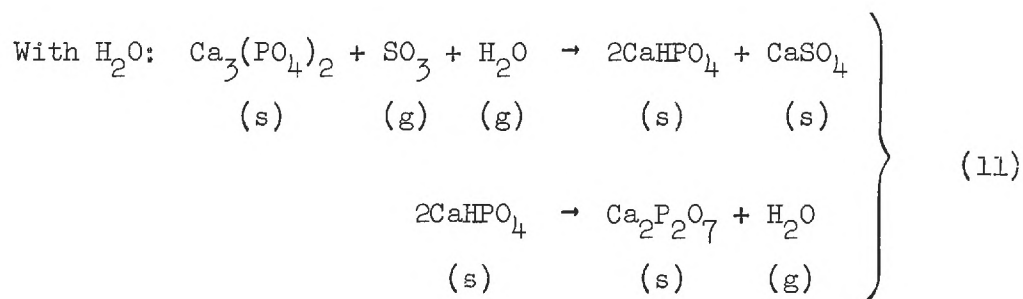
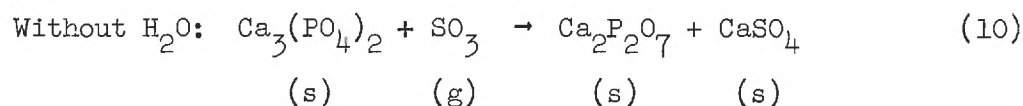
In 1939 Baumgarten and Brandenburg³⁰ demonstrated that sulfur trioxide possessed the ability to combine with anhydrous salts, including phosphates, with liberation of free phosphorus oxide. This was demonstrated for three potassium salts according to the following mechanisms:



The reactions all occur with liquid sulfur trioxide at about 60°C . The authors remark that "presence of sufficient sulfur trioxide and not too high temperatures" are required, and that phosphorus oxide recombines with the pyrosulfate product from about 400°C onward. No information on yields is presented, and details on identification of P_2O_5 in the product are likewise omitted.

In 1962 Pompowski³¹ reopened the question of sulfur dioxide reactions with phosphate rock. His viewpoint is that high SO_2 concentrations are industrially infeasible, and likewise the two-thirds maximum theoretical yield (due to the $2\text{SO}_3 + \text{S}$ shift) is uneconomical. Pompowski used excess oxygen, and SO_2 concentrations of only about five per cent. Maximum conversion occurs at 700° to 720°C . If water is introduced, a ratio of SO_2 to H_2O of 1.0 results in best conversion. The results are

explained by postulating the following reactions:



Reaction time is not explicitly stated, but the reported figures allow an estimate of about 170 hours to achieve 86 per cent conversion of solid. Pompowski points out that the percentages of SO_2 in the range he investigated are close to those obtained in industrial burner gas.

Pompowski apparently overlooks the German patent of Scheel³² issued in 1947 for a process involving dilute SO_2 gas mixtures above 500°C . In this patent a product containing $\text{Ca}_3(\text{PO}_4)_2 + \text{CaSO}_4$ is claimed.

It is known that the Tennessee Valley Authority investigated sulfur oxide processes at one time, but the results were never published.³³

In summary, sulfur trioxide is seen to be the true reactant in all the processes reported. Investigators often cite calcium pyrophosphate, $\text{Ca}_2\text{P}_2\text{O}_7$, as the product obtained. The presence of water is strongly suggested as favorable for conversion of phosphate rock. Contact times are an uncertain quantity, but they may be favorable to industrial application. Finally, there is one reported instance of phosphorus oxide product, from the reaction of liquid sulfur trioxide with anhydrous metal phosphates.

3. Thermodynamic Equilibrium Analysis

Introduction. The calculation of the thermodynamic equilibria of the processes discussed here has only become possible in recent years, with the publication of improved experimental values for heats of formation and standard entropies of the compounds involved. The present investigation is the first to benefit from these data, so far as is known.

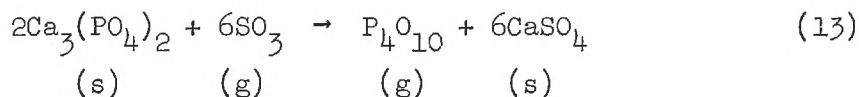
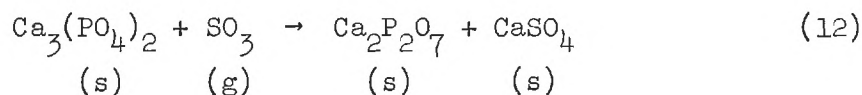
It is worthwhile, in advance of presenting the results, to consider what may be expected of equilibrium calculations. Thermodynamic quantities furnish quantitative values of driving forces from processes relative to each other and predict limiting equilibrium states. However, the calculated equilibrium state depends on the assumed reaction mechanism, and thermodynamics by itself throws no light on the correctness of the assumption. Some clues concerning probability of a given reaction's occurrence can often be obtained from consideration of chemical structures. Experiment is ultimately required for explanation of what takes place in systems as complex as those considered here. In the calculations of this section, possible mechanisms are explored in terms of structure and their standard free energies ΔF_T° and equilibrium constants K at various temperatures.

Consideration of Mechanisms. In all calcium phosphates, including fluorapatite, calcium ions occur interstitially between $(\text{PO}_4)^{3-}$ tetrahedra. As shown in Figure 1, the $(\text{PO}_4)^{3-}$ tetrahedra in the fluorapatite crystal are shielded from the force fields of fluorine ions, and thus it is reasonable to consider reaction mechanisms as concerning only tricalcium phosphate.

When a molecule of SO_3 attacks this structure and combines with a Ca-O unit to form calcium sulfate, there are three possible basic configurations which the residual P-O structure may assume: (1) chain structure (see discussion under "Phosphoric Acid and Polyphosphates," above); (2) ring structure,³⁴ trimeric, with a Ca/P ratio of 1/2; and (3) sheet structure^{18,35} consisting of an infinite network of P and O atoms in the ratio $\text{P/O} = 2/5$, in other words a polymeric form of P_4O_{10} , as shown in Figure 3.

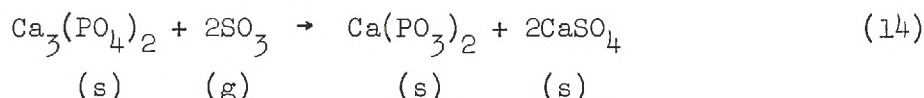
The ionic chain structure of P-O-P linkages is theoretically capable of extending to indefinite length. It has been shown that branching is unusual and very unstable compared to the linear chain configuration.³⁶ The chain formed from two $(\text{PO}_4)^{3-}$ tetrahedra defines the pyrophosphate radical, $(\text{P}_2\text{O}_7)^{4-}$, which is well known. Infinite length of the chain conforms to a ratio $\text{P/O} = 1/3$, the same ratio as metaphosphate, as mentioned above.

The reactions of formation of $\text{Ca}_2\text{P}_2\text{O}_7$ and P_4O_{10} may be written respectively as

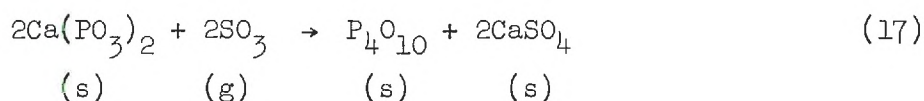
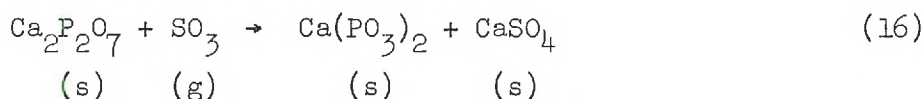
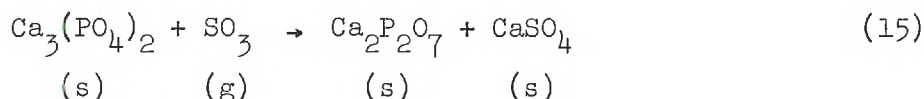


Equation 13 is the ultimate desired result, with the product written as P_4O_{10} because this accords with the true molecular state of free phosphorus oxide. Thermodynamic data are unavailable for the polyphosphates which would be expected in actuality.

The ring structure has a ratio $P/O = 1/3$, which defines the metaphosphate radical. The reaction of formation may be written



The stepwise sequence of reactions describing the progressive degradation of the apatitic calcium phosphate to free phosphorus oxide may be written as follows (again ignoring the Ca-F relationship):



Calcium pyrophosphate, as pointed out above, has a chain structure embodying two P atoms. Accordingly, it would be expected that the next product in the sequence would be the next member of the chain series, $\text{Ca}_5(\text{P}_3\text{O}_{10})_2$, instead of the metaphosphate with ring structure. The sequence shown, however, is the only one for which existing data permit equilibrium calculations.

Calculation of the standard free energy of these postulated mechanisms* yields the following figures for the standard free energy in kcal/mole, with the equation written for a product containing 4P in every case (in order to permit comparison with P_4O_{10}).

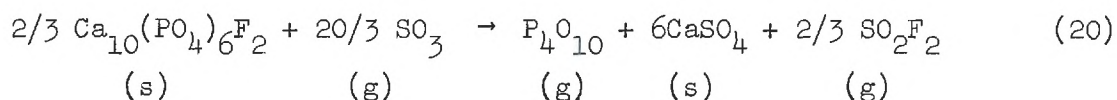
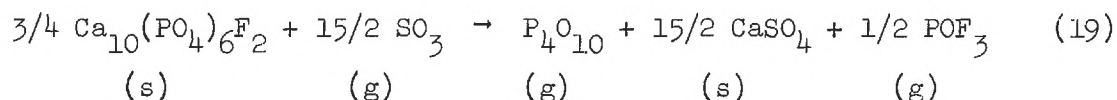
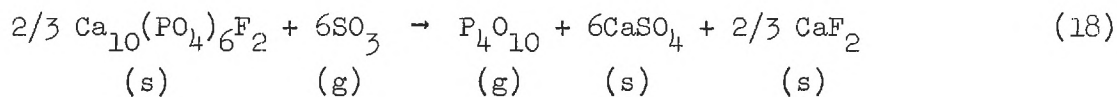
*Complete computational details and sample calculations are presented in Appendix B.

| Reaction | Temperature °K | | |
|---------------------|----------------|-------|-------|
| | 298.15 | 500 | 1000 |
| Overall (Eqn. (13)) | -135.9 | -88.1 | +29.0 |
| Eqn. (15) | -100.0 | -81.1 | -22.8 |
| Eqn. (16) | -46.6 | -28.0 | +4.1 |
| Eqn. (17) | +10.8 | +21.0 | +47.8 |

The overall process presents an attractive picture and will feature a good equilibrium constant up to temperatures where a good rate might be expected.

However, consideration of the individual steps presents a different prospect. The reactions forming pyrophosphate and metaphosphate will feature attractive equilibrium constants, but the final step, P_4O_{10} formation, features a vanishingly small equilibrium constant. In actuality a high molecular weight polyphosphate structure is expected, and the figures for equation (17) suggest that there is a high thermodynamic barrier between this structure and free phosphorus oxide.

If fluorapatite is considered as the starting material instead of tricalcium phosphate, there are at least three possible overall mechanisms which may account for the final state of the fluorine:



The standard free energies of these reactions are as follows:

| <u>Reaction</u> | <u>Temperature °K</u> | | |
|-----------------|-----------------------|------------|-------------|
| | <u>298.15</u> | <u>500</u> | <u>1000</u> |
| Eqn. (18) | -101.8 | -54.7 | +61.8 |
| Eqn. (19) | -132.9 | -76.5 | +63.4 |
| Eqn. (20) | -101.7 | -48.6 | +83.4 |

All three mechanisms will have favorable equilibria to fairly high temperatures. On mechanistic grounds, equation (20) is probably to be preferred, since CaF_2 is capable of reaction with SO_3 ,³⁷ and the unit cell configuration of fluorapatite is such that the P-O bonds are shielded from fluorine, so as to discourage phosphorus oxyfluoride formation.

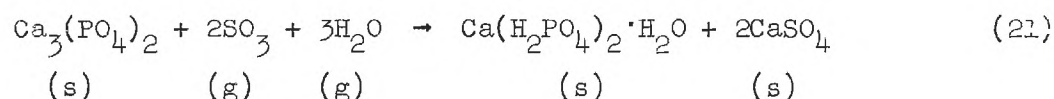
As in the case of the hypothetical tricalcium phosphate mechanisms discussed above, the fluorapatite mechanisms would logically proceed through successive linkage of phosphate tetrahedra to form anions of increasing molecular weight, either chains or sheets. Once again the overall equilibria are favorable but the respective final steps will have very discouraging equilibrium constants.

Sulfur dioxide can be substituted for SO_3 in all the above equations, with either CaSO_3 or CaSO_4 plus free sulfur in the product. These equilibria are uniformly less attractive than those involving SO_3 .

Up to this point the role of water has been ignored. It is possible that water exerts a catalytic effect in the initial attack of the calcium phosphate structure by SO_3 , and water may provide hydrogen ions to terminate the P-O-P linkages formed by the reaction. There is evidence from some of the works cited above^{29,31} that water enhances the reaction, sometimes to a degree which cannot be explained by assuming water as a

reactant. The present investigation has also accumulated some data to this effect, which are discussed in Chapter V.

If water is taken as a gas-phase reactant in company with sulfur trioxide, the phosphoric product can be assumed as monocalcium phosphate, phosphoric acid, or any of the series of acid phosphates which are known. Monocalcium phosphate is certainly the most likely, since (1) it is the lowest member of the acid phosphate family and (2) phosphoric acid would be expected to react further with the solid present. A typical hypothetical mechanism is



It is interesting to recall that Pompowski³¹ achieved optimum results with a 1:1 ratio of SO_2 to H_2O , while Hughes and Cameron²⁹ used a 1:1 SO_3 - H_2O ratio. Unfortunately, thermodynamic data for $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ are available only at 298.15° K; however, the equilibrium according to equation (21) is strongly favored at that temperature.

4. Rate Theory of Noncatalytic Gas-Solid Reactions

Reactions between inorganic substances are often very rapid compared to the mass transport required to bring the substances together. Thus the normal superphosphate process is believed to be controlled by a film of calcium sulfate which forms on the phosphate rock granules, inhibiting the contact of acid with the rock. Hughes and Cameron²⁹ also demonstrate the presence of an inhibiting coating in the gas-solid contact of phosphate rock with sulfur dioxide. Frear and Hull,³⁸ in fixed-bed studies of the reaction of phosphate rock with phosphorus pentoxide, show

that the liquid film formed on the rock particles controls the reaction rate. Many other examples could be cited from processes involving other materials.

In fluidized-bed processes, with the gas concentration constant and good agitation provided, the particle may be expected to contribute the major resistance to diffusion of reactant gas, and thus to reaction. The mathematics of this situation is complex, and data are generally insufficiently precise to permit choosing any one model over another. For example, a shrinking-core spherical model, with certain simplifying assumptions, leads to the following equation for uptake M of diffusing material:

$$M = -D \int_0^t \left(\frac{\partial C}{\partial r} \right) dt = at^{3/2} + bt + ct^{1/2}$$

where M = amount of reactant gas absorbed in time t

D = diffusion coefficient

C = concentration of diffusing material

R = particle radius

a,b,c = constants.

This equation was derived by the present author. However, such a three-constant formula can be forced to fit virtually any monotonic function. Furthermore, data of the present investigation do not justify development of mathematical models.

5. Preliminary Investigations

In the summer of 1962 Mr. David Bowen, Jr., of the Georgia Institute of Technology contacted phosphate rock with sulfur trioxide in

a series of exploratory experiments.³⁹ His procedure consisted of introducing liquid SO_3 into an ampoule containing phosphate rock at room temperature, then sealing the ampoule and heating the portion containing the rock, while holding another portion in contact with room air.

A white powder, hygroscopic, acid in character, and giving a positive phosphomolybdate test, was observed to condense in the cool part of the ampoule in some of the experiments. The temperature at which this deposit appeared was not closely observed; maximum temperature of the heated portion of the ampoule was about 600°C . It was observed that if the phosphate rock was dried before contact with SO_3 , no white deposit was produced.

The white deposit was judged to be phosphorus pentoxide. The influence of water was not explained, but was conjectured to be catalytic in nature.

6. Experimental Plan

The objective of this investigation was to alter the nature of phosphate rock by means of contact with sulfur oxides, with the ultimate view of providing a source of soluble or available phosphorus competitive with existing fertilizers. A particular objective of the investigation was to produce pure phosphorus pentoxide if possible.

The literature has revealed that processes conducted at high temperatures are too slow, while thermodynamic equilibrium calculations predict that the maximum feasible temperature for the desired mechanisms is relatively low. Preliminary experiments indicate that phosphorus pentoxide can be produced in the presence of moisture.

With these guidelines, the general experimental plan was set forth as follows:

(1) Determine the conditions (temperature, time moisture) under which phosphorus pentoxide can be produced.

(2) Determine the parameters for fluidized-bed operation of the process.

The details of the conduct of the investigation are developed in Chapters IV and V, following.

CHAPTER II

EXPERIMENTAL MATERIALS AND EQUIPMENT

A. Materials1. Sulfur Trioxide

Properties of Sulfur Trioxide. Sulfur trioxide is a very reactive material. Its affinity for water is such that it will combine instantly with atmospheric moisture (forming sulfuric acid), is more hygroscopic than P_2O_5 (i.e., will dehydrate phosphoric acid) under certain conditions, and will displace certain nonmetallic oxides from metal salts. It is also a powerful oxidizing agent.

This vigorous reactivity has been attributed to an electron deficiency of the sulfur atom.⁴⁰ The central sulfur atom is surrounded by an electron sextet, which tends to seek an electron octet configuration analogous to the noble gas atomic arrangement. The sulfur trioxide molecule has the configuration of a planar equilateral triangle with the sulfur atom at the center, the S-O bond distance being 1.43 Å, and the bonding mechanism featuring resonance forms.⁴¹

The common physical properties of sulfur trioxide are as follows:⁴²

| | |
|---------------------------|-----------------|
| Boiling point | 44.8° C |
| Molecular weight | 80.06 |
| Density (liquid at 20° C) | 1.9224 |
| Freezing point | 16.8° C |
| Heat of vaporization | 11,900 cal/mole |

The vapor pressure of sulfur trioxide is summarized in Reference 43.

Sulfur trioxide will polymerize, under the catalytic influence of traces of moisture, into a sequence of forms that are successively more stable.⁴⁴ These are the so-called γ , β , and α forms, which melt at 16.8° C, 32.5° C, and 62.3° C respectively. The γ form is a trimeric ring; the β form is a chain structure of indefinite length; the α form, finally, is a layered chain structure. The polymerization may be inhibited and the liquid "stabilized" by addition of a small quantity of inhibitor, of which many are known, including carbon tetrachloride, boric oxide, sulfur dioxide, and a number of other inorganic compounds.

The corrosive properties of sulfur trioxide toward metals are not severe if the system is anhydrous. However, if water is present even in small quantity, the problem is one of sulfuric acid. Liquid and gaseous sulfur trioxide will attack all known plastic materials of construction, including Teflon, but glass is completely unaffected.

Oleum. Oleum is the name given to a solution of sulfur trioxide in sulfuric acid. The commonest commercial mixture is "20 per cent oleum," containing 20 weight per cent free SO_3 . The corrosive and desiccant properties of oleum are similar to those of sulfuric acid.

The vapor pressure of sulfur trioxide over oleum solutions at various temperatures is given in References 45 and 46.

Safety Considerations. Sulfur trioxide and oleum present a considerable safety hazard because of the highly corrosive fumes which they give off. These fumes always consist of droplets of sulfuric acid formed by the instantaneous reaction of atmospheric moisture with the oxide, and they are always visible. The mist so formed is very difficult to filter, which makes conventional fume masks and respirators unreliable (see below). There is no alternative except for workers to avoid inhaling the

fumes. The dangers of these sulfuric materials are summarized in References 47 and 48.

Polymerized sulfur trioxide presents an unusual hazard. The solid α form melts at 62.3°C , which is above the boiling point of the liquid. Accordingly, the vapor pressure instantaneously exceeds one atmosphere, and the resulting " SO_3 pop" is an explosion hazard in glass equipment.

Sulfur Trioxide Mist. The mist which sulfur trioxide forms with moisture, mentioned above, is a fine aerosol difficult to collect by filtering or absorption. Particle sizes range from $1/2$ micron to 10 microns.⁴⁹ In sulfuric acid plants this mist is an air pollution and safety hazard, while in the laboratory it is a hazard and a nuisance to collect for analysis. However, its appearance is a useful and unfailing indication of sulfur trioxide in the atmosphere.

Source of Sulfur Trioxide for Reaction. Although sulfur trioxide is available as stabilized liquid from the General Chemical Division of Allied Chemical Corporation, this has not proved a feasible source for the present study. The liquid is shipped either in one-pound glass bottles with fused necks or in 55-gallon drums. If liquid is drawn from either source into glass vessels for subsequent vaporization, moisture is absorbed and polymerization soon converts the liquid to solid. In addition, the glass bottles are relatively expensive as a day-to-day source.

It has proved more expedient to generate sulfur trioxide as needed from oleum supplied in bottles by the Tennessee Corporation. A single charge of oleum can be used to generate sulfur trioxide over and over until the boiling point of the oleum rises to nearly 200°C , which is

about the limit of laboratory convenience. This method is simple, relatively rapid, and very flexible. Details of the technique are given in Chapter III.

2. Sulfur Dioxide

Properties. Sulfur dioxide is much easier to handle than sulfur trioxide, since it is a gas to much lower temperatures and is less vigorous chemically. The common physical properties of sulfur dioxide are as follows:⁵⁰

| | |
|------------------------|------------|
| Boiling point | -10° C |
| Molecular weight | 64.06 |
| Density (gas at 20° C) | 2.927 gm/l |
| Freezing point | -72.7° C |

The vapor pressure of sulfur dioxide is given in Reference 51.

The corrosive properties of sulfur dioxide are relatively mild. Sulfur dioxide is a reducing agent and forms a weak acid in aqueous solution, but is not a corrosive substance above the boiling point of water. Glass and most synthetic resins are inert to sulfur dioxide.

Safety Considerations. Sulfur dioxide is a highly toxic gas, requiring a special respirator for workers who handle it. Its strong, unmistakable odor gives ample warning of its presence. Adequate ventilation is normally sufficient protection against its hazards.

Source of Sulfur Dioxide for Reaction. Sulfur dioxide is readily obtainable in metal cylinders. For this investigation, a 100-pound cylinder of sulfur dioxide purchased from the Matheson Co., with a Matheson pressure regulator, model 13-660, was the sole source of sulfur dioxide.

3. Phosphate Rock

Properties. Phosphate rock in the form of a free-flowing powder is the normal raw material for superphosphate fertilizer manufacture. Several grinds are used,⁵² the commonest probably being a grade designated as "90 per cent through 100 mesh." The chemical nature of phosphate rock has been described in Chapter I. Phosphate rock is not a safety hazard.

Source. For the present investigation a quantity of about 50 pounds of acidulation grade phosphate rock was drawn from the pile of the Tennessee Corporation's plant in East Point, Georgia, and stored in a fiber drum. This supply was the sole source of phosphate rock for the investigation. Analyses of blanks at intervals throughout the course of the investigation assured that the composition of this rock did not vary, within the limits of experimental error.

The phosphate rock employed in this investigation contained approximately 0.67 per cent free moisture. Typical analyses of the composition of this rock are given in Table 1.

The fluidizing properties of this phosphate rock are relatively good for all the gases (air, nitrogen, steam, sulfur trioxide, sulfur dioxide) employed in this investigation, provided that certain precautions are observed. The precautions are necessary because of the following properties of the rock:

- (1) a tendency to stick to walls, especially if cold rock is introduced into a hot tube;
- (2) a tendency for gas to channel through the charge of rock without fluidizing, especially in the zone immediately above the supporting screen or plate;

- (3) a tendency to form pellets of about millimeter size, which do not break up during fluidization, especially in the portion of rock immediately above the supporting screen or plate.

The first effect is easily avoided by introducing a cold charge of rock into a cold reactor, then heating the reactor. The second and third effects can be avoided by employing a layer of material between the supporting screen or plate and the charge of phosphate rock. This material must be chemically inert and maintain its position and integrity during fluidization. Ottawa sand, as described below, meets these requirements. A bed of sand beneath the charge of rock fluidizes independently; and if it is uniformly larger than the rock in size it will not mix with the rock, but will provide oscillatory vertical motion and uniform gas distribution to the smaller particles of rock powder above it. These characteristics guarantee good fluidization behavior of the phosphate rock.

4. Minor Materials

Sand. The sand used in this investigation was Ottawa sand from the stockroom of the School of Chemical Engineering. The sand was approximately uniform in grain size, about 20 mesh. Before the sand could be used in contact with sulfur trioxide, washing with 97 per cent sulfuric acid was required in order to remove the small quantity of gel-forming material present. Otherwise, as was observed several times, the rock would stick and lose its fluidization characteristics.

Fluorapatite. The fluorapatite for this investigation was purchased from Ward's Natural Science Establishment in Rochester, New York. This fluorapatite was mineral in nature instead of synthetic, and was

labeled "asparagus stone." There were probably impurities present as a result. For example, the P_2O_5 analysis of this fluorapatite was 37.1 per cent by weight, compared to 39.8 per cent based on the theoretical formula.

Phosphoric Acid. For experiments in dehydration of phosphoric acid, a "superphosphoric acid" containing 76.2 weight per cent P_2O_5 was used. This acid was provided to Mr. W. H. Burrows of Georgia Tech by the Tennessee Valley Authority, and by Mr. Burrows to the author.

B. Reaction System

1. Description of Apparatus

Fluidized-Bed Reactor System. The position of this reactor in the system is shown in Figure 8, and the reactor is shown in cross section in Figure 9. The reactor is a tube of 316 stainless steel 22 inches long, 0.43 inch inside diameter and 0.50 inch outside, joined at each end by silver solder to $\frac{1}{2}$ 19/38 stainless steel outer joints designed to mate with glass equipment, the overall length being 25-1/4 inches. At a point 3 inches above the base, a stainless steel ring is positioned inside the reactor by means of three circumferential punches applied externally. A circular screen of 100-mesh 316 stainless steel, closely fitting the reactor diameter, is positioned against the lower edge of the ring and held in place by a plug of stainless steel wool.

The steam inlet, visible in Figure 9, is 4-5/8 inches above the base, fastened by silver solder. This inlet port is intended to admit steam or air-steam mixtures into the sand bed of the reactor charge. A short length of 1/8-inch stainless steel tubing, with 1/8-inch copper fittings at either end, is screwed to the steam inlet.

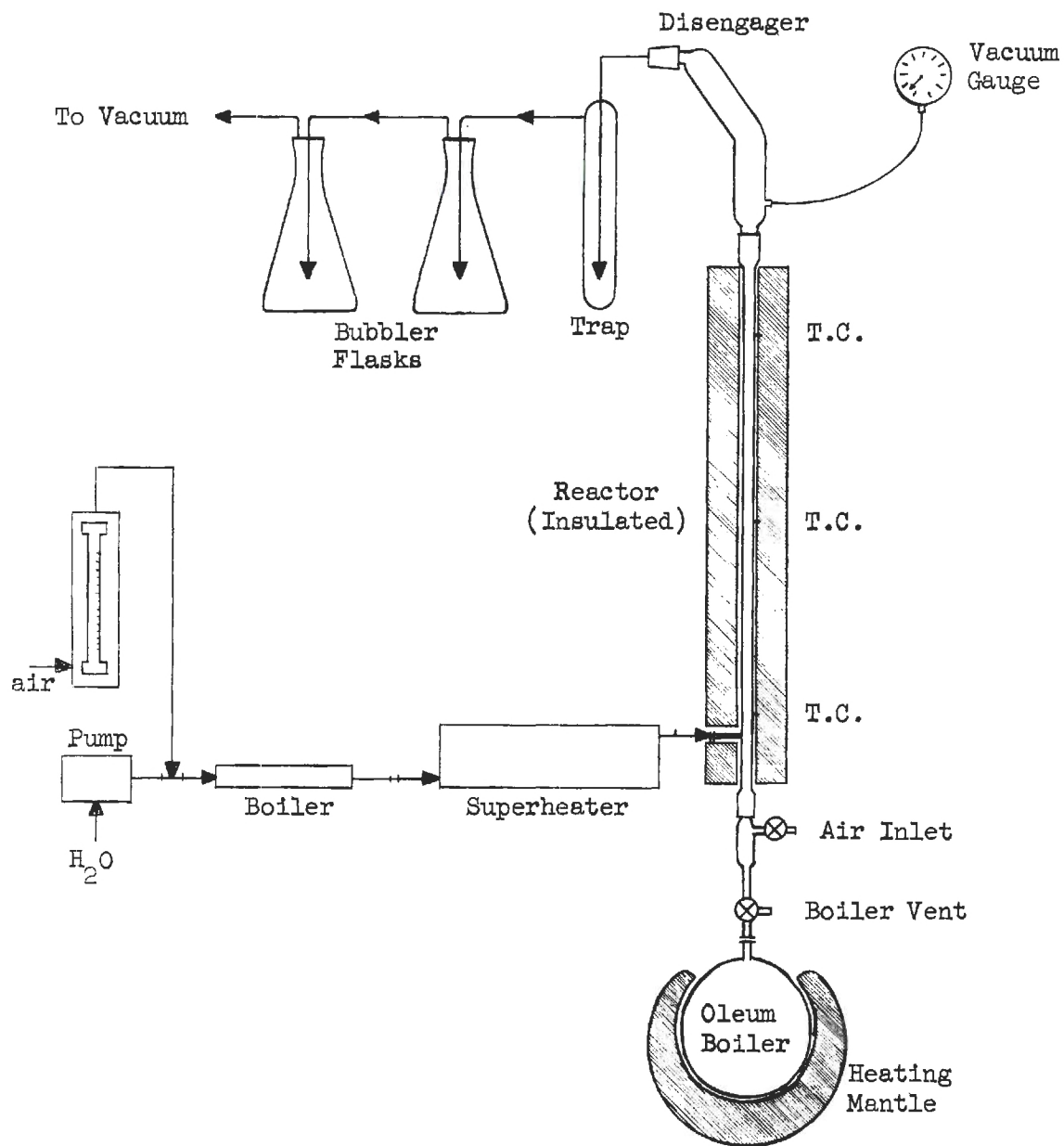


Figure 8. Fluidized-Bed Reaction System.

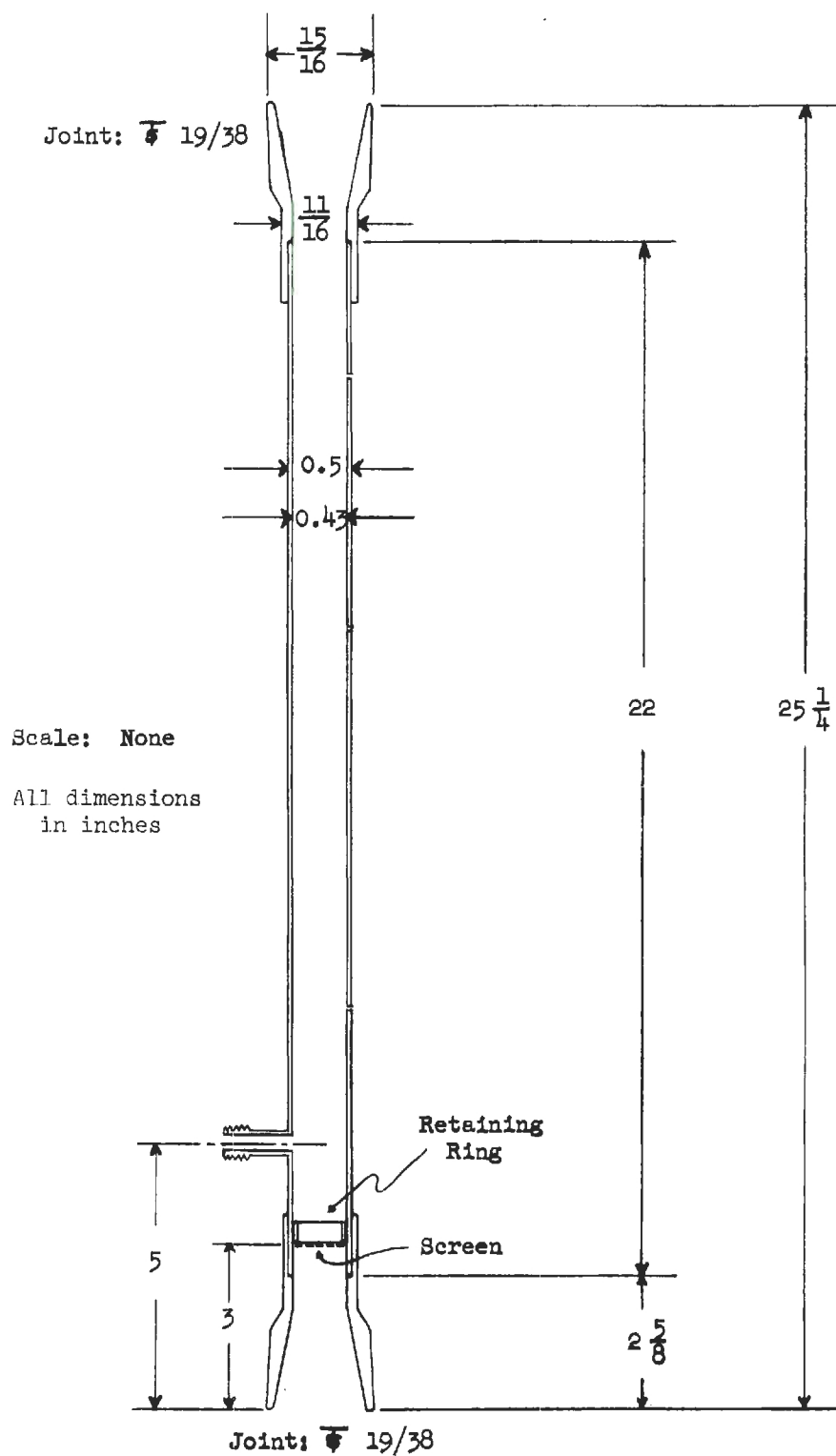


Figure 9. Cross Section of Fluidized-Bed Reactor.

Three holes for thermocouple insertion are positioned at 6-1/2, 13, and 19-1/2 inches above the reactor base. The thermocouples are chromel-alumel of 28 gauge, coated with a layer of fused Teflon for corrosion protection. They are inserted approximately to the center of the reactor bore, and held by Sauereisen cement.

The glass piece immediately above the reactor has the function of providing a space for the fluidized charge of phosphate rock to disengage from the gas stream and fall back into the reactor. Figure 8 shows the position of the disengager above the reactor. The principles of disengager design are as follows:

- (1) the fluidized stream enters a larger cross section, and gas velocity is no longer sufficient for fluidization;
- (2) the path of gas travel in the disengager changes direction, which gives entrained solid particles additional opportunity to strike the wall and return to the reactor.

The disengager is of glass so that the fluidization can be observed at the reactor exit.

In practice, the disengager proved to be the most critical portion of the assembly. Six different pieces were employed as disengagers during the investigation and were successively replaced as breakage or frosting of the glass ruined them for use. Early models were of insufficient diameter, but it became evident that there was a maximum size for practical utility.

The final disengager design was 3/4 mm inside diameter, 13-1/2 inches overall height, and 9 inches from the base to the elbow. A nipple

shown in Figure 8 leads to the vacuum gauge whose function is described in Chapter III. An indentation about 1/2 inch in depth was provided in most models to hold a thermocouple. The joints are both $\frac{1}{8}$ 19/38. Construction was of Pyrex, except for one Vycor model.

Downstream of the disengager, the process stream flows to a water aspirator through a one-liter flask which serves to check backflow of water. In those runs where it was desired to collect the sulfur trioxide, an absorption train was constructed as shown in Figure 8, consisting of a bubbler trap and two 500-ml bubbler flasks. All three of these vessels were packed with Pyrex wool at their outlets, in order to filter out the acid mist formed by sulfur trioxide. The entire system from reactor to aspirator was drained and washed when acid recovery was desired.

Fixed Bed Reactor Systems. Several configurations of glass tubing were employed in the fixed bed reaction systems. These were constructed as required from glass tubing. All of these had the common feature that phosphate rock (5 or 6 grams) was held in position in the tube by plugs of Pyrex wool. Heat was provided either by windings of nichrome wire on the outside of the tube or by an electric furnace of folding construction, of the type used in mineral and metallurgical combustion analysis. High temperature experiments were conducted in a 1/2-inch steel tube.

Connections were usually glass joints, but rubber stoppers were occasionally used and discarded afterward. Some arrangements were designed to have liquid sulfur trioxide drip on the charge, but most were vapor contact reactors. Temperature was always measured by an indentation in the reactor wall, into which a thermocouple was inserted.

Sulfur Trioxide Production System. Sulfur trioxide was always produced, after the very earliest exploratory experiments, by boiling

oleum in a one-liter boiling flask. The resulting vapor stream was always adequate to fluidize the charge in the fluidized-bed reactor. When liquid sulfur trioxide was desired, the stream was condensed into a receiver, with precaution taken to vent the system to the atmosphere through a bed of silica gel.

Figure 8 shows the oleum boiler in position below the fluidized-bed reactor. A conventional heating mantle provides heat.

Above the boiler is a three-way Teflon stopcock, which serves as a valve for flow of sulfur trioxide. When this valve is closed, the boiler is vented through a water-coated condenser connected to the boiler. This condenser is always closed to the atmosphere at the same moment the valve is opened. A plug of Pyrex wool is inserted in the condenser near the outlet, in order to keep atmospheric moisture from entering the condenser and boiler.

Several attempts were made to immerse nichrome wire into the oleum as a means of rapid heat input. The wire was welded to electrodes inserted through a glass joint. These attempts were unsuccessful because the nichrome was prone to corrosion at the vapor-liquid interface.

Steam Delivery System. Steam delivery to the fluidized-bed reactor was one of the major problems of the investigation. The final arrangement, shown in Figure 8, consisted of the following elements:

- (1) a Beckman solution metering pump, model 746,
with 0 to 5 ml per minute variable delivery
rate;
- (2) a boiler consisting of a bored-out platen
from a small printing or typewriting machine,

machine, intended to provide and expanded portion of the line in which water can be boiled;

- (3) a superheater tube five feet long, of 1/4-inch copper tubing, packed with pumice stone.

The pump has inlet and outlet fittings compatible with 1/4-inch copper fittings, and the boiler inlet and outlet tubular sections are exactly 1/4 inch in outside diameter. Thus the entire steam delivery system is joined by 1/4-inch copper fittings. At the end of the superheater, a thermocouple is inserted and sealed with Sauereisen cement. Standard reducing connections provide the transition to the 1/8-inch fittings of the reactor steam inlet.

In some arrangements, a tee is placed immediately downstream of the boiler in order to receive air flow into the superheater and ultimately into the reactor.

The steam delivery system is designed to provide continuous delivery of steam at constant rate to the reactor. The pump delivers intermittently at a rate of ten strokes per minute, but the boiler, superheater, and fittings provide sufficient resistance to damp out fluctuations in steam flow. Admission of air into the tee further improves the smoothness of flow.

Heat Supply and Temperature Control. A total of seven heater rheostats and one Meker burner is employed to provide heat to the fluidized-bed reaction system. These are applied as described in the following paragraphs.

The fluidized-bed reactor is heated by a total of three heater windings. The first is a bare nichrome wire wound the length of the reactor on a layer of asbestos paper. This winding is heated at constant voltage in the range of 20 to 30 volts and is designed to heat the reactor to about 250° C. The second and third are nichrome wires, shielded by ceramic ferrules 1/8 inch long, about 1-1/2 mm inside diameter, and about 3 mm outside diameter, wound on the upper and lower halves of the reactor respectively. These latter two heater windings are controlled by the temperature controllers described below, and carry 55 volts intermittently. These windings provide fine control to supplement the first overall (unshielded) winding.

One nichrome winding heats the disengager at constant voltage. The disengager is wrapped with asbestos paper before the winding is applied. The lowest one inch of the disengager (above the joint) is not wrapped with asbestos paper, although the heater wire is shielded and is wound on the disengager at this point. The purpose of this arrangement is to leave this section free for observation of the plume of fluidized solids from the reactor, but experience has demonstrated the necessity of providing heat at this point, and this is the reason for the presence of the shielded winding. The disengager is always heated to a temperature above 360 degrees centigrade, for reasons discussed in Chapter V.

The steam superheater is heated by two windings of nichrome over approximately each half of its length. A layer of asbestos paper is again interposed between the tubing and the winding, and the nichrome wire is shielded by ceramic ferrules. A constant voltage of 100 volts in these windings is required to deliver an outlet steam (or steam-air) temperature of about 360 degrees centigrade.

The last rheostat heats the oleum boiler, at 60 to 70 volts. The heating of oleum can be accelerated by packing asbestos paper around the top of the mantle to preserve heat.

The nichrome wire used in the investigation was of two grades. Wire of one ohm per foot resistance was the type most often used, but some windings were constructed of wire of 0.783 ohm per foot resistance in the early stages of the investigation.

The steam boiler was heated by direct flame from a Meker burner.

Two fundamental types of insulation were applied to the reaction system. The reactor is shielded by two semicylindrical sections of pressed asbestos. The disengager and superheater are individually wrapped with asbestos tape. Other portions of the system are uninsulated.

Temperature control to the reactor is provided by two Sim-Ply-Trol pyrometer controllers manufactured by Assembly Products, Inc., of Chesterland, Ohio. These controls operate on the principle of voltage amplification. The thermocouple output from the reactor upper section (controller no. 1) and base (controller no. 2) produces a reading on the limit meter (millivoltmeter) of the controller. When the set point is achieved, a relay is actuated, which in turn actuates another relay, and then finally the power supply relay that supplies the reactor heater.

These controllers were originally equipped with 10-ohm meter shunt resistors, which provided a maximum operating point of 250° C. They were also each equipped with electric motor-driven cams, which provided one temperature check each minute. The controllers were modified in this investigation by insertion of 30-ohm resistors instead of 10-ohm, which raised the maximum operating point to about 450° C, and by insertion of

cams with eight notches, which would consequently provide eight temperature checks per minute. At steady state, temperature could be controlled within $\pm 5^\circ \text{C}$ in the range from 300° to 360°C .

A Leeds and Northrup millivolt potentiometer, model 8686, was used to read temperatures. The two thermocouple leads to the controllers were led through knife switches, which made it possible to divert the thermocouple outputs to the potentiometer when desired. Other thermocouple outputs were fed directly to positions of a ten-position selector, to which the potentiometer was connected. The potentiometer was periodically checked by comparison with a glass thermometer at readings of 300°C and above; the agreement was always within $\pm 5^\circ \text{C}$.

Utilities. As mentioned above, seven sources of 110 volt AC power were employed for the various heaters, and one more source to drive the water metering pump. One gas source fed the Meker burner to heat the water boiler. Two sources of water were required: one for aspiration of system vacuum and one for the water-cooled condenser at the oleum boiler. Air was drawn from a 150-psi (gauge) line. Steam was available at 25 psi (gauge), but was not used in the investigation.

2. Establishment of Scale of Operation

It was originally envisaged that the fluidized-bed reactor would be about one inch in diameter. Preliminary experiments in fluidization of the phosphate rock were conducted in tubes of this size. It was soon realized, however, that fluidization on this scale would require prohibitive quantities of sulfur trioxide and necessitate an elaborate arrangement to insure uniform gas feed distribution for fluidization.

Eventually a reactor inside diameter of 0.4 inch, or as close

thereto as possible, was decided upon. This would make possible the consumption of reasonable quantities of sulfur trioxide, would make the fluidizing, heating, and recovery operations practical with conventional laboratory equipment, and would result in an experimental apparatus that would fit inside a standard laboratory ventilation hood.

This scale of operation justified expectations, but introduced predictable disadvantages. Most important, the phosphate rock sample size now became a maximum of about six grams, which meant that a high yield was necessary for analytical purposes. The other major drawback was the difficulty of temperature control on such a relatively small scale, where the mass of the system was in high ratio to the throughput. The sensitivity of the vacuum arrangement was also increased due to the relatively small system volume. Reactor plugging became a problem. Several other minor problems were also introduced by the reduced scale of operation.

3. Selection of Materials of Construction

An all-glass reaction system is the ideal situation for this process. Qualitative effects can then be observed more easily, and there are no difficulties with thermal expansion differentials from piece to piece.

All fixed-bed reactors except those employed for high temperature experiments were manufactured from glass and joined to glass connectors and vessels. However, all attempts to produce an operable glass fluidized-bed reactor were unsuccessful. The major obstacle was the difficulty in mounting the fluidizing screen; a structural weakness at this point could not be avoided. Only two fluidized experiments were

conducted in glass reactors, but they were valuable for the information they provided on the qualitative features of sulfur trioxide fluidization (see Chapter III).

A metal fluidized bed was necessary, and grade 316 stainless steel was selected because of its availability and good corrosion resistance. Joints were also available in this material. The screen was likewise fabricated from 316 stainless steel.

All other process vessels that contact sulfur trioxide were made of glass, except for lengths of copper and tygon connecting line downstream of the bubbler trap, where the sulfur trioxide concentration was decreased. Pyrex was the standard grade of glass for this investigation.

The steam system was copper. Teflon was used at several points in the system; for example, all stopcocks used in the investigation were Teflon; sleeves of Teflon were used over the glass joints at both ends of the reactor; a Teflon vent line was used with the sulfur trioxide distillation system employed with fixed-bed systems (see above); and other short connecting lines in contact with sulfur trioxide were of Teflon. After a period of use, Teflon was always badly charred by contact with sulfur trioxide, but was not deformed or corroded.

Sauereisen cement was used to fix thermocouples in place in the fluidized-bed reactor. Sauereisen proved to have excellent refractory properties and excellent corrosion resistance. However, it was a poor dielectric and could not be used to shield heated metal parts from the nichrome windings.

Pyrex wool was used extensively for plugs. It was used to position the charge in fixed-bed arrangements (see above), to filter particles of

phosphate rock at the disengager exit, and to perform filtering functions wherever acid mist was encountered, as described above.

C. Laboratory Facilities

1. Experimental Arrangements

Original Laboratory Arrangement. The experiments of this investigation were originally conducted in a standard laboratory hood made available in the Industrial Products Branch of the Engineering Experiment Station by the generosity of Mr. W. H. Burrows. This hood is approximately 24 inches deep, 47-1/2 inches wide, and 55 inches high, with a frontal access opening 43 inches wide by 31-1/2 inches high. A safety glass door slides up and down to provide shielding. A supporting frame of wood and perforated angle iron (Handy Angle) was constructed in the hood to hold the apparatus.

After several months of experimentation, the investigation outgrew the space available in these quarters. In addition, the ventilation here was barely adequate for safety, and utilities were inadequate.

Specially Constructed Arrangement. A specially designed, high-ventilation hood was constructed for this investigation. The overall height is 7 feet 7-1/2 inches, the operating area is 59-1/2 inches high, 41-1/2 inches wide, and 24 inches deep. The base is constructed from an old laboratory table with transite top, and the sides and roof are plywood. The doors are plexiglass. These doors do not provide complete shielding, but they shield the experimenter at the shoulder and head level, and they provide an enhanced draft when closed.

The ventilation opening of the hood is at the experimenter's left, and measures 22 inches in height, 12 inches in width. Ductwork leads from

this opening to a fan driven by a one-horsepower electric motor. The draft from this arrangement was a great improvement over the laboratory hood, and provided safety in the most severe upsets encountered.

Another improvement of this arrangement was the availability of running water in a sink immediately behind the experimenter. Two windows close by were likewise very advantageous for ventilation.

2. Auxiliary Laboratory Support

Throughout the investigations the laboratories of the Industrial Products Branch of the Engineering Experiment Station were available for auxiliary requirements such as analysis, and for materials and equipment not available from the School of Chemical Engineering. Late in the investigation, the chemical process laboratory under the directorship of Dr. G. L. Bridger of the School of Chemical Engineering became available for auxiliary assistance to the investigation.

CHAPTER III

EXPERIMENTAL PROCEDURE

A. Fixed-Bed Experiments

1. Gas Contact Experiments

These experiments were almost entirely exploratory, and therefore the arrangement was seldom exactly the same. The charge of phosphate rock was held in glass tubes of diameter from 0.4 inch to 1.5 inches inside diameter, usually held in place by plugs of Pyrex wool, although in some vertical arrangements the upper surface of the charge was free. The reaction tube was directly connected to the oleum boiler by tubing several inches in length. The arrangement was vented either to atmosphere or to a condenser and receiver, but the sulfur trioxide was not usually measured.

Time of contact was not a critical factor in these experiments, so a valve arrangement for admission of sulfur trioxide was not employed. Heat was provided as described in Chapter II, either at constant temperature or over a range of temperatures. Sulfur trioxide was removed after reaction by heat and by addition of sweep nitrogen or air at a point between the boiler and the charge.

Water was added by dripping through a tube above the charge, or in the form of steam by insertion of a tube below the charge, which delivered steam from a boiler.

The time-temperature gradient under constant heating voltage was measured in several experiments in the search for exothermic effects. In

this case the heater was set at constant voltage, and temperature was measured at regular intervals.

2. Liquid Contact Experiments

In these experiments the charge of phosphate rock was positioned downstream from an oleum still and water-cooled condenser, in order to receive condensed liquid sulfur trioxide. In most experiments the charge was held in vertical position by plugs of Pyrex wool, but in some experiments the upper surface of the charge was free.

The procedure consisted of adjusting the temperature of the charge as desired, then beginning production of sulfur trioxide by inducing boiling of oleum. Visual observation was necessary to decide when the sulfur trioxide had penetrated completely through the charge.

3. High Temperature Experiments

A small number of experiments was conducted at temperatures in the neighborhood of 800° C. The procedure consisted of placing a charge of about two grams of phosphate rock in the center of a horizontal 1/2-inch steel tube about two feet long, then heating the charge to desired temperature by means of a tubular furnace of folding design, and finally introducing sulfur trioxide or dioxide. The charge was not held by plugs of glass wool in this case, and care was taken to insure a space above the charge so that gas flow would not dislodge the phosphate rock.

A thermocouple was inserted into the reaction tube at the position of the charge and held in place by Sauereisen cement. Since the bore of the furnace was larger than the diameter of the reaction tube, asbestos tape was wrapped around the tube at both ends of the furnace in order to conserve heat.

The gas stream was introduced by a glass tube connected to the oleum boiler or the sulfur dioxide cylinder, as the case might be. An exact fit was not sought because of thermal expansion problems, but an effort was made to exclude air by tilting the reactor tube and assuring that gas flowed outward around the inlet joint. The outlet was vented to the atmosphere.

Maximum temperature was sought in these experiments, so the furnace was heated to 110 volts AC without temperature control and allowed to achieve steady state. Gas throughput was measured only with sulfur dioxide.

4. Experiments with Phosphoric Acid and Sulfur Trioxide

These experiments were designed to contact liquid phosphoric acid with liquid sulfur trioxide at various temperatures, to ascertain whether phosphorus oxide could be liberated. The phosphoric acid was held in the base of test tubes or small boiling flasks, which were heated by nichrome windings, and liquid sulfur trioxide was added dropwise from a graduated receiver downstream of an oleum still and condenser.

When the desired temperature was reached, sulfur trioxide was added a drop at a time, at intervals determined by the resultant fuming. The top of the reaction vessel was sealed by rubber stoppers, which often caused black fluid to drip into the charge of phosphoric acid. An opening in the insulation was maintained so that the state of the phosphoric acid could be observed. Temperature was measured by a thermocouple inserted into an indentation in the reaction vessel.

B. Fluidized-Bed Experiments

1. Operations Preliminary to Contact

Assembly of Apparatus. The reaction system was disassembled between individual runs for removal of sample from the reactor and recovery of sulfur trioxide from the absorption train. The reactor and disengager were also washed to remove phosphate rock that remained. Accordingly, the reactor required reattachment of electric leads and replacement of insulation before each run, and the disengager was also reinsulated and sometimes rewound with nichrome each time. Reactor heater windings were replaced after about eight runs, when the condition of the asbestos paper made this necessary.

The reactor was held in vertical position by an adjustable metal strap, held in place by a clamp at the supporting grid. The disengager was supported only by its two joints. Consequently, much of the weight of the reaction assembly rested on the connecting line from the oleum boiler, below the reactor.

Charging. The reactor was almost always charged cold, since otherwise there was risk of phosphate rock sticking to the wall. Sand was charged in approximately the same volume as the six-gram charge of rock, but was not weighed. After the sand, the rock was charged. During charging, the reactor was in its assembled position, and the solids were charged through a funnel inserted in the top. Then the disengager was placed in position and joined to the bubbler trap, and the tubing to the vacuum gauge was connected to the disengager.

The oleum was replaced after an average of about four runs. This operation always took place with maximum safety precautions: ventilation

fan operating, full protective clothing, and presence of a second person.

Heating. With the assembly complete, the constant-voltage winding of the reactor was set at 30 volts and water was allowed to flow past the aspirator in order to induce light fluidization. While the reactor was heating, it was necessary to check the fluidization characteristics of the charge continually in order to assure that no sticking occurred. During this time, the oleum in the boiler below the reactor was brought to boiling and flow of steam (if used) through the steam system was initiated. In early experiments, before the sulfur trioxide valve was introduced, the oleum was brought to boiling only after full temperature and fluidizing conditions were established.

The two controlled heater windings on the reactor were next turned on. The reactor was heated to 360°C and allowed to reach a steady condition. If steam was to be introduced, it was introduced at this time by connecting the superheater to the reactor (see Figure 8).

Initiation of Fluidization. During heating, when the aspirator was turned on, air was drawn through the still open steam inlet and through the stopcock shown in Figure 8 between the reactor and the sulfur trioxide valve. It was very important to have the disengager fully heated during this preliminary fluidization, because otherwise a slight amount of rock would stick to the disengager wall. This would later become the nucleus for additional sticking during the reaction and would sometimes lead to shutdown due to severe sticking.

The vacuum required for this preliminary fluidization was too small to register on the vacuum gauge, i.e., was significantly below one inch of mercury.

2. Conduct of Gas-Solid Contact

Introduction of Sulfur Trioxide. With the reactor at desired temperature and steam (if desired) flowing, sulfur trioxide was introduced by simultaneously (1) opening the valve, (2) closing the oleum boiler vent condenser, and (3) closing the air inlet stopcock below the reactor. The immediate next step was to adjust the fluidization by regulating the flow of water past the aspirator.

Fluidization Criteria. The fluidization was adjusted by visual inspection of the conical plume of fluidized solids at the top of the reactor. Under best conditions, this plume would be about one inch high, oscillating slightly.

Pressure drop was considered as a criterion for fluidization, but was rejected because of the practical difficulties involved and because constant visual inspection of the reactor is required anyhow.

Temperature Measurement and Control. The reactor temperature was measured at intervals during reaction by switching the reactor thermocouple outputs to the millivolt potentiometer and reading temperatures there. This operation was conducted rapidly during a moment when the power relay of the controller was open, i.e., when control would not be disturbed. Other temperatures were measured when convenient.

As discussed in Chapters IV and V, the usual operating temperature was around 325° C. Because of difficulties associated with operation below the boiling point of sulfuric acid, temperature control in this region is crucial to steady conduct of the reaction. The usual procedure consisted of heating the reactor to 360° C before introducing sulfur trioxide, then lowering the temperature to the desired point either before

or during introduction of sulfur trioxide. The latter method is more conducive to stability, but opens questions concerning the actual time of effective reaction.

Another method of temperature control that proved successful consisted of employing a thermal gradient in the reactor. The lower section (base) at the point of thermocouple entry, for example, would be at the desired operating temperature, while the upper section would be at 360°C or above. Results obtained with this method agreed with results obtained at uniform temperature. This method was occasionally employed to combat sticking at the reactor-disengager joint, which is a critical point because of the difficulty of effective insulation.

The center temperature of the reactor was not always recorded. As expected, it tended to be higher than either the upper or lower section temperature, but at steady operation it would agree closely with the others. The temperature of the steam or steam-air mixture was 360°C or above during reaction, in order to assure that no condensation occurred at the inlet point. Early attempts to introduce steam and/or air at lower temperatures encountered difficulty due to condensation of liquid in the reactor.

The disengager was also held at 360°C or above, to discourage condensation. Any condensation in the disengager was a threat to smooth operation. In the exit region of the disengager, it was not always possible to hold this temperature level, and any particles that reached this region were prone to stick to condensed liquid on the wall. This effect was occasionally a cause of early shutdown, if the Pyrex wool plug at the disengager exit became blocked. At all times this was the source of

greatest product loss.

Vacuum. The reaction system was always operated under light vacuum, since this proved to be the easiest method of adjusting the flow of sulfur trioxide. Whenever a positive pressure of sulfur trioxide developed, there was danger of leaks.

In order to prevent sunction of undesired air into the reactor, care was taken that all joints of the oleum boiler were moist with liquid acid, and the reactor joints were protected by a Teflon sleeve between inner and outer parts. Leakage at points downstream was not a problem.

Upset Criteria. The most frequent reason for premature shutdown was loss of fluidization. There are several possible causes:

- (1) blocking of the Pyrex wool plug at the disengager exit (see above);
- (2) sticking of phosphate rock in the disengager, with the result that moist powder returns to the reactor and plugs the exit throat;
- (3) condensation of liquid in the base section;
- (4) loss of heat, due to burned-through connections, inadvertent controller shutoff, or short circuits.

Loss of fluidization is immediately observable in the lower section of the disengager, which is kept free of insulation for this purpose. If the disengager exit is blocked, fluidization can sometimes be retrieved by increasing the vacuum.

3. Shutdown Operations

Postheat. When the supply of sulfur trioxide is shut off, the fluidization is continued with air until the reactor is free of the

reactant gas. It is necessary to raise the temperature above 340°C for this operation, or else the product will be observed to give off fumes and take on a moist appearance, when the phosphate rock is removed. This postheat procedure requires three to five minutes.

Sample Removal. The reactor was disconnected from the assembly after the run had been completed and the charge was poured on an 80-mesh screen. Shaking the screen separated the reacted rock, which passed the screen, from the sand, which was retained.

Cleanup. The reactor interior is the first concern after completion of a run. If there is sticking to the walls, doubt is cast on the assumption of uniform fluidization and reaction. Therefore an immediate inspection and washing of the reactor is mandatory.

The disengager is next washed to recover acid, and the downstream lines and vessels are similarly treated. The washings are collected and aliquoted for analysis.

C. Analytical Methods

1. General

Present Status of Phosphate Rock Analysis. Although phosphate rock is a member of the apatite family, which has so many members, as discussed in Chapter I, the difficulty of assigning any formal stoichiometry is reflected in the empirical nature of the analytical methods used in its analysis. The Association of Official Agricultural Chemists (AOAC) has long been the greatest influence on the development of analytical methods in the fertilizer industry in the United States, and the Association has developed "official" methods for P_2O_5 ⁵³ and sulfur⁵⁴ in fertilizer, but not for fluorine or calcium, to name the four principal

constituents of phosphatic fertilizers. Fertilizer constituents which are not the subject of official methods are determined as elements (or oxides, in the case of metals and carbon) by various methods of wet quantitative analysis.

Methods. A comprehensive discussion of phosphate evaluation up to 1953 is given by Jacob and Hill.⁵⁵ Their conclusions are still largely valid, the major exception being the growing realization that the alkaline ammonium citrate test is probably a better index of crop response to phosphorus than the neutral ammonium citrate test. Jacob and Hill address their review entirely to wet quantitative analytical methods, in relation to types of phosphate fertilizer and crop response.

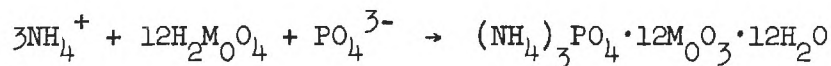
Other methods have not been applied to fertilizers on a large scale. X-ray diffraction, for example, can provide quantitative measurement of undegraded (i.e., unavailable) crystalline apatite in phosphatic materials, but there is only one major published study related to fertilizers.⁵ Infrared methods likewise are unexplored.

Chromatography is another possible analytical tool for estimating compounds. To date, no studies on fertilizer materials seem to have been published. There are several investigations on polyphosphoric acids (see for example the review by Van Wazer⁵⁶), and these methods might be of particular interest in studying products resulting from investigations similar to the present study. The fate of the phosphorus content of the reacted phosphate rock could perhaps be studied closely by chromatography.

2. Analysis for P_2O_5 by AOAC and Related Methods

Official AOAC Methods. The best known and most often used method of phosphate analysis is the volumetric method, based on analysis of the

yellow ammonium phosphomolybdate precipitate resulting from the following reaction:⁵⁷



The three other official methods include the spectrophotometric method based on the same reaction, the magnesium ammonium phosphate gravimetric method, and the quinoline molybdate method. It should be remarked, however, that the volumetric method of analysis has come under sharp attack,⁵⁸ because the nature of the precipitate is not as well known as the equation implies. It is merely known that orthophosphate is quantitatively precipitated, and responds quantitatively to sodium hydroxide titration, in the absence of excessive interfering materials. A defense of the volumetric method has also been published.⁵⁹ Details of the methods can be found in the Official Methods of Analysis.

Method of This Investigation. For this investigation the classical volumetric method involving sodium hydroxide titration of the ammonium phosphomolybdate precipitate was employed by this author.

Two slight modifications were introduced. Instead of caustic of 0.324 normality, which is equivalent to one milligram of P_2O_5 per milliliter, a strength of 0.300 was used because of the difficulty of three-figure volumetric measurement with the equipment available. The other modification consisted of the use of 0.100 N hydrochloric acid for back-titration of samples carried past the NaOH-molybdate end point; this latter end point is slow to develop, and it proved much easier to overrun it and then titrate back. Both modifications are acceptable to AOAC participants.

The simplicity of the volumetric method makes it still the most widely used method among laboratories of the author's acquaintance. It seems likely that modifications will be adopted to improve the accuracy of the method. Complexing of ammonia with formaldehyde, using excess nitric acid to eliminate sulfate interference, using a glass-fiber filtration pad, and using a mixed indicator are the principal improvements suggested. By these means the accuracy may be improved by about three per cent.⁶⁰

Method Employed by the Tennessee Corporation. Many of the analyses reported in the present investigation were performed by the Tennessee Corporation in their College Park, Georgia, laboratories, directed by Mr. W. D. Warriner. The method used by this organization is the official AOAC quinoline molybdate method.

The Tennessee Corporation prefers this method because of the fewer possibilities of error. It has been termed "idiot-proof." The results of this method, however, are intrinsically only slightly divergent from those of the volumetric method,⁶¹ and these differences are within the accuracy required for the present study.

Citrate Solubility. The solubility of fertilizer materials in neutral ammonium citrate solution is the standard United States method of correlating the water-insoluble P_2O_5 content of fertilizers with expected crop response. The background of this "availability" determination was discussed in Chapter I.

In general, fertilizer materials are extracted with water, then with neutral ammonium citrate at 65° C for one hour with agitation. The sum of both solubilities (weight per cent) is then termed the "available"

P_2O_5 . The comparison of this figure with total P_2O_5 determined from digestion in strong oxidizing acid is the most common index of fertilizer phosphate values. The present investigation has relied extensively on this comparison.

In practice, citrate-insoluble P_2O_5 is usually determined by digestion and total analysis of the residue from citrate extraction. Most laboratories prefer to determine total P_2O_5 separately, but it is permissible to determine water solubility, citrate solubility, and citrate insolubility from a single sample, then to add these for determination of total P_2O_5 . This procedure was occasionally used in the present investigation when sample size was small.

Alkaline Citrate (Netherlands) Method. The relation of this method to P_2O_5 availability and crop response has been discussed in Chapter I. The latest variation of this method, and the one that seems destined to prevail in the United States, was recently set forth by Brabson and Burch.⁶² The major difference among existing alkaline citrate methods is the extraction time or temperature, which bear an inverse relation. For example, Brabson and Burch recommend two hours at 65° C, while the Netherlands standard calls for 15 hours at room temperature plus one hour at 40° C.⁶³

The "standard" product of the present investigation (see Chapter IV) was analyzed by the procedure of Brabson and Burch in the laboratories of the Tennessee Corporation; data are given in Table 12.

3. Analysis for Other Major Constituents

Sulfur. This element was determined according to the method described by Barker,⁵⁴ with omission of the step in which bromine is added

to oxidize elemental sulfur. In outline, the method consists of precipitating sulfate by the familiar method of adding barium chloride, and determining the sulfur gravimetrically as barium sulfate.

Fluorine. Fluorine is determined by the method described in standard textbooks,⁶⁴ involving removal of F as fluorosilicic acid, followed by thorium nitrate titration to a color comparison with an alizarine lake. There is no official AOAC method for fluorine. Comparison of the determinations reported for the several blanks (Table 1) casts doubt on the consistency of the fluorine determination.

Calcium. This element is determined by gravimetry as CaCO_3 after calcium oxalate precipitation and firing, as described by Snell and Biffen.⁶⁵ There is presently no official AOAC method for calcium. The method is regarded as highly accurate.

4. Measurement of Gaseous Reactants

Sulfur Trioxide. It has already been described how acid is recovered from the absorption train, disengager, and lines of the assembly after reaction. The most serious concern is to be certain that all the sulfur trioxide is absorbed in the vessels designed for the purpose.

The criterion for complete recovery was the absence of acid mist in the vacuum flask at the end of the vacuum line, immediately ahead of the aspirator. Under normal steady conditions, mist did not appear there, being absorbed completely in the three bubblers. Even when acid mist filled this vessel, most of the acid which entered this vessel was probably absorbed by the water which was maintained in the base of the vessel. The volume of this vessel (two liters) permitted gas to flow at a relatively slow velocity, which would permit appreciable acid recovery.

Steam. Steam input at a known rate was always assured by use of the metering pump. This pump was calibrated and found to deliver water at the design rate over the entire range (0 to 5 ml per minute). Because of lag in the length of the boiler and superheater, a known rate was only safely assumed under steady-state conditions.

Air. Air was drawn from the compressed air line through a metering valve, which reduced the pressure from 150 psig to essentially atmospheric. A rotameter, No. 3202, size No. 2, purchased from the Cole-Parmer Instrument and Equipment Co., was used to measure air flow rate. The rate was variable from 0 to 2000 ml per minute (air at STP). The most common rate was 280 ml per minute, which coincided with a reading of 20 on the rotameter. Oscillations around this point were on the order of ten per cent.

5. Extraction Procedures

The products of this investigation have not been regarded as materials directly suitable for fertilizer use. However, they are potentially useful in combination with other materials or as sources of extractable phosphorus for solutions. Accordingly, a series of extraction experiments was designed to explore the properties of the reaction products. The types of products studied included (1) the standard product (see Chapter IV, section B) of the fluidized-bed series of experiments, and (2) the products of three different experiments (experiments 11 and 13 of Table 2, and experiment 26 of Table 4) where the phosphate rock had been exhaustively contacted with sulfur trioxide.

A total of three series of extractions was conducted. The standard product was subjected to extraction by several solutions of salts which

are related to fertilizer components--chiefly ammonium and potassium salts--and was also subjected to extraction by sulfuric acid of two concentrations. The exhaustively reacted samples were subjected to extractions with sodium hydroxide solutions of two compositions, ammonia solutions, and a very dilute hydrochloric acid solution intended to promote hydrolysis.

These three series of extractions are described below.

Salt Solution Extraction of Standard Product. The aqueous solutions chosen for extraction of standard product were as follows, always in proportions of 100 ml of solution per gram of sample:

ammonium carbonate (saturated at 25° C)

ammonium nitrate (saturated at 65° C)

ammoniacal ammonium nitrate (70 parts of 60% NH_4NO_3 solution plus 30 parts of 32% NH_3 solution) ³

ammonium nitrate-urea (45% NH_4NO_3 , 35% urea, 20% H_2O , at 65° C) ³

potassium carbonate (a) saturated at 25° C
(b) saturated at 65° C
(c) saturated at 100° C

potassium chloride (saturated at 65° C)

potassium hydroxide (20% solution at 65° C)

sodium carbonate (saturated at 65° C)

water (65° C)

The extractions were conducted in 300-ml Erlenmeyer flasks, with agitation provided by a laboratory wrist-action shaker. The temperature of 65° C, chosen to provide direct comparison with the AOAC citrate-solubility determination, was achieved by a water bath heated by a Meker burner, manually regulated. Extraction time was always one hour.

The extraction with potassium carbonate at 100° C was conducted in a large test tube heated by a nichrome winding, with temperature control provided by a thermocouple connected to a Sim-Ply-Trol controller of the type described in Chapter II.

In all cases, the extract was aliquoted and tested for P_2O_5 by the AOAC volumetric procedure for P_2O_5 . The citrate-soluble extract was aliquoted and digested according to the procedure of Gehrke and Johnson⁶⁶ to destroy the citrate, then analyzed as usual by the AOAC volumetric procedure.

Sulfuric Acid Extraction of Standard Product. On the premise that the standard product of this investigation might be a superior charge for existing superphosphate or triple superphosphate processes, a procedure was devised to test the product's extraction properties with sulfuric acid of 97 and 70 weight per cent concentrations.

The procedure consisted of shaking one gram of sample in a 200-ml flask, in a wrist-action shaker, in contact with 10 ml of 97 or 70 per cent sulfuric acid. This quantity of acid was chosen such that the concentration would not be appreciably diluted by the reaction with the solid. Shaking time was one hour. After shaking, the slurry of acid and solid residue was filtered through glass wool and washed as rapidly as possible until the residue on the filter was free of acid. Both fractions were collected for analysis: the extract for total P_2O_5 analysis, and the residue for citrate-solubility analysis.

Extraction of Exhaustively Reacted Products. The extractions here were limited to sodium hydroxide and ammonium hydroxide solutions, and a weak acid solution (0.001 molar) designed to promote hydrolysis rather

than reaction by substitution. Sample size was one gram per 100 ml of solution. The small quantities of sample available limited the extractions to the following schedule:

| <u>Sample</u> | <u>10% NaOH</u> | | <u>0.5% NaOH</u> | <u>Acid</u> | <u>32%</u> |
|-----------------|-----------------|-------------|------------------|-------------------|----------------|
| | <u>1 hr</u> | <u>2 hr</u> | <u>1 hr</u> | <u>Hydrolysis</u> | <u>Ammonia</u> |
| 11 (Table 2) | x | | | | |
| 13 (Table 2) | x | x | x | | x |
| 26 (Table 4) | x | | x | x | x |

Sodium hydroxide extractions were conducted at 65° C, ammonia extractions at room temperature, and hydrolysis was conducted for five days, during which the sample was held at boiling-water temperature for a total of eight hours. All extractions were conducted with agitation provided by a laboratory wrist-action shaker.

6. X-Ray Diffraction Analysis

Analysis of phosphate rock and the standard product of the investigation was carried out in the X-ray diffraction laboratory of the Engineering Experiment Station, with the kind permission of Dr. R. A. Young, head of the Solid State Branch, and the assistance of his staff.

In brief, the procedure consists of grinding samples to -300 mesh, mounting them in sample holders (sample weight approximately 1 gram), and mounting them in a goniometer. This instrument is a Philips X-ray basic unit goniometer and circuit panel combination, employing Cu K α radiation which is measured by a scintillation counter and recorded on a strip chart. A pulse height analyzer is integral with the assembly.

The chart records diffraction peak heights at various incident angles of the radiation, in a continuous scan, from 0 to 90° of arc. The

angles corresponding to significant peaks can then be converted by means of charts into the equivalent crystalline interplanar spacings corresponding to the measured interference peaks. The pattern of peaks so obtained can then be compared to known X-ray powder diffraction patterns⁶⁷ of various compounds.

CHAPTER IV

EXPERIMENTAL RESULTS

A. Fixed-Bed Experiments1. Sulfur Trioxide and Phosphate Rock

Liquid Contact. These experiments are of special interest for two reasons. First, they are the only experiments in which the maximum degree of reaction between phosphate rock and sulfur trioxide could be consistently obtained, as evidenced by sulfur uptake and lowered total P_2O_5 concentration. Second, they are the only experiments in which the white powder believed to be phosphorus oxide was ever observed as product. Table 2 records the results of this series of experiments.

The maximum degree of reaction obtained is exemplified by experiment 10 of Table 2. In this experiment, a deliberate effort was made to react the phosphate rock exhaustively, by repeated contact with excess sulfur trioxide for an extended time. The result was that total P_2O_5 in the product was 17.5 per cent, the lowest recorded in the investigation, and sulfur content was 14.55 per cent, exceeded by only three experiments (15.60 per cent is the highest S analysis achieved, in experiment 13 of Table 4). Analysis revealed that some of the P_2O_5 was insoluble in aqua regia but soluble in hot 20 per cent sodium hydroxide solution.

Two samples from experiment 10 and one from experiment 11 were heated in a muffle furnace to a temperature above $2000^{\circ} F$ (chosen for reasons explained in Chapter V) and their weight checked at various stages, as recorded in Table 3. The second sample from experiment 10

(fired at 1650° F) contained 10.1 per cent sulfur and 25.45 per cent total P_2O_5 after firing. This points to some loss of sulfur, but no loss of P_2O_5 .

Whenever white powder appeared in this series of experiments, it always appeared between 320° C and 325° C, spontaneously, as a ring of solid on the reactor wall, a distance of a few millimeters downstream from the charge of phosphate rock. In Table 2,* the instances when this white powder was observed are noted.

If exposed to air, the white deposit showed definite hygroscopicity. If allowed to remain in the reactor, the deposit was eventually wet with sulfur trioxide, and lost its integrity. The deposit yielded a positive test with ammonium molybdate, i.e., a yellow precipitate. The amount of the deposit was always small, and was never accurately measured, because of interference from phosphate rock particles and from the preponderance of sulfur trioxide in the system.

Table 2 records only those experiments where data were sufficient for meaningful interpretation, omitting several early experiments which were insufficiently precise for recording. In general the experiments with liquid sulfur trioxide were the earliest of the investigation.

Gas Contact. Table 4 reveals that this group of experiments also was largely exploratory. The white powder discussed above also appeared in a few experiments of this group, but not under predictable conditions.

In general, the product of these experiments is disappointing. The available P_2O_5 (sum of water-soluble and citrate-soluble, by AOAC

*For explanation of the abbreviations used in the tables, see page 113.

definitions) is low, except where initial temperature of contact is so low as to suggest liquid sulfur trioxide as the real reactant. The desired white powder likewise made its appearance in experiments where initial temperature of contact was low.

Experiments 13-15 of Table 4 are of special interest because they were the first to achieve a product with P_2O_5 availability above 50 per cent. They also led directly to the realization that the apparent lower limit of total P_2O_5 , often observed at about 20 per cent, agreed closely with the value calculated on the assumption that all calcium in the rock was converted to calcium sulfate. This point is developed further in Chapter V, along with the question which is immediately raised, namely, what is the fate of the phosphate?

High temperature experiments, nos. 31 and 32, do not yield conversions as good as those reported by Hughes and Cameron.²⁹ However, when those investigators mention "sulfate trioxide," they refer to an equimolar gaseous mixture of SO_3 and H_2O .

2. Sulfur Dioxide and Phosphate Rock

As revealed by Table 5, sulfur dioxide hardly affected phosphate rock in any of the experiments, even at high temperature. It is unfortunate that citrate solubility was not followed more closely, but the fluidized-bed runs reported below confirm this general conclusion.

In the high-temperature experiment, a deposit of white material of nonhygroscopic character, presumably sulfur, was observed at 400° C. This is the range where Hughes and Cameron²⁹ report the same phenomenon. The sulfur uptake by the rock, however, was slight.

3. Sulfur Trioxide and Phosphoric Acid

The series of experiments reported in Table 6 was undertaken to determine whether or not sulfur trioxide would liberate free phosphorus oxide, P_4O_{10} , from phosphoric acid. No white subliming solid was produced in these experiments.

A series of increasingly viscous materials was obtained. These showed a strong tendency to react with the Pyrex reaction vessels at temperatures of about 350°C and above. The normal product was an opaque viscous liquid, and it is likely, on the basis of observation of the vessels, that any solid product results from hot spots at the vessel wall which exceed the recorded temperature of 400°C .

B. Fluidized-Bed Experiments

1. Sulfur Trioxide and Phosphate Rock

Sulfur Trioxide with no Admixtures. As with the entire series of fixed-bed experiments (see Section A, above), the experiments with sulfur trioxide in the fluidized bed were largely exploratory. When experiment 1 (Table 7) was conducted successfully after many false starts, the results were disappointing: no evidence of free P_4O_{10} in spite of good gas-solid contact; little or no loss of fluorine; no enhancement of citrate solubility.

The series of vacuum runs, nos. 2-7, was then undertaken in the hope of reducing the total pressure below the vapor pressure of P_4O_{10} , and causing the P_4O_{10} to sublime at a greatly enhanced rate. Once more there was no P_4O_{10} observed, and little conversion in the majority of cases, but it was noticed that presence of leakage around the reactor

correlated with conversion. Two possible explanations of this were (1) moisture in the leakage air and (2) condensation of sulfur trioxide to liquid droplets, or to droplets of sulfuric acid if moisture was sufficient.

Experiment 8 sought to isolate the effect of moisture. It was considered a great success (conversion of P_2O_5 :89.2%) but it could not be reproduced. However, experiment 4 is very similar. These results will be studied with regard to possible mechanisms in Chapter V.

Experiments 6, 7, 10, 11, and 18 demonstrate a consistent pattern of P_2O_5 availability rising to 8-9 per cent, independent of contact time. This phenomenon is also examined closely in Chapter V.

The reaction temperatures of the experiments reported in Table 7 were chosen around 325° C, in view of the significance of that temperature for appearance of free phosphorus oxide (see Section A). Later on, a temperature of about 350° C was found to be more significant, as described in Chapter V. Table 7 testifies to the difficulty of stable operation in this general temperature region.

Sulfur Trioxide and Air. This series of experiments (Table 8) was an outgrowth of the vacuum experiments with sulfur trioxide alone (see above). It seemed possible that air moisture might be sufficient to provide the water necessary for successful conversion of the phosphate rock, since the influence of small amounts of water had been noticed from the very earliest days of the investigation (see Chapter I).

The absence of fluorine and sulfur analyses in these experiments indicates the increased tempo of the investigation, as increased P_2O_5 availability became the major process criterion. On balance, none of

these experiments was judged significantly better than those with sulfur trioxide alone. Several experiments, with available P_2O_5 about 8.5 per cent, are very reminiscent of the experiments with SO_3 alone.

Sulfur Trioxide and Steam. These experiments are largely distinguished by their inherent instability, as revealed by Table 9. Upsets are the rule rather than the exception. The reported experiments include only those in which fluidization was established for any length of time at steady state, and in which the product was largely free of sticking to the reactor and disengager walls.

Only one experiment of the series was carried through to 30 minutes of steady operation. In this experiment (no. 7, Table 9) the available P_2O_5 was 46 per cent of the total in spite of somewhat reduced sulfur trioxide throughput. In experiment 5, for example, conversion was 60 per cent, achieved in two-thirds the time. Experiment 9 is even better, but the results are of doubtful validity due to sticking of product in the reactor.

Sulfur Trioxide, Steam, and Air. This series was generally the last to be performed in the investigation. By this time the importance of water vapor had been realized, and air had been found useful to increase the stability of the fluidized system. Likewise the techniques necessary for introducing these gases had been improved.

The ultimate capabilities of the SO_3 - H_2O -air system were soon established, as revealed by experiments 2, 3, 4, and 7 of Table 10. Within five minutes, about half (or slightly better) of the P_2O_5 content of the phosphate rock can be converted to available form. If too much air is present, the results are much poorer (experiment 1), while the

ratio of water to SO_3 seems less critical. Increased contact time does not improve the conversion.

The minimum contact time seems to be about three minutes (experiment 8). However, any contact at all results in some conversion (experiments 9 and 10), and it should be mentioned that the measured time is the time between opening and closing of the admission valve (see Chapter III), whereas sulfur trioxide is always present in the system for a minute or two after the valve is closed.

Experiments 7 through 13 are recognizable as timed runs under closely similar conditions. For the final series of experiments, a set of conditions was adopted as standard, and runs conducted until the accumulated product amounted to about 40 grams. These conditions were modeled after those of experiments 3 and 4 and included the following:

water rate: 0.1 ml/min (liquid)

air rate: 250 ml/min (gas at STP) line air at 6%
relative humidity

temperature: $325 \pm 5^\circ \text{C}$

time: 15 min.

postheat: 360°C for 5 min.

The results from samples 14, 15, and 16 show that the standard conditions produced the expected product, featuring 53 to 55 per cent of the P_2O_5 present in available form. A curious feature is the disagreement in sulfur analysis between 14 and 15, both of which are carefully proportioned composite samples of the series of standard experiments.

2. Sulfur Dioxide and Phosphate Rock

The experiments reported in Table 11 present a clear picture of unsuccessful attempts to convert phosphate rock into an available form

of P_2O_5 by means of contact with sulfur dioxide. Up to 60 minutes of fluidized contact proved insufficient to increase the P_2O_5 availability more than 1 to 2 per cent. The water solubility of the product is especially poor, which is interesting by comparison with the results of Hughes and Cameron,²⁹ discussed in Chapter I (see Chapter V for further explanation).

Experiment 2 is an apparent exception to the general pattern, but the low sulfur uptake, and the citrate solubility essentially unchanged from that of raw rock, suggest strongly that an analytical error has occurred.*

Experiment 10 is suggestive of the influence of water in the form of rock moisture (see by comparison no. 8, Table 7).

C. Extraction Experiments

1. Salt Solution Extraction of Standard Product

All but one of these experiments with the standard product result in an availability (solvent-soluble plus citrate-soluble) less than the availability measured by the AOAC and Netherlands methods, according to the results in Table 12. Potassium sulfate is the exception, and is therefore the most effective extractant of the series. In general, the extracts of $pH < 7$ (i.e., acid solutions) are the most effective (potassium and ammonium sulfate) and the basic solutions generally reduce the available P_2O_5 , as does hot water.

The four potassium carbonate experiments were intended to check the effect of temperature. Overall, very little effect is evident.

* Analysis was not performed by the author.

2. Sulfuric Acid Extraction of Standard Product

These results are reported in Table 13. They show that the phosphate values of the standard product are significantly less extractable than those of the raw rock.

If the P_2O_5 content of extract and residue are added, the total approximates the total P_2O_5 reported for the standard product (~24%). However, the citrate-soluble portion, which measured about 12 per cent of the standard product, is not entirely separated into either fraction, although most of it is evidently extracted by the acid. This raises the question of what comprises the remainder of the residue, which is neither acid-soluble nor citrate-soluble. This question is examined in Chapter V.

It was observed that the standard product did not foam at all when contacted by the acid, whereas the raw phosphate rock foamed vigorously.

3. Extraction Experiments with Exhaustively Reacted Samples

In these experiments, as described in Chapter III, samples from three experiments featuring prolonged contact of phosphate rock with sulfur trioxide were subjected to extraction with sodium hydroxide, ammonium hydroxide, and very dilute hydrochloric acid. As discussed in Chapter V (below), the P_2O_5 in such samples is believed to be present in the form of highly polymerized phosphorus oxide in infinite-sheet form.

The supposed acid nature of this material suggested alkaline extraction. On the other hand, based on evidence summarized by Van Wazer,⁶⁸ hydrolysis by solutions of $pH < 7$ was suggested. The extraction experiments of Table 12 likewise pointed to the advantages of acid medium.

The results are reported in Table 14. An immediate conclusion is that ammonia is without effect. Likewise, little encouragement is

offered by sodium hydroxide solutions. Acid hydrolysis, however, looks very promising; more than half the total P_2O_5 is extracted, and in fact the extracted P_2O_5 is about the same as the percentage of citrate-soluble P_2O_5 .

D. Material Balance

The two experiments conducted for the purpose of obtaining a formal material balance are reported in Table 15. Both experiments were conducted under standard conditons, with the exception that experiment 1 lasted only ten minutes instead of fifteen.

The figures of Table 15 were obtained by the procedure described below. Methods of analysis have been described in Chapter III.

Original Charge. Percentages are average of phosphate rock analyses conducted by the Tennessee Corporation and the author (Table 1).

Reacted Charge. Percentages were obtained by the Tennessee Corporation. Total weight was obtained by the author.

Disengager Solid Residue. Solids in the disengager were washed free, filtered, and recovered from the filter paper after drying. Weight and P_2O_5 analysis were obtained by the author.

Disengager Filtrate. The filtrate from the step immediately above was collected, made up to volume, aliquoted, and analyzed for P_2O_5 (by the official AOAC volumetric method) and for sulfuric acid (by phenolphthalein-indicator titration with NaOH).*

Absorption Train. The absorbing liquid solutions were collected, made up to volume, and analyzed for P_2O_5 and for sulfuric acid.

* Sulfuric acid titrations were corrected for presence of H_3PO_4 , with allowance for the fact that only two H^+ ions of the H_3PO_4 appear at the phenolphthalein end point.

Entrained solids recovered from the disengager were insufficient in amount to permit analysis for calcium, fluorine, or sulfur. The liquid portions (last two above) are not capable of analysis for fluorine or calcium, because of sulfuric acid interference.

Recoveries of various constituents according to the figures of Table 15 are as follows (weight per cent):

| <u>Experiment</u> | <u>P₂O₅</u> | <u>Ca</u> | <u>F</u> |
|-------------------|-----------------------------------|-----------|----------|
| 1 | 92 | 96 | 66 |
| 2 | 90 | 96 | 79 |

It should be noted that the recorded P₂O₅ recovery is based entirely on analysis, while the Ca figures depend on an assumption regarding the fate of calcium in solids which were entrained into the disengager. Some loss of fluorine has definitely occurred in both experiments.

The P₂O₅ analyses in particular indicate that some product has been lost. Possible sources of loss include (1) holdup of solids in reactor; (2) handling losses associated with removing solids from the reactor, weighing, etc.; (3) washing inefficiencies in the case of recovered liquids.

The high calcium recovery is possibly suspect in view of the P₂O₅ recovery. Since some Ca probably washed into the filtrate from the disengager solids, the estimate of Ca recovery would be expected to be conservative. Accordingly, the most likely source of error would seem to be the original analysis of Ca in the phosphate rock. Reliable calcium analysis depends on a muffle furnace which is capable of reliable control, and it is possible that the furnace available to the author was prone to overheating and consequent decomposition of the

calcium carbonate on which analysis depends.

E. X-Ray Diffraction Analysis

The measured results of the X-ray diffraction analysis are reported in Table 16. The major diffraction peaks are reported, with their position given in terms of crystalline planar spacing equivalent to the measured angles, and their size given as intensity ratio, I/I_1 , according to ASTM definitions.⁶⁷ The pattern for fluorapatite is also given for comparison.

The raw phosphate rock pattern shows great similarity with that of fluorapatite, except that spacings disagree by about two per cent (measured spacings lower than reported spacings⁶⁷). The standard product, however, evidences significant changes from phosphate rock. Major peaks have all declined, and the peak at $d = 3.4241 \text{ \AA}$ now predominates.* Several new peaks have also appeared.

A search through patterns reported in the literature indicates that the enhanced peak agrees closely with the single major peak reported for calcium sulfate (anhydrite). The other new peaks, however, cannot be easily identified.

*In fact, this peak greatly exceeds in size any peak in the raw material.

CHAPTER V

DISCUSSION OF EXPERIMENTAL RESULTS

A. Introduction

The objective of this chapter is to explain the results reported in Chapter IV. For this purpose, the material balance derived from the analysis of reaction products is fundamental. With these figures, plus the accumulated knowledge of phosphates due to previous investigators, and other measurements obtained from the investigation, an explanation of the processes taking place between phosphate rock and sulfur oxides can be advanced.

B. Material Balance1. Calcium Balance

Of the major elements present in phosphate rock, calcium is the least likely to be lost by conversion to volatile compounds. Therefore it was expected that calcium would provide the most reliable index to gain or loss of weight by the sample as a whole.

The first indication of the correctness of this expectation was provided by fixed-bed experiments, in which no materials were observed to volatilize (except P_4O_{10} in certain cases, as discussed below). If it is assumed that all original calcium is still present in the product of these experiments, then the material balance for P_2O_5 and S, as shown above, accords well with a postulated reaction mechanism in which all absorbed S appears as $CaSO_4$.

The material balance experiments recorded in Table 15 reinforce the assumption that no Ca is lost. Even though the results of this table are subject to error, as described in Chapter IV, it is clear that Ca is conserved, within the limits of analytical accuracy.

Finally, the results of X-ray diffraction analysis as reported in Table 15 strongly support the CaSO_4 hypothesis.* After reaction, the recorded diffraction peak corresponding to a lattice spacing of 3.4241 \AA shows a very great increase, to a height much greater than any other peak of raw material or product. This peak agrees closely with the major peak reported for CaSO_4 (anhydrite) at $d = 3.498 \text{ \AA}$ (discrepancy $\sim 2\%$). Major peaks previously present in the raw material (phosphate rock) are all reduced in height. From these results it is permissible to postulate that the calcium in the phosphate rock has been converted to CaSO_4 to a significant extent.

2. Sulfur Balance

As explained above, the observed increase in S on the part of reaction products is believed due to formation of CaSO_4 . In fixed-bed experiments, where no sample is displaced and no significant volatilization observed, assumption of SO_3 uptake equivalent to the total Ca content of the phosphate rock, and reacting solely to form CaSO_4 , leads to the following calculated compositions** (basis: Table 1):

* These results were obtained with the standard reaction product from a fluidized bed. However, the conclusions should be applicable to fixed-bed results, because the temperatures, reactants, and times are comparable.

** Also assumed: no loss of F by volatilization.

| <u>Constituent</u> | <u>Original Content</u> (wt %) | <u>Final Content</u> (wt %) |
|-------------------------------|-----------------------------------|--------------------------------|
| Ca | 40.9 | 22.5 |
| P ₂ O ₅ | 33.9 | 18.7 |
| S | 0.37 | 18.2 |
| F | 3.25 | 1.79 |

However, if Ca is assumed to take up an amount of SO₃ equivalent to the total P₂O₅ in the rock, assuming that the P₂O₅ is present solely as (PO₄)³⁻ ions, the new composition becomes:

$$\begin{aligned}
 \text{Ca} &= 26.0\% \\
 \text{P}_2\text{O}_5 &= 21.5 \\
 \text{S} &= 14.8 \\
 \text{F} &= 2.06
 \end{aligned}$$

The latter hypothesis leads to a fair approximation of the results for sulfur (Table 2, expts. 10, 11, 12; Table 4, expts. 13, 14, 15), which never exceeded 15.60 per cent. Likewise, except for experiment 10 of Table 2, the observed P₂O₅ percentages also agree better with the latter assumption. Experiment 10 of Table 2 is probably exceptional, as explained below.

The sulfur balance in fluidized-bed experiments, including the two formal material balances, agrees roughly with the CaSO₄ mechanism discussed above, insofar as the solid, free-flowing product from the reactor is concerned. Assuming that the sulfur uptake amounts to 10 per cent of the product (expts. 13-15, Table 10; expts. 1-2, Table 15), the new totals for Ca and P₂O₅ should be

$$\begin{aligned}
 \text{Ca} &= 32.8\% \\
 \text{P}_2\text{O}_5 &= 27.1
 \end{aligned}$$

These are slightly higher than the measured figures. Assumption of some H_2O uptake would revise them downward; however, some loss of F has probably occurred (see Chapter IV, section D), which would partially compensate for H_2O uptake. Possible explanations include low sulfur analysis, loss of Ca and P_2O_5 , or presence of S in a form which defies analysis. There is no reason to suppose volatilization of Ca or P_2O_5 , and thus the other explanations must be considered.

The overall fluidized-bed material balance reveals little concerning the fate of sulfur in the product, because unreacted SO_3 enters the analysis at all points beyond the reactor.

3. Phosphorus Balance

The calcium and sulfur balances reported above support the interpretation that (a) Ca forms $CaSO_4$ to a considerable extent and (b) no significant quantity of material (except possibly F) is volatilized from the solid product. This interpretation immediately raises a fundamental question: What is the fate of the phosphate originally associated with calcium?

In superphosphate processes, hydrogen becomes the new partner for phosphate, either in monocalcium phosphate or phosphoric acid. In the present study, monocalcium phosphate is the most likely explanation for whatever water solubility the product has acquired. Water solubility is generally observed to the extent that the sample has been allowed to absorb atmospheric moisture, as for example in experiments 13 and 15 of Table 4, which were exposed to air at length after wetting with sulfur trioxide.

On the other hand, citrate solubility is generally the result of dry contact with SO_3 or heating of the product after contact with SO_3 and moisture. Experiment 14 of Table 4 is an example of a product heated after "moist" exposure. The available (water-soluble plus citrate-soluble) P_2O_5 appears to reach a maximum close to 50 per cent of the total P_2O_5 in those cases where atmospheric moisture has been excluded; most of this is citrate solubility. The compounds which might account for this are numerous, and are probably found largely among the spectrum of polyphosphates. This point is developed further under "Reaction Mechanism" below.

Within the limits of experimental error, the analyses always support the conclusion obtained from direct observation: there is no measurable volatilization of phosphoric material from the reacted solid. This has been mentioned above in connection with the Ca and S balances.

Strong support for this conclusion is obtained from Table 3 (see Chapter IV, section A). When the product of experiment 10, Table 2, was fired to 1650°F in the muffle furnace, the P_2O_5 content rose to 25.45 per cent as a result of weight loss by the sample. The weight loss was 26.4 per cent, so that the P_2O_5 (if none is lost) should be increased to

$$14.5 \times \frac{100}{100-26.4} = 23.8\%$$

which, although not a perfect check, indicates that no P_2O_5 has volatilized. The results of Table 6 reinforce this conclusion; no P_2O_5 is volatilized from phosphoric acid as a result of contact by SO_3 at temperatures up to 400°C .

The material balance of Table 15 yields P_2O_5/Ca ratios as follows for the standard product:

Experiment 1 Ratio = 0.843

Experiment 2 Ratio = 0.795.

The average is 0.819, which agrees well with the P_2O_5/Ca ratio of the unreacted charge, which is 0.830. This provides additional evidence that the P_2O_5 is conserved. As an attempt to recover P_2O_5 in the system exhaustively, however, the material balance is barely satisfactory.

4. Fluorine Balance

Fluorine is often considered the key to P_2O_5 availability. Accordingly, the fluorine content of reacted samples received special attention throughout the investigation.

Unfortunately no consistent pattern can be inferred from the results. The difficulty begins with the raw phosphate rock, in which fluorine content was reported from 3.25 to 4.10, while P_2O_5 was always nearly the same. The most reasonable value for F is probably 3.80 per cent, since that figure is most consistent with other results, and was reported in more than one blank.

Moisture is conducive to fluorine loss, which is expected from superphosphate experience. Moisture followed by heating resulted in virtually complete F loss in two cases (13 and 14, Table 4). The fluorine content, however, tells very little about the nature of the phosphate content.

C. Mechanism of Sulfur Trioxide Reaction with Phosphate Rock

1. Stationary (Fixed-Bed) Contact

General. The material balance considered in section B, above,

has thrown considerable light on possible mechanisms that might explain the observed results. There is strong evidence that Ca reacts with SO_3 to form CaSO_4 . There is also strong evidence that the $\text{P}_2\text{O}_5/\text{Ca}$ ratio remains constant under all conditions of reaction, which implies that no P_2O_5 is lost during reaction.

In section B, 2. above, it was shown that an assumption of Ca reaction with SO_3 only to the extent that Ca is associated with P_2O_5 leads to good agreement with experiment, as follows:

| | <u>P_2O_5 (wt %)</u> | <u>S (wt %)</u> |
|--------------------|---|-----------------|
| Assumption (above) | 21.5 | 14.8 |
| 10, Table 2 | 17.5 | 14.55 |
| 11, Table 2 | 20.7 | 13.9 |
| 12, Table 2 | 21.2 | 15.0 |
| 13, Table 4 | 19.37 | 15.60 |
| 14, Table 4 | 27.09 | 15.20 |
| 15, Table 4 | 20.92 | 14.10 |

These are the experiments where exhaustive contact was attempted. Only the next-to-last result (14, Table 4) is seriously out of line; in fact, the two figures given are contradictory,* and an analytical error is suspected.

These figures are considered sufficient evidence for assuming that the calcium does indeed react with SO_3 to a maximum extent equivalent to the calcium phosphate in the phosphate rock.

* A sulfur uptake of 15.20 per cent would lower P_2O_5 to 21.0 per cent, assuming no weight loss.

The respective fates of Ca and S in the reaction are now reasonably accounted for. The P_2O_5 is evidently liberated from association with Ca. In the case of reaction with liquid SO_3 , there are no cations to receive the $(PO_4)^{3-}$ ions as partners, and the inevitable conclusion is that free P_2O_5 is formed. In a few cases, a white subliming powder has been observed whose properties all agree with those of P_4O_{10} , as indicated in Tables 2 and 4 (see also discussion below), but in most cases the product is not volatile. The conclusion emerges that the form of P_2O_5 which usually appears is highly polymeric, presumably the infinite-sheet form (O or O', or a mixture; see Chapter I and Figure 3).

"White Powder" Form of P_4O_{10} . The conditions under which white powder has been observed as a reaction product are worthy of examination, since there is no mention of these phenomena in the literature. To begin with, the character of this white powder leaves little doubt that it is free P_4O_{10} : hygroscopic, acid, subliming, and yielding a positive orthophosphate test. The conditions of formation seem to be the following:

- (1) moisture present in phosphate rock^{*}
- (2) contact with liquid SO_3 in excess^{**}
- (3) rapid temperature rise to 320-325° C

The first criterion was observed by Bowen³⁶ prior to this investigation, as mentioned in Chapter I.

^{*}Note exceptions: expts. 5, 6, and 7 of Table 2. This condition is therefore questionable.

^{**}Note exceptions in Table 4, where presence of condensed SO_3 is nevertheless suspected.

The temperature of appearance of this compound is explained by assuming that the phenomenon is one of phosphoric acid decomposition. Phosphoric acids comprise a continuous spectrum of P_2O_5 - H_2O compositions, with boiling points typically as follows, at one atmosphere:⁶⁹

| <u>P_2O_5 (wt %)</u> | <u>Boiling Point ($^{\circ}C$)</u> |
|--|---|
| 61.6 | 154.2 |
| 72.4 (stoichiometrically equivalent to H_3PO_4) | 255.3 |
| 76.3 | 325.1 |
| 79.7 (stoichiometrically equivalent to $H_4P_2O_7$) | 427.3 |

The temperature of $325^{\circ}C$ definitely falls between the two most likely compositions to be expected, i.e., orthophosphoric acid and pyrophosphoric acid. Therefore the phenomena is not to be explained by boiling of one of these.

An experiment was conducted in which H_2SO_4 was used to wet the phosphate rock, followed by liquid sulfur trioxide. When the temperature was raised, the liquid boiled at $320^{\circ}C$ and yielded a deposit of white powder overhead. The temperature could not be raised past $320^{\circ}C$ while liquid was still present.

The interpretation of the "white powder" phenomenon is likely to be found in existence of an H_2SO_4 - H_3PO_4 azeotrope. Boiling phosphoric acid always yields P_4O_{10} in measurable quantity, and in a system of powerful desiccants such as these it may be that the H_3PO_4 is partially freed of water. In summary, SO_3 would be conjectured to combine with

moisture in the phosphate rock to yield H_2SO_4 , which in turn yields H_3PO_4 ; at 320°C the mixture boils, and the vapor overhead contains P_4O_{10} which will condense on a cold surface. The literature yields no information on such an azeotrope.

Another possible explanation is that SO_3 , being in excess, dehydrates the nascent phosphoric acid or, alternatively, prevents the $(\text{PO}_4)^{3-}$ ions from polymerizing, with the result in either case that the $(\text{PO}_4)^{3-}$ tetrahedra cannot form chains or sheets. Then at 320°C the sublimation point of the phosphorus oxide is attained, and it sublimates. There are two objections to this mechanism: (1) it cannot explain the H_2SO_4 - SO_3 liquid contact experiment described above, and (2) no known form of P_4O_{10} volatilizes at 320°C . With respect to the second point, the lowest crystalline form (i.e., the H-form) of P_4O_{10} sublimates at 360°C ,¹⁹ and if amorphous forms arise they will certainly have lower sublimation temperatures than this, perhaps as low as 320°C .

The small quantity of P_4O_{10} produced is indicative of some limiting factor. This factor is probably moisture in the phosphate rock, if the P_4O_{10} is produced from dehydration of phosphoric acid, as explained above. In all cases the loss of P_4O_{10} is too small to be detected definitely with the analytical methods employed on the residual rock. Neither could the P_4O_{10} be collected and analyzed, because of practical problems with particles of phosphate rock and the predominance of SO_3 in the vicinity.

High-temperature Experiments. These experiments (31 and 32 of Table 4) did not yield as high conversions of P_2O_5 to available form as

those of Hughes and Cameron,²⁹ who used a much longer contact time (5 hours). The low total P_2O_5 percentage of experiment 31 suggests a considerable uptake of SO_3 , in which case the available P_2O_5 would normally be expected to be higher, unless conversion of P_2O_5 to a form which resists digestion and analysis by conventional methods has occurred.

Sulfur Dioxide Experiments. These experiments (Table 5) uniformly indicate very little uptake of sulfur and therefore little reaction. Extended contact time might have produced some conversion of P_2O_5 into available forms, as in the literature.^{29,31} Hughes and Cameron²⁹ obtained only 5.30 per cent availability after one hour, which is comparable with experiment 1 of Table 5.

Sulfur Trioxide and Phosphoric Acid. These experiments were designed to provide information on the behavior of these materials in contact, free from interfering solids. The results indicate that the product is a phosphoric acid increasingly high in P_2O_5 content as contact temperature is raised. Experiments 9 and 11 of Table 6 seem to indicate that no P_2O_5 is lost.

As noted in Table 6, there were three experiments (2, 3, 5) in which a white deposit was produced. In experiment 5, the entire product was solid, whereas in 2 and 3 the white deposit was less than half the total product. These white solid products are insoluble in aqua regia, and must be digested with hot sodium hydroxide solution. The reported behavior of the $H_2O-P_2O_5$ system⁶⁹ does not reveal any solids at temperatures in the range of Table 6; in the $H_2O-P_2O_5-SO_3$ system, however, it is possible that sulfur trioxide dehydrates the phosphoric acid appreciably at temperatures in the range of Table 6. Unfortunately the

region of high P_2O_5 content in the $H_2O-P_2O_5$ system is little known, and the nature of the species to be expected is uncertain. The possibility therefore exists that free P_2O_5 is present in the product as well as high-molecular-weight phosphoric acids.

2. Fluidized Contact

General. The product obtained from fluidized contact of sulfur trioxide and phosphate rock features certain differences from the product of stationary contact:

(1) The conversion of phosphate rock in fluidized contact is limited, as evidenced by lower sulfur uptake and higher total P_2O_5 .

(2) The product of fluidized contact is free-flowing and not greatly altered in physical appearance, whereas stationary contact generally produces a fused mass.

(3) The best obtainable conversion in the fluidized system is reached very rapidly, after about two minutes, while stationary contact requires much longer.

The best conversion of phosphate values to available forms obtainable in the fluidized bed is exemplified by the standard product (experiments 14-16, Table 10). This falls short of exhaustive reaction of the phosphate rock, as evidenced by the total P_2O_5 and sulfur analyses (see section C, 1. above).

Furthermore, even this conversion is only obtainable when the reactant gas is a mixture of sulfur trioxide and steam (with or without air). These phenomena are examined in detail in the sections below. To begin with, however, the reasons for selection of a reaction temperature of $325^\circ C$ will be examined.

Reaction Temperature. It has already been mentioned that a temperature of 320°C to 325°C is often associated with appearance of free P_4O_{10} as a subliming white powder, but this is not the reason for the choice of 325°C as reaction temperature in the fluidized bed. The reason lies in an apparent conversion threshold at about 340°C ; above this temperature, it was noticed that P_2O_5 availability seemed to reach a maximum of about 8.5 per cent, indicating low sulfur uptake. Experiments 9 and 11 of Table 8 were performed specifically to check this observation.

It was also noticed that operation above 340°C was always stable in the fluidized system, and a product reacted below 340°C was always fuming and hygroscopic. This led to the hypothesis that 340°C was approximately the maximum temperature in the vapor-liquid region of the $\text{H}_2\text{O}-\text{SO}_3$ system. The latest published studies on this system⁷⁰ indicate that the maximum temperature in the vapor-liquid region is 338.8°C , the boiling point of the constant-boiling mixture (98.3% H_2SO_4) at one atmosphere.

The following reasoning was adopted as a result of this discovery:

(1) The conversion limit above 340°C is probably due to absence of liquid, since the fluidizing phase cannot wet the rock above this temperature. Accordingly:

(2) Operation should be conducted below 340°C with water (steam) added to the gas stream, but conducted close to 340°C so that stable fluidization can be maintained.

If hypothesis (1) above is correct, then a limited conversion would also be expected to result when water is excluded from the

fluidizing phase, since the fluidizing gas will then be dry sulfur trioxide. This premise is examined below.

In conclusion, regarding reaction temperature in the fluidized system, a temperature of 325°C was adopted as standard. Tables 7-10 feature temperatures largely around this value. If temperature was allowed to fall toward 300°C , instability and upset were likely, as observed in several cases. Observation of the fluidizing system on numerous occasions led to the conclusion that above 340°C operation was always stable; from 340°C to 315°C operation was usually stable; and below 315°C stability was problematical.

Pure Sulfur Trioxide Contact. Among these experiments, reported in Table 7, two stand out as anomalous (4 and 8). In both, total P_2O_5 is about as low as with the exhaustively reacted samples (contacted with liquid SO_3) discussed in section C, 1. above, but the water-soluble P_2O_5 content is exceptionally high. These two similar results were arrived at quite differently (see Table 7). Since high water solubility of P_2O_5 is always thought to be associated with presence of monocalcium phosphate (or phosphoric acid), it is believed that both these samples were wet with SO_3 and water (moisture) prior to development of reaction temperature. These results could never be duplicated satisfactorily, due to difficulty of fluidization after low-temperature contact with sulfur trioxide.

The remainder of the stable experiments reported in Table 7 (3, 6, 7, 10, 11, and 18)* seem to feature an upper limit of available

*Experiment 1 is excluded because of varying temperature.

P_2O_5 near 9 per cent. This is in apparent agreement with the hypothesis advanced in the preceding section ("Reaction Temperature") to the effect that absence of liquid, whether due to high temperature or exclusion of water from the fluidizing phase, limits the conversion.

However, the conversion to 9 per cent indicates that some reaction always takes place. If water is the limiting factor, it is of interest to calculate how much water is required for this limited conversion. Adopting experiment 11 of Table 7 for example, and taking 100 grams of product as basis,

$$\%H_2O = (9.04 - 2.42 \times \frac{31.24}{33.88}) \times \frac{1}{142} \times 2 \times 18 \times \frac{1}{100} \times 100 = 1.98\%$$

(A) (B) (C) (D) (E) (F)

A--weight gain in P_2O_5 availability (based on Table 1)

B--molar gain in P_2O_5 availability

C--moles H_2O corresponding to gain

D--weight H_2O corresponding to gain

E--fraction H_2O corresponding to gain

F--percentage of H_2O required in sample.

This calculated water content is higher than the measured free moisture content (0.67 per cent), even if preheating were not applied. It is possible that $(CO_3)^{2-}$ or $(OH)^-$ inclusions in the crystal lattice provide points of attack for the SO_3 ; the CO_2 is measured (Table 1) as 1.46 per cent in unreacted rock.

Contact with Sulfur Trioxide and Admixtures. The considerations discussed above led to experiments on two methods of introducing water

into the fluidizing phase: introduction of humid air, and introduction of steam. As will be seen, best results were obtained by introducing a combination of air and steam.

Air introduced into the fluidizing stream of sulfur trioxide does not significantly enhance the conversion of P_2O_5 to available forms, as revealed in Table 8. Experiments 6 and 7 are the only ones in which results are measurably better than with sulfur trioxide alone.

When steam was added to the fluidized system, a series of upsets occurred until the method of injection was perfected. The single stable experiment of this table (expt. 7) was a slight improvement over the case of sulfur trioxide alone. Experiment 6 is interesting because it demonstrates that liquid acid, followed by heating above $340^\circ C$, produces a material in which P_2O_5 is apparently converted to a form which does not respond to standard methods of analysis.

When air as well as steam is injected into the fluidized system, conversion is generally improved, as shown in Table 10. Stability is improved and conversion is only affected at low SO_3 concentration. Experiment 1 of Table 10 is discouraging to direct use of lean gas ($<5\% SO_3$) for this process; experiment 2, at 9.4 mole per cent SO_3 , yields results comparable to the rest. Taken altogether, the results recorded in Table 10 testify to the insensitivity of product composition to a wide range of gas compositions.

In the SO_3 -steam-air system, a maximum conversion is evident, at about 13.5 per cent available P_2O_5 . This situation is more difficult to interpret than the case of exhaustive reaction discussed in section C, 1. above. In the first place, it is not clear why the total P_2O_5 declines

only to about 24 per cent, at most. Second, the sulfur uptake is at most about two-thirds the amount recorded in the case of exhaustive (stationary) contact. The sulfur uptake is questionable (compare experiments 14 and 15 of Table 10), but the higher figure of 10.3 per cent is preferred on the basis of comparison with experiment 13 of Table 10 and experiment 7 of Table 9. If this figure is adopted, the P_2O_5 should be, based on the same mechanism as in the case of exhaustive contact (basis 100 gm original sample):

$$\%P_2O_5 = \frac{33.88}{100 + 10.3 \times \left(\frac{100}{100-10.3} \right) \times \frac{80}{32}} = 26.4\% ,$$

which is at variance with the measured total P_2O_5 which averages only 23.9 per cent for the experiments under standard conditions. This may mean (1) that some P_2O_5 in the standard product does not respond to conventional analytical methods or (2) that a different reaction mechanism is at work.

The evident incompleteness of the gas-solid reaction may be due to formation of a layer of product on the particles of phosphate rock. Presumably a layer of product also forms on the particles of phosphate rock in the case of contact with liquid sulfur trioxide, but this layer may be more permeable to the high concentration of sulfur trioxide present in the case of liquid contact, compared to the concentration present in the gaseous mixture. In fact, exhaustive reaction is obtained only with difficulty even in the case of liquid sulfur trioxide contact. If a layer of product is the inhibiting mechanism, it still must be asked which one--calcium sulfate or the phosphatic product--forms the barrier

to further reaction.

It is clear from Table 10 (experiments 4, 7, and 8) and Figure 10 that maximum conversion in the fluidized bed is achieved within five minutes, possibly within three minutes. This is especially interesting by comparison with the very long contact times reported by previous authors^{29, 31} (see also Figure 7).

D. Extraction Experiments

1. Standard Product

From Table 12, it is evident that basic extractants generally reduce the availability of P_2O_5 in the standard product. This is presumably due to formation of insoluble apatites, a phenomenon which is well known.⁷¹ Neutral solutions (e.g., ammonium nitrate) seem to have no effect on the availability. Acid solutions, on the other hand, improve the availability of the standard product. Potassium sulfate (pH ~ 4) was the most effective of all the extractants, extracting about two-thirds of the P_2O_5 .

The observed conversion of about two-thirds of the P_2O_5 , discussed above, seems to correspond to the two-thirds maximum extractability. In fact, the P_2O_5 extracted by potassium sulfate exceeds the available P_2O_5 measured by AOAC methods.

The sulfuric acid extractions reported in Table 13 yield very little more available P_2O_5 than the potassium sulfate extraction of Table 12. This is surprising, since the standard product seems to consist of some unreacted phosphate rock, which the sulfuric acid would be expected to extract along with most of the citrate-soluble fraction.

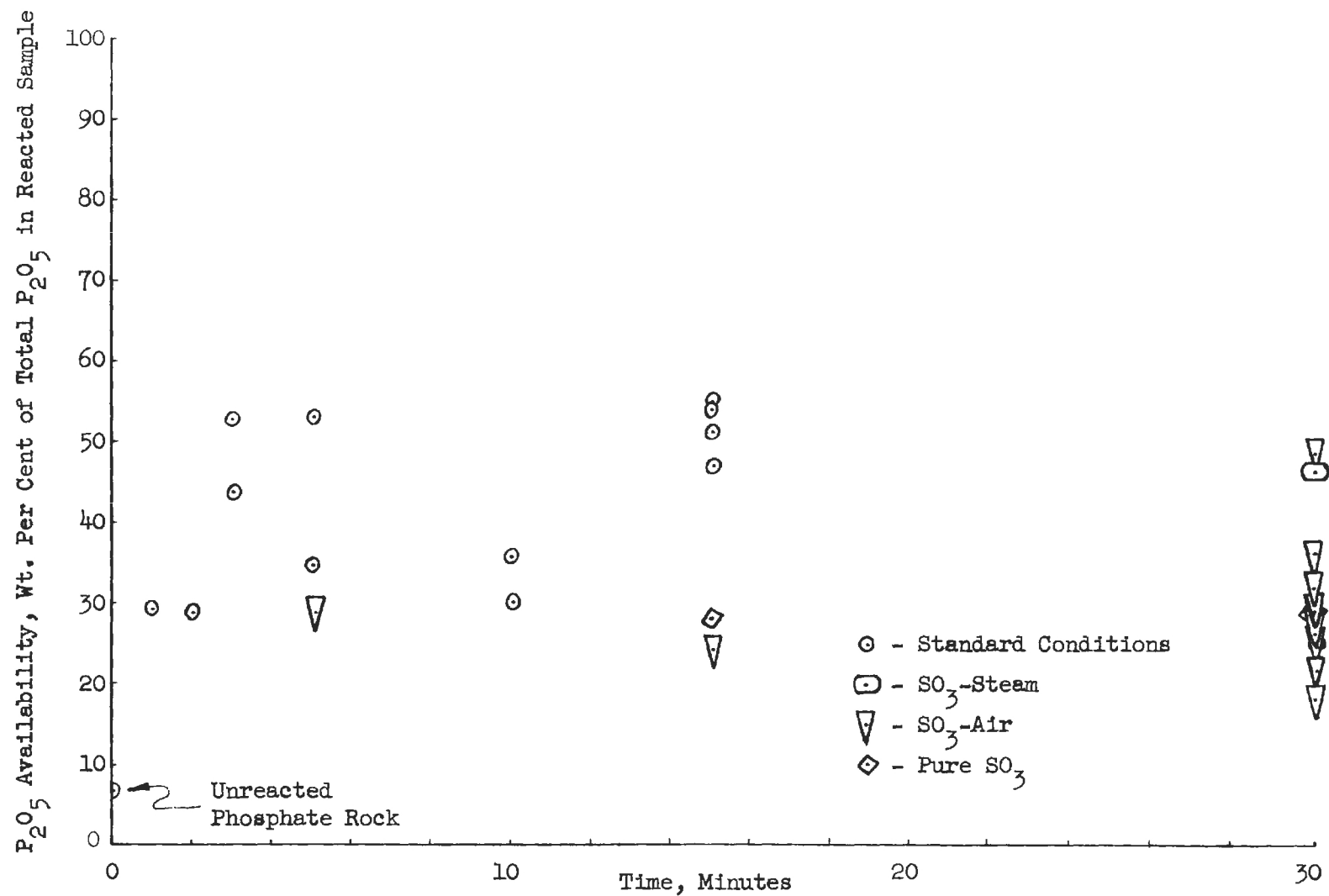


Figure 10. Conversion of Phosphate Rock to Available Form by Reaction with Sulfur Trioxide in a Fluidized Bed, with Various Gas Admixtures.

The residual P_2O_5 from sulfuric acid extraction is plainly present in a form inaccessible to the acid, but it is not clear whether unreacted rock is being extracted, leaving behind high polymerized P_2O_5 , or whether the polymeric P_2O_5 is being extracted, while the unreacted rock is for some reason no longer accessible to the sulfuric acid. A possible reason for inaccessibility might be that converted P_2O_5 at the particle surface is only incompletely soluble, and the remainder is shielded from contact.

If the potassium sulfate-extracted P_2O_5 is just that P_2O_5 which has been converted by reaction (as suggested by their approximate numerical equivalence), then the extract includes the citrate-soluble fraction. In that case the residue would consist of unreacted phosphate rock. Since the H_2SO_4 likewise extracts most of the citrate-soluble P_2O_5 , it would seem that the residue from this extraction may also be unreacted phosphate rock also.

2. Exhaustively Reacted Product

In these experiments, reported in Table 13, basic solutions were again ineffective in extracting phosphate values from the product. However, acid solutions again appear promising.

In the exhaustively reacted experiments, sulfur trioxide uptake has been shown (above) to be approximately equivalent to the Ca associated with P_2O_5 , computed as $Ca_3(PO_4)_2$. However, the best extraction only removes slightly more than one-half of the P_2O_5 . This is presumable due to (a) the presence of P_2O_5 in the form of high-molecular-weight sheets which hydrolyze only slowly, (b) hindrance of diffusion by $(SO_4)^{2-}$ or P_2O_5 sheets within the crystal, or (c) a hindering layer on the particles of product caused by the extractant.

With alkaline extractants, (c) is likely. With weak acid, (a) is the most likely explanation. With regard to (a), quantitative data are available on hydrolysis of P-O-P linkages in long-chain phosphates.⁶⁸ Such hydrolysis displays a considerable temperature coefficient, which suggests that the product of experiment 26, Table 4, could be extracted more quickly and to greater extent by application of pressure and high temperature.

E. Practical Possibilities

1. General

Industrial phosphate processes require essentially complete conversion of P_2O_5 to available forms. Furthermore, modern trends call for high P_2O_5 analysis, which means that even a more economical product equivalent to normal superphosphate (16-18 per cent total P_2O_5) is of less interest than formerly.

The products studied in this investigation include (1) the exhaustively reacted product of contact with liquid SO_3 and phosphate rock, and (2) the standard product of fluidized contact. The former has about the same P_2O_5 content as normal superphosphate, but less available P_2O_5 , and in particular much less water solubility. Therefore it is of little potential industrial use.

The standard product contains only about 55 per cent available P_2O_5 by AOAC definitions. However, this product can be obtained under process conditions which are very attractive: very short contact times; contacting gas very dilute in SO_3 ; relatively low temperature; convenience of fluidized-bed operation. If the product could be enhanced in P_2O_5

availability, or if an economical method of extracting the P_2O_5 values could be devised, this material might then be industrially attractive.

2. Enhancement of Conversion

Evidence has been obtained that the P_2O_5 conversion can be enhanced by finer subdivision of the phosphate rock, so that a film of product does not form a barrier film of thickness sufficient to hinder the reaction, or by grinding the product and recontacting it with reactant gas. In this way the P_2O_5 availability might be induced to approach 100 per cent. Another possible means of promoting increased conversion is application of pressure to the process.

However, the product is at best equivalent to normal superphosphate in total P_2O_5 , and will always have much lower water solubility. Only its potential economy of manufacture renders it attractive. Potentially, this might mean that the process would be more attractive in other countries than the United States, since the U. S. phosphate market is demanding even more specialized products and higher analysis.

3. Extraction of P_2O_5

The ease of manufacturing the standard product of this investigation suggests that, if the phosphate values could be extracted, the overall process might provide an economical source of either phosphoric acid or soluble phosphate for liquid fertilizers.

The second alternative is exemplified by the potassium sulfate extraction reported in the investigation (Table 12), in which the P_2O_5 was apparently extracted to the extent to which it had been converted by reaction. The essential feature of this extraction seemed to be the

mild acid nature of the extractant. Therefore it is possible that any fertilizer solution of acid character could be enriched in P_2O_5 by contact with the standard product. Most fertilizer solutions, of course, are basic or neutral, but the basic constituents could certainly be added after extraction in mild acid medium.

Experience with the exhaustively reacted product is suggestive of the power of weak acid to take P_2O_5 into solution. Exhaustively reacted samples are believed to consist of highly polymerized P_2O_5 , which can be regarded as a limiting state for the compounds occurring in decomposed phosphate rock. If acid solutions are capable of hydrolyzing P_2O_5 in infinite-sheet form, the spectrum of compounds in the fluidized-bed product should be susceptible to essentially complete extraction by hydrolysis. This extraction could probably be performed very rapidly by use of pressure and elevated temperature.

CHAPTER VI

CONCLUSIONS

The investigation described in the preceding Chapters I through V has led to the following conclusions concerning the behavior of phosphate rock in contact with sulfur dioxide and trioxide.

1. Exhaustive reaction of phosphate rock and liquid sulfur trioxide produces essentially quantitative conversion of the P_2O_5 content of the rock to nonvolatile, highly polymeric forms of P_4O_{10} . The absorption of sulfur trioxide is apparently quantitatively equivalent to the calcium which was associated with the P_2O_5 in the phosphate rock.

2. In the case of exhaustive reaction with liquid sulfur trioxide the calcium content of the phosphate rock is converted to $CaSO_4$ to an extent equivalent to the P_2O_5 content of the rock.

3. The fluorine content of the phosphate rock is very sensitive to presence of water during reaction. If water is absent, fluorine is conserved. In presence of sufficient water, fluorine can be quantitatively removed during contact with sulfur trioxide.

4. A single contact of phosphate with sulfur trioxide gas in a fluidized bed at atmospheric pressure results in conversion of about two-thirds of the P_2O_5 , at most.

5. The degree of conversion of phosphate rock by gaseous sulfur trioxide in a fluidized bed can be increased by grinding the product and

reacting it a second time under the same conditions.

6. The phosphate rock of this investigation, nominally 90 per cent through 100 mesh, is difficult to fluidize by itself in small laboratory columns. However, the rock can easily be fluidized with air, nitrogen, sulfur dioxide, or sulfur trioxide, provided that the bed of solids rests on a layer of sand of significantly larger particle size, which maintains its integrity during fluidization and provides uniform gas distribution and agitation to the bed of phosphate rock above.

7. The reaction between phosphate rock and sulfur trioxide in a fluidized bed is enhanced by presence of water (steam) in the fluidizing stream. The amounts of water required are only a small fraction of that equivalent to the SO_3 , and much less than the amount of P_2O_5 involved in the reaction. In absence of water, the maximum obtainable conversion is significantly lower.

8. Maximum conversion of phosphate rock by sulfur trioxide in the fluidized bed is achieved within five minutes.

9. The best temperature for contact of phosphate rock with sulfur trioxide in a fluidized bed is below 340°C , but close enough to 340° that wetting of particles is not a problem of fluidization. A temperature of 325°C to 330°C is concluded to be optimum.

10. The rate of conversion and final composition of the product of contact of phosphate rock with sulfur trioxide in a fluidized bed are insensitive to SO_3 composition of the gas (a mixture of SO_3 , air, and H_2O) down to SO_3 compositions on the order of five mole per cent.

11. Addition of air to the fluidizing gas mixture of SO_3 and H_2O in the fluidized-bed contact of phosphate rock is conducive to stable fluidization.

12. Sulfur dioxide contact with phosphate rock under stationary or fluidized conditions produced negligible conversion of P_2O_5 to available forms in the temperature range 200-500° C, with contact times up to one hour.

13. The P_2O_5 content of the "standard" product of fluidized-bed contact between sulfur trioxide and phosphate rock is extractable to an extent greater than the availability according to AOAC definitions if the extractant is saturated potassium sulfate solution at 65° C, with pH slightly acid. If neutral salt solutions are employed for extraction, the availability is essentially unchanged. If basic solutions are employed, availability falls below the AOAC availability.

14. The P_2O_5 content of the "standard" product of fluidized-bed contact between phosphate rock and sulfur trioxide in a fluidized bed can be extracted in an amount about two-thirds of the total P_2O_5 of the product. The citrate solubility (by AOAC definition) of the residue from extraction is significantly reduced from that of the product.

15. The P_2O_5 content of exhaustively reacted product of contact between sulfur trioxide and phosphate rock can be extracted to an extent slightly more than 50 per cent by a weak (0.001 M) acid solution at 100° C for 8 hours, with agitation.

16. From the practical point of view, the most notable finding of the investigation seems to lie in the favorable technical aspects of the fluidized-bed contact: rapid conversion, moderate temperatures, simple operation, feasibility of dilute SO_3 gas mixtures, all at atmospheric pressure. If the product could be enhanced in P_2O_5 availability, or if an economical method of P_2O_5 extraction could be devised, this material might then be industrially attractive.

CHAPTER VII

RECOMMENDATIONS

The investigation described in Chapters I through V is heavily exploratory. Several avenues of investigation have been pursued in an effort to obtain greater understanding of the processes taking place when phosphate rock is contacted by sulfur trioxide. This approach has inevitably left some avenues incompletely explored, and it has raised suggestive possibilities which merit extensive investigations in their own right. The following recommendations are therefore intended to provide directions to future investigators who may explore some of these promising areas of investigation.

1. In order to isolate the fundamental processes which take place when phosphate rock and sulfur trioxide are contacted, pure tricalcium phosphate should be used in place of industrial phosphate rock. With the influence of fluorine and impurities removed, it is possible that the compounds which arise could be closely characterized, and a clear understanding of the reaction mechanism obtained.

This would permit meaningful studies by means of X-ray methods, microscopic (optical and electron) methods, and perhaps chromatography. Likewise the reaction equilibria could possibly be studied quantitatively, and heat effects isolated.

The use of pure fluorapatite for such a fundamental study is not recommended, because it is not reactive.

2. Fluidized-bed contact of phosphate rock (or tricalcium phosphate, as in recommendation 1) deserves closer study in view of the utility of the method and the advantages found with this system which are discussed in Chapter V. It is likely that conversion can be improved significantly beyond the point achieved in this investigation, by means of finer particle sizes or grinding of product followed by recontact. Evidence for this viewpoint has been discussed above.

If the observed limitation on conversion is found to consist of a film of product on the particles, as believed, it might be possible to study the diffusion process quantitatively. The literature reveals that the diffusion problem is often encountered in systems of reacting particles, but has not received significant study. The importance of a fundamental study of this type can easily be imagined.

3. The hydrolysis of polymeric P_2O_5 in products of sulfur trioxide reaction merits serious study in view of its interest to the phosphate industry. If the fluidized-bed reaction explored in this investigation produces P_2O_5 principally in the form of infinite-sheet polymer, hydrolysis might be the means of converting it to usable form.

4. The area of high temperatures has been largely neglected in this investigation. Although the studies reported in the literature are not encouraging, because of the times required, the fluidized bed offers a technique for greatly improving the contact between gas and solid. The effect of water at high temperatures is also little known.

APPENDIX A

TABLES

Notes:

1. W.S. denotes water-soluble according to AOAC standard methods.
2. C.S. denotes citrate-soluble according to AOAC standard methods.
3. A.P.A. is "available phosphoric acid," defined as the sum of W.S. and C.S.
4. White powder was observed to appear only in those experiments where it is mentioned under "Remarks."
5. Temperatures are $\pm 5^{\circ}$ C except where otherwise specified.

Table 1

Typical Analysis of Phosphate Rock Employed in the Present Investigation

| <u>Constituent</u> | <u>Weight (%)</u> |
|----------------------------|-----------------------|
| P_2O_5 | 33.88 |
| Ca | 40.9 |
| F | 3.25 |
| S | 0.37 |
| SiO_2 | 4.67 |
| Al | 0.373 |
| Fe | 0.855 |
| MgO | 0.361 |
| CO_2 | 1.46 |
| Free moisture | 0.67 |
| Water-soluble $P_2O_5^*$ | 0.02 |
| Citrate-soluble $P_2O_5^*$ | 2.42 |

* By AOAC official method.

Table 2

Liquid Sulfur Trioxide Contact With Phosphate Rock in Fixed Bed

| No. | Charge (gm) | Temp.* (°C) | Pre- drying (°C) | Analyses (wt %) | | | | | Remarks |
|-----|----------------|----------------|------------------------|---|---------------------------------------|---------------------------------------|------------------|-------------------------------|---|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | Other | |
| 1 | 5 | 380 (max) | None | — | — | — | — | — | White powder at 320° C. |
| 2 | 10 | 350 (max) | None | 32.56 | — | — | 21.96 | — | — |
| 3 | 3 | 380 | 380 | 24.48 | 2.83 | — | — | — | Contact at 380° C. 6.8 ml SO ₃ . |
| 4 | — | 320+ | None | 22.8 | 1.10 | — | — | — | — |
| 5 | 5 | 350 | 110 | 26.57 | — | — | 10.42 | — | Predried 4 hrs. White powder (small amt.) at 320° C. |
| 6 | 5 | 340 (max) | 105 | 23.13 | — | — | 14.40 | — | Predried 5 days. 5 ml SO ₃ . White powder (temp. uncer- tain). |
| 7 | 5 | 85-335 | 120 | 31.65 | — | — | — | — | Predried 8 hrs. 5 ml SO ₃ . White powder at 320° C. |
| 8 | 5 | 84-387 | 110 | 20.8 | 2.19 | — | — | — | Elaborate predrying, > 24 hrs. 4 ml SO ₃ . |
| 9 | 3 | 380 | 110 | 27.44 | — | — | — | — | Predried several days. 7.2 ml SO ₃ . |
| 10 | 5 | 350 (max) | None | (1) 16.6 (2) 16.2 (3) 15.5 [†] 17.5 ^{††} | — — — — | — — — — | — — — — | (1) — (2) — (3) S=14.55 | Contacted three times, heated between. |

(continued)

Table 2 (continued)

| No. | Charge (gm) | Temp.* (°C) | Pre- drying (°C) | Analyses (wt %) | | | | | Remarks |
|-----|----------------|----------------|------------------------|--|---------------------------------------|---------------------------------------|--------|----------|--|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | Other | |
| 11 | 5 | 375 | None | 20.7 | — | 13.4 | — | S = 13.9 | — |
| 12 | 5 | 350 | None | 21.2 | 2.76 | — | — | S = 15.0 | Water (as steam) 3 gm; SO ₃ = 17.9 gm. |
| 13 | 10 | appr. 500 | None | 25.0 | — | 6.65 | — | S = 11.2 | — |

* All contact was performed at room temperature except as otherwise noted.

† Acid digestion.

†† Caustic digestion.

Table 3

Weight Loss at High Temperature of Samples
Contacted with Liquid Sulfur Trioxide

| <u>Source of Sample</u> | <u>Temp.</u> (°F) | <u>Sample</u> (gm) | <u>Loss</u> (wt %) |
|-------------------------|----------------------|-----------------------|-----------------------|
| Expt. 10, Table 2 | Room | 0.4075 | 0.0 |
| | 1200 | 0.3789 | 7.0 |
| | 1450 | 0.3284 | 19.4 |
| | 2010 | 0.2943 | 27.8 |
| Expt. 10, Table 2 | Room | 0.7229 | 0.0 |
| | 1650 | 0.5319 | 26.4 |
| Expt. 11, Table 2 | Room | 0.3746 | 0.0 |
| | 1200 | 0.3421 | 8.7 |
| | 1450 | 0.2955 | 21.1 |
| | 2010 | 0.2643 | 29.5 |

Table 4

Gaseous Sulfur Trioxide Contact with Phosphate Rock in Fixed Bed

| No. | Charge (gm) | Temp. (°C) | Predrying (°C) | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | Other | Remarks |
|-----|----------------|---------------|-------------------|--|---------------------------------------|---------------------------------------|--------|-------------------|---|
| 1 | — | 315±10 | None | 33.9 | — | — | 6.3 | F=3.84 | White powder (small amount). |
| 2 | 13.4 | 180 | None | 31.6 | — | — | 9.1 | F=3.60 | 2.8 ml SO ₃ (liq.). |
| 3 | 15 | 245 | None | 33.2 | — | — | 5.9 | F=3.76 | 6.9 ml SO ₃ (liq.). |
| 4 | — | 498 (max) | None | 29.62 | 2.63 | 8.02 | 10.65 | — | Contact at 85° C, Postheat to 498° C. |
| 5 | — | 73-350 | None | 23.89 | 2.95 | 8.76 | 11.71 | — | — |
| 6 | — | 85-420 | None | 23.23 | 7.42 | 4.87 | 12.29 | — | — |
| 7 | — | 85-430 | None | 26.52 | 2.50 | 8.39 | 10.89 | — | White powder when flow reversed, 429° C. |
| 8 | — | 78-500 | None | 26.58 | 2.90 | 10.99 | 13.89 | — | — |
| 9 | — | 50-400 | None | 28.69 | 1.54 | 7.15 | 8.69 | — | — |
| 10 | — | 82-568 | None | 22.77 | 1.90 | 9.42 | 13.32 | — | — |
| 11 | — | 197-487 | None | 30.30 | 0.95 | 2.60 | 3.55 | F=2.90 S=2.77 | — |
| 12 | — | 150-477 | None | 26.15 | 0.17 | 7.00 | 7.00 | F=2.70 S=6.63 | — |
| 13 | 6 | 75-400 | None | 19.37 | 15.21 | 4.08 | 19.24 | F<0.05 S=15.60 | Rock removed, reground once. Product heated to dryness over flame. |

(continued)

Table 4 (continued)

| No. | Charge (gm) | Temp. (°C) | Predrying (°C) | Analyses (wt %) | | | | | Remarks |
|-----|----------------|---------------|-------------------|--|---------------------------------------|---------------------------------------|--------|-------------------|---|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | Other | |
| 14 | 6 | 215-400 | None | 27.09 | 1.34 | 19.43 | 20.77 | F<0.05 S=15.20 | Rock removed, ground twice. Contact at (1) 215° C, (2) 100+° C, (3) 350-400° C. Postheat 350° C all three runs. |
| 15 | 6 | 200-320 | 250, 8 hrs. | 20.92 | 9.32 | 4.98 | 14.30 | F=1.54 S=14.10 | Rock removed, reground twice. Contact at 200-250° C all three runs, postheat to 320° C. |
| 16 | — | 360-400 | 200, 1 hr. | 28.77 | 5.07 | 4.20 | 9.27 | — | — |
| 17 | — | 450 (max) | 110, 1/2 hr. | 30.47 | 5.37 | 4.26 | 9.63 | — | Contact at 96-118° C, 1 hr. Postheat to 450° C. |
| 18 | — | 625 (max) | 174, 4 hrs. | 30.18 | 0.32 | 2.82 | 3.14 | F=2.24 S=3.99 | Contact at 170°C, 1/2 hr. Postheat to 675° C. White powder when flow reversed, at 393° C. |
| 19 | 5 | 350 | None | 33.2 | 10.0 | — | — | — | Vacuum 24.6 in Hg. Time 1 hr. |
| 20 | 5 | 320 | None | 31.6 | 1.5 | — | — | — | Vacuum 24 in Hg. Time 1/2 hr. |
| 21 | 5 | 330 | None | 33.5 | 2.1 | — | — | — | Vacuum 27.7 in Hg. Time 1/2 hr. |
| 22 | 5 | 320 | None | 33.6 | 3.90 | — | — | S=9.87 | Precautions to retain rock moisture. White powder observed. Time 15 min. |
| 23 | 5 | 400 | None | 27.2 | 0.35 | — | — | — | Precautions to retain rock moisture. Vacuum 22 in Hg. |

(continued)

Table 4 (continued)

| No. | Charge (gm) | Temp. (°C) | Predrying (°C) | Analyses (wt %) | | | | | Remarks |
|-----|----------------|---------------|-------------------|--|---------------------------------------|---------------------------------------|--------|---------|---|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | Other | |
| 24 | 5 | 400 | None | 27.4 | 0.85 | — | — | S=10.50 | Precautions to retain rock moisture. Vacuum 21 in Hg. Time 1/2 hr. |
| 25 | 5 | 390 | None | 28.6 | 0.46 | — | — | S=3.94 | Vacuum varied. Time 15 min. |
| 26 | 5 | 375 | None | 18.5 | 0.5 | 10.9 | 11.4 | — | H ₂ O admitted by dripping. |
| 27 | 6 | 330 | None | 26.5 | 4.39 | — | — | — | H ₂ O admitted by dripping. |
| 28 | 6 | 330 | None | 22.6 | 0.0 | — | — | — | H ₂ O admitted by dripping. Postheat 4 hrs. at 375° C. |
| 29 | 6 | 330 | None | 25.5 | 0.8 | — | — | — | H ₂ O admitted by dripping. |
| 30 | 2 | 725 | None | — | (lost) | — | — | — | — |
| 31 | 2 | 825 | None | 23.3 | 0.0 | 4.30 | 4.30 | — | Time 40 min. |
| 32 | 4 | 450-830 | None | 29.6 | 0.04 | 5.10 | 5.14 | — | Time 30 min. Post at 870° C. |

Sulfur Dioxide Contact with Phosphate Rock in a Fixed Bed

Table 5

| No. | Charge (gm) | Temp. (°C) | Analyses (wt %) | | | | | Remarks |
|-----|-------------|------------|-------------------------------------|------------------------------------|------------------------------------|--------|------|---|
| | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | F | |
| 1 | — | 425 | 34.5 | — | — | 4.6 | 3.85 | Very early experiment. |
| 2 | 5 | 400 | 34.2 | — | — | — | — | — |
| 3 | 5 | 500 | 35.0 | 1.0 | — | — | — | — |
| 4 | 5 | 500 | 34.7 | — | — | — | — | — |
| 5 | 5 | 840 | 34.6 | — | — | — | 1.46 | White deposit of S observed-- 400° C. |
| 6 | 6 | 330 | 33.5 | — | — | — | — | Molar ratio H ₂ O/SO ₂ : 0.086. |
| 7 | 5 | 400 | 34.2 | — | — | — | — | Predried. Vacuum 28.1 in Hg. |
| 8 | 5 | 500 | 35.0 | 1.0 | — | — | — | — |
| 9 | 5 | 500 | 34.7 | — | — | — | — | — |

Table 6

Liquid Sulfur Trioxide Contact with Phosphoric Acid

| No. | Phosphoric Acid | SO ₃ (ml) | Temp. (°C) | Description of Contact | Description of Product |
|-----|--|-------------------------|---------------|---|--|
| 1 | 3.5 ml, 75.2% (wt) P ₂ O ₅ | 1.4 | 375 max | Room temperature contact. Fuming at 60.80° C, unidentified liquid volatilizes at 250° C. No reaction observed upon initial contact. | Viscous white opaque liquid. |
| 2 | 1.2 ml, 75.2% (wt) P ₂ O ₅ | 4.2 | 370 max | Room temperature contact. Immiscible layers disappear only at ~ 150° C. White deposit in vessel at 250° C. | Viscous gray; white liquid and white water-insoluble deposits on wall. |
| 3 | 5 ml, 75.2% (wt) P ₂ O ₅ | 5.8 | 345 max | Contact first at 200° C. | Viscous gray liquid. White deposit at liquid level formed at 320° C. Deposit soluble in NaOH solution. |
| 4 | 1.1 ml, 75.2% (wt) P ₂ O ₅ | — | 320 | Contact at 320° C. | Similar to (3). |
| 5 | 2.3 ml, 75.2% (wt) P ₂ O ₅ | 5 | 390 | Contact at 390°-400° C. | Dry white deposit, soluble in hot NaOH solution. |
| 6 | 3 ml, 85% H ₃ PO ₄ | 4.6 | 320 | Contact at 320° C. | Viscous white liquid. |
| 7 | 3 ml, 85% H ₃ PO ₄ | 4.2 | 320 | Contact at 320° C. | Viscous white liquid. |

(continued)

Table 6 (continued)

| No. | Phosphoric Acid | SO_3 (ml) | Temp. (°C) | Description of Contact | Description of Product |
|-----|---|-----------------------|---------------|------------------------|---|
| 8 | 3 ml, 85% H_3PO_4 | 11.5 | 350 | Contact at 350° C. | Viscous white liquid. |
| 9 | 2 ml, 85% H_3PO_4 | 9.5 | 400 | Contact at 400° C. | Viscous white liquid. Total P_2O_5 = 62.3% (wt). |
| 10 | 2 ml, 85% H_3PO_4 | 9.0 | 400 | Contact at 400° C. | Viscous white liquid. |
| 11 | 2 ml, 75.2% (wt) P_2O_5 | 10.5 | 400 | Contact at 400° C. | Viscous white liquid. Total P_2O_5 = 71.2% (wt). |

Table 7

Fluidized-Bed Experiments. Phosphate Rock Contacted with Pure Sulfur Trioxide

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt. %) | | | | | | Remarks |
|-----|---------------|---------------|----------------|--|---------------------------------------|---------------------------------------|--------|------|------|--|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | F | S | |
| 1 | 250-500 | — | 6 | 30.42 | 6.01 | 2.65 | 8.66 | 3.10 | 4.01 | Fluidized in glass reactor. Pre-heated to 500° C. |
| 2 | 280-300 | — | 6 | — | — | — | — | — | — | Vacuum run. Upset due to leaks. |
| 3 | 310 | 30 | 6 | 32.68 | 0.65 | 4.93 | 5.58 | 3.84 | 1.65 | Vacuum run, varying pressure. Leaks. |
| 4 | 300-332 | 30 | 6 | 20.57 | 13.9 | 0.91 | 14.81 | 2.00 | 6.29 | Vacuum run, 15-18 in. Hg. Leaks |
| 5 | 286-320 | 30 | 6 | 27.89 | 6.21 | 2.28 | 8.99 | 3.10 | 1.76 | Vacuum run. Upset due to leaks. |
| 6 | 297-324 | 30 | 6 | 30.76 | 1.69 | 6.97 | 8.66 | 3.80 | 3.49 | Vacuum run, 22-23 in. Hg. Leaks. |
| 7 | 275-331 | 30 | 6 | 30.43 | 1.65 | 6.88 | 8.53 | 3.60 | 4.14 | Vacuum run, 7.5 in. Hg. Leaks. Postheat 360° C. |
| 8 | 325 | 30 | 6 | 20.00 | 13.99 | 3.85 | 17.84 | 3.10 | 6.18 | Elaborate care to preserve rock moisture. Postheat 360° C. Contact with SO ₃ before fluidization. |
| 9 | 300 | 15 | 6 | 31.85 | 7.38 | — | — | — | — | Upset--poor SO ₃ production. |
| 10 | 294-302 | 30 | 6 | 31.44 | 1.45 | 7.79 | 9.24 | 3.60 | 3.13 | Charge dried 30 min at ave. 310° C before contact. Vacuum 25 in. Hg. |

(continued)

Table 7 (continued)

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt %) | | | | | | Remarks |
|-----|---------------|---------------|----------------|--|---------------------------------------|---------------------------------------|--------|------|-------|--|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₃ | C.S. P ₂ O ₅ | A.P.A. | F | S | |
| 11 | 327-332 | 15 | 6 | 31.24 | 1.20 | 7.84 | 9.04 | 3.44 | 3.73 | Charge dried 30 min at 320° C. |
| 12 | 330 | 30 | 5 | 33.1 | 4.80 | — | — | — | — | Unsatisfactory fluidization. |
| 13 | 330 | 15 | 6 | 30.9 | 1.38 | — | — | — | — | Poor SO ₃ production. |
| 14 | 400 | — | 6 | 29.7 | 1.36 | — | — | — | 11.57 | Upset-plugging. Attempt to retain rock moisture. |
| 15 | 320 | 15 | 6 | 31.5 | 9.10 | — | — | — | — | Upset-plugging. Entrainment of oleum encouraged. |
| 16 | 340 | — | 6 | 20.5 | 7.47 | — | — | — | — | Upset--severe plugging. |
| 17 | 300 | — | 6 | 29.1 | 0.45 | 8.0 | 8.45 | — | — | Upset--no steady state obtained. |
| 18 | 320 | 30 | 6 | 30.3 | 0.12 | 7.6 | 7.72 | — | — | Molar ratio SO ₃ /Ca = 10.35. |

Table 8

Fluidized-Bed Experiments. Phosphate Rock Contacted with Mixtures of Sulfur Trioxide and Air

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt %) | | | | | | Molar Ratio $\text{H}_2\text{O}/\text{SO}_3$ | Molar Ratio Air/ SO_3 | Remarks |
|-----|---------------|---------------|----------------|---------------------------------|--------------------------------|--------------------------------|--------|---|---|---|-----------------------------------|--|
| | | | | Total P_2O_5 | W.S. P_2O_5 | C.S. P_2O_5 | A.P.A. | F | S | | | |
| 1 | 330 | 10 | 6 | — | 2.29 | — | — | — | — | 0.0070 | 3.3 | Upset--sticking. |
| 2 | 330 | 15 | 6 | 28.6 | 0.79 | 6.1 | 6.9 | — | — | — | — | — |
| 3 | 325 | 15 | 6 | 30.2 | 1.02 | 6.5 | 7.5 | — | — | — | — | Vacuum 8 in. Hg. Leaks. |
| 4 | 330 | 30 | 6 | 29.6 | 0.83 | 7.8 | 8.6 | — | — | 0.35 | 9.9 | Vacuum 2.5-4 in. Hg. Upper section 360° C. |
| 5 | 310 | 10 | 6 | 30.15 | 1.61 | 15.5 | 17.1 | — | — | — | — | — |
| 6 | 320 | 30 | 6 | 28.2 | 3.18 | 10.5 | 13.7 | — | — | 0.015 | — | — |
| 7 | 300-325 | 30 | 6 | 29.5 | 1.64 | 9.4 | 11.0 | — | — | — | — | — |
| 8 | 300-325 | 25 | 6 | 29.4 | 0.0 | — | — | — | — | — | — | Unstable run. |
| 9 | 360 | 30 | 6 | 31.9 | 0.0 | 8.4 | 8.4 | — | — | 0.29 | 8.1 | — |
| 10 | 315 | 30 | 6 | 24.0 | 3.16 | — | — | — | — | — | — | Unstable run. |
| 11 | 360 | 40 | 6 | 31.3 | 0.79 | — | — | — | — | — | — | — |
| 12 | 325 | 30 | 6 | 21.1 | 6.18 | 4.7 | 10.9 | — | — | 0.043 | 1.1 | Low temperature at one point. Molar ratio $\text{SO}_3/\text{Ca} = 4.52$. |

(continued)

Table 8 (continued)

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt %) | | | | | | Molar Ratio $\text{H}_2\text{O}/\text{SO}_3$ | Molar Ratio Air/ SO_3 | Remarks |
|-----|---------------|---------------|----------------|---------------------------------|--------------------------------|--------------------------------|--------|---|---|---|-----------------------------------|--|
| | | | | Total P_2O_5 | W.S. P_2O_5 | C.S. P_2O_5 | A.P.A. | F | S | | | |
| 13 | 315 | 30 | 6 | 28.8 | 1.02 | 8.2 | 9.2 | - | - | 0.147 | 0.19 | Saturated air. Post- heat 360° C. Molar ratio $\text{SO}_3/\text{Ca} = 10.9$. |
| 14 | 320 | 30 | 6 | 30.6 | 0.20 | 6.5 | 6.7 | - | - | — | — | Molar ratio $\text{SO}/\text{Ca} = 9.7$. Postheat 360° C. |
| 15 | 315 | 30 | 6 | 31.0 | 0.16 | 5.5 | 5.7 | - | - | — | — | Molar ratio $\text{SO}/\text{Ca} = 12.4$. Postheat 360° C. |
| 16 | 330 | 30 | 6 | 28.3 | 0.79 | 6.1 | 6.9 | - | - | 0.033 | 0.84 | — |
| 17 | 325 | 30 | 6 | 30.2 | 1.02 | 6.5 | 7.5 | - | - | 0.033 | 0.92 | Molar ratio $\text{SO}_3 = 0.49$. Postheat 360° C. Saturated air, pre- heated. |
| 18 | 325 | 5 | 6 | 29.1 | 0.45 | 8.0 | 8.5 | - | - | 0.062 | 1.7 | Molar ratio $\text{SO}_3/\text{Ca} = 0.40$. Postheat 360° C. Saturated air, pre- heated. |
| 19 | 320 | 10 | 6 | 29.6 | 0.83 | 7.8 | 8.6 | - | - | — | — | Upset--plugging. |

Table 9

Fluidized-Bed Experiments. Phosphate Rock Contacted with Mixtures of Sulfur Trioxide and Steam

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt %) | | | | | | Molar Ratio H ₂ O/SO ₃ | Remarks |
|-----|---------------|---------------|----------------|--|---------------------------------------|---------------------------------------|--------|---|---|---|---|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | F | S | | |
| 1 | 200 | — | 6 | 34.3 | 29.2 | — | — | — | — | — | Upset--poor SO ₃ production. |
| 2 | 400 | 8 | 6 | 28.8 | 1.38 | 6.8 | 8.2 | — | — | — | Upset--plugging. |
| 3 | 400 | 7 | 6 | 28.0 | 3.0 | 5.8 | 8.8 | — | — | — | Upset--plugging. 10 min fluidiza- tion with SO ₃ along prior to steam. |
| 4 | 400 max | 15 | 6 | 30.6 | 1.02 | 7.1 | 8.1 | — | — | — | Upset--temperature varying widely. Molar ratio SO ₃ /Ca = 6.9. |
| 5 | 320 | 20 | 6 | 21.7 | 1.03 | 11.9 | 12.9 | — | — | 0.84 | Upset--control problems. Molar ratio SO ₃ /Ca = 6.9. |
| 6 | 360 | — | 6 | 8.71 | 3.39 | 1.69 | 5.08 | — | — | — | Immediate upset. Sample fused. |
| 7 | 350 | 30 | 6 | 24.9 | 1.53 | 10.0 | 11.5 | — | — | 8.1 | Molar ratio SO ₃ /Ca = 0.81. |
| 8 | 330 | 8 | 6 | 25.14 | 5.14 | 2.82 | 7.96 | — | — | — | Upset--plugging. |
| 9 | 335 | 15 | 6 | 18.5 | — | 13.5 | — | — | — | 0.41 | Upset--plugging. Varying tempera- ture. Molar ratio SO ₃ /Ca = 8.0. |

Table 10

Fluidized-Bed Experiments. Phosphate Rock Contacted with Mixtures of Sulfur Trioxide, Steam, and Air

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt %) | | | | | | Molar Ratio H ₂ O/SO ₃ | Molar Ratio Air/SO ₃ | Remarks |
|-----|---------------|---------------|----------------|--|---------------------------------------|---------------------------------------|--------|---|---|---|------------------------------------|---|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | F | S | | | |
| 1 | 315 | 30 | 6 | 32.6 | 0.0 | 5.55 | 5.55 | - | - | 2.7 | 10.2 | Molar ratio SO ₃ /Ca = 1.22. Vacuum 3.5 in. Hg. |
| 2 | 320 | 15 | 6 | 22.1 | 0.27 | 10.19 | 10.46 | - | - | 4.3 | 5.3 | Molar ratio SO ₃ /Ca = 0.76. Vacuum 1.0 in. Hg. |
| 3 | 325 | 15 | 6 | 24.4 | 2.57 | 10.17 | 12.74 | - | - | 1.24 | 1.24 | Molar ratio SO ₃ /Ca = 2.66 |
| 4 | 325 | 5 | 6 | 23.8 | 0.36 | 12.4 | 12.76 | - | - | 0.805 | —† | Molar ratio SO ₃ /Ca = 1.35. Excess air drawn in by leaks. |
| 5 | 320 | 22 | 6 | 21.4 | 3.28 | 10.4 | 13.68 | - | - | 0.55 | —† | Molar ratio SO ₃ /Ca = 8.5. Upset-plugging. |
| 6 | 330 | 17 | 6 | 21.8 | 0.29 | 13.2 | 13.49 | - | - | 0.27 | —† | Molar ratio SO ₃ /Ca = 7.1. Upset-plugging. |
| 7 | 335 | 3 | 6 | 23.1 | 0.50 | 11.8 | 12.30 | - | - | 0.43 | —† | Molar ratio SO ₃ /Ca = 1.35. |
| 8 | 330 | 3 | 6 | 26.0 | 0.17 | 11.3 | 11.47 | - | - | 3.02 | 0.64 | Molar ratio SO ₃ /Ca = 1.0. |

(continued)

Table 10 (continued)

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt %) | | | | | | Molar Ratio $\text{H}_2\text{O}/\text{SO}_3$ | Molar Ratio Air SO_3 | Remarks |
|-----|---------------|---------------|----------------|---------------------------------|--------------------------------|--------------------------------|--------|------|------|---|----------------------------------|--|
| | | | | Total P_2O_5 | W.S. P_2O_5 | C.S. P_2O_5 | A.P.A. | F | S | | | |
| 9 | 330 | 1 | 6 | 31.4 | 0.10 | 9.3 | 9.40 | — | — | 0.61 | 0.95 | Molar ratio $\text{SO}_3/\text{Ca} = 0.18.$ |
| 10 | 330 | 2 | 6 | 30.5 | 0.14 | 8.8 | 8.94 | — | — | 0.53 | 1.01 | Molar ratio $\text{SO}_3/\text{Ca} = 0.41.$ |
| 11 | 320-340 | 5 | 6 | 28.8 | 1.19 | 8.9 | 10.09 | — | — | 0.69 | 1.28 | Molar ratio $\text{SO}_3/\text{Ca} = 0.81.$ |
| 12 | 325 | 10 | 6 | 31.2 | 0.16 | 9.4 | 9.56 | — | — | 0.97 | 1.07 | Molar ratio $\text{SO}_3/\text{Ca} = 1.12.$ |
| 13 | 330 | 10 | 6 | 29.3 | 0.20 | 10.4 | 10.60 | 2.98 | 10.0 | 2.10 | 3.96 | Molar ratio $\text{SO}_3/\text{Ca} = 0.52.$ |
| 14 | 325 | 15 | 6 | 23.7 | 1.02 | 12.1 | 13.12 | 1.70 | 10.3 | — | — [†] | Standard condi- tions. |
| 15 | 325 | 15 | 6 | 24.7 | 0.93 | 12.8 | 13.73 | 1.70 | 5.6 | — | — [†] | Standard condi- tions. |
| 16 | 325 | 15 | 6 | 23.4 | 0.83 | 11.5 | 12.33 | — | — | — | — [†] | Standard condi- tions. |
| 17 | 325 | 15 | 6 | 23.0 | 1.08 | 13.1 | 14.18 | 1.32 | 7.98 | — | — [†] | Standard condi- tions. Product reground and re-reacted. |

[†]Air was not metered.

Table 11

Sulfur Dioxide Contact with Phosphate Rock in a Fluidized Bed

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt %) | | | | | | Remarks |
|-----|---------------|---------------|--------------------------------------|--|---------------------------------------|---------------------------------------|--------|------|------|--|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | F | S | |
| 1 | 400 (max) | 30 | 6 | — | — | — | — | — | — | Four runs for observational purposes no analysis. One SO ₂ alone, two SO ₂ --air, one SO ₂ --O ₂ . |
| 2 | 500 (max) | — | 6 | 20.15 | 0.13 | 2.43 | 2.56 | 2.40 | 0.05 | Error in analysis suspected. |
| 3 | 186-210 | 45 | 6 gm rock 1.3 gm SiO ₂ | 28.22 | 0.01 | 3.22 | 3.23 | 3.12 | 0.2 | — |
| 4 | 220-250 | 60 | 6 | 33.91 | 0.40 | 3.51 | 3.91 | 3.90 | 0.2 | — |
| 5 | 240-265 | 60 | 6 | 34.07 | 0.01 | 3.77 | 3.78 | 4.00 | 0.26 | — |
| 6 | 300 | 10 | 6 | 33.89 | 0.05 | 3.49 | 3.54 | 3.50 | 0.33 | Predried 30 min. |
| 7 | 300 | 30 | 6 | 34.29 | 0.08 | 3.69 | 3.77 | 4.06 | 0.36 | Predried 30 min. |
| 8 | 300 | 60 | 6 | 34.22 | 0.06 | 4.22 | 4.28 | 4.04 | 0.36 | Predried 30 min. |
| 9 | 300 | 30 | 6 gm rock 1 gm SiO ₂ | 22.99 | 0.03 | 3.29 | 3.32 | 2.96 | 0.2 | Predried 30 min. |
| 10 | 300 | 30 | 6 | 34.33 | 0.03 | 6.53 | 6.56 | 3.90 | 0.34 | Effort to retain rock moisture. |
| 11 | 320 | 60 | 6 | 34.20 | — | — | 3.58 | — | — | Predried 15 min. |

(continued)

Table 11 (continued)

| No. | Temp. (°C) | Time (min) | Charge (gm) | Analyses (wt %) | | | | | | Remarks |
|-----|---------------|---------------|--|--|---------------------------------------|---------------------------------------|--------|---|---|--|
| | | | | Total P ₂ O ₅ | W.S. P ₂ O ₅ | C.S. P ₂ O ₅ | A.P.A. | F | S | |
| 12 | 320 | 30 | 6 | 34.28 | — | — | 3.58 | — | — | Predried 15 min. |
| 13 | 320 | 15 | 6 | 34.19 | — | — | 3.62 | — | — | Predried 15 min. |
| 14 | 250 | 60 | 6 | 34.07 | — | — | 3.41 | — | — | Predried 15 min. |
| 15 | 250 | 30 | 6 | 33.91 | — | — | 3.87 | — | — | Predried 15 min. |
| 16 | 250 | 60 | 6 | 34.07 | — | — | 4.11 | — | — | Predried 15 min. |
| 17 | 300 | 60 | 6 | 34.31 | — | — | 3.92 | — | — | Two runs 30 min. each, rock re-ground between runs. Predried 15 min. |
| 18 | 300 | 30 | 6 gm rock 1 gm K ₂ CO ₃ | 33.91 | — | — | 3.60 | — | — | Predried 15 min. |

Table 12

Extraction of Standard Product[†] with Various Solutions

Extraction time: 1 hr. (except as noted)

Extractant volume: 100 ml per gm sample

| Extraction Solution | Conc. (gm/100 gm H ₂ O) | Temp. (°C) | Extractable | | Total Available P ₂ O ₅ (wt %) |
|---|--|---------------|---|--|---|
| | | | P ₂ O ₅ (wt %) | C.S. P ₂ O ₅ (wt %) | |
| Ammonium carbonate | 29.8* | 65 | 1.84 | 8.59 | 10.43 |
| Ammonium nitrate | 456* | 65 | 1.37 | 11.05 | 12.42 |
| Ammonium nitrate + urea (30-0-0 soln.) | (98 ml soln.) | 65 | 1.78 | 9.46 | 11.24 |
| Ammonium nitrate (ammoniacal) | (70 ml 60% NH ₄ NO ₃ soln.; 30 ml 32% NH soln.) | 25 | 0.54 | 10.17 | 10.71 |
| Ammonium sulfate | 92* | 65 | 6.94 | 4.48 | 11.42 |
| Potassium carbonate (1) | 53* | 65 | 7.59 | 0.34 | 7.93 |
| Potassium carbonate (2) | 56* | 65 | 7.61 | 0.27 | 7.88 |
| Potassium carbonate (3) | 53* | 25 | 3.92 | 3.39 | 7.31 |
| Potassium carbonate (4) | 61* | 100 | 6.00 | — | — |
| Potassium chloride | 47* | 65 | 1.52 | 9.50 | 11.02 |
| Potassium sulfate | 19* | 65 | 11.70 | 4.37 | 16.07 |
| Potassium hydroxide | 25 | 65 | 11.33 | — | — |
| Sodium carbonate (1) | 46* | 65 | 5.65 | 5.52 | 11.17 |
| Sodium carbonate (2) | 46* | 65 | 5.08 | 3.29 | 8.37 |
| Water | (100 ml) | 65 | 3.05 | 5.52 | 8.57 |
| AOAC official method | — | 65 | — | 12.1 | 13.1 |
| Netherlands method** | — | 65 | — | 12.05 | 14.29 |

[†]Total P₂O₅: 23.9 wt % (average)

*Approximately saturated solution at 65° C.

**Citrate extraction: 2 hrs. with alkaline ammonium citrate.⁶²

Table 13

Extraction of Standard Product with Sulfuric Acid,
Compared to Extraction of Unreacted Phosphate Rock

Room Temperature
Time: 1 hour
Solution volume: 10 ml
Sample weight: 1 gm

| <u>Sample</u> | <u>Acid Strength (wt %)</u> | <u>Total P₂O₅ in Sample (wt %)</u> | <u>P₂O₅ Extracted (wt %)</u> | <u>P₂O₅ in Residue (wt %)</u> | <u>C.S. P₂O₅ in Residue (wt %)</u> |
|------------------|-------------------------------------|--|--|---|--|
| Standard product | 97 | 23.9 | 15.94 | 7.41 | 2.68 |
| Standard product | 70 | 23.9 | 12.88 | 12.51 | 4.85 |
| Phosphate rock | 97 | 33.9 | 34.6 | < 1.0 | — |
| Phosphate rock | 70 | 33.9 | 33.1 | < 1.0 | — |

Note: See Table 10, experiments 14-16, for complete composition of standard product.

Table 14

Extraction Experiments with Exhaustively Reacted Samples

Room Temperature

Solution Volume: 100 ml per gm sample

Time: 1 hour (except as noted)

| Sample | Total P_2O_5 (wt %) | C.S. P_2O_5 (wt %) | Caustic-Extractable P_2O_5 | | | P_2O_5 from Acid Hydrolysis ^{††} (wt %) |
|-------------------|--------------------------|-------------------------|------------------------------|----------------------------|-------------------------|--|
| | | | NH_4OH^* (wt %) | $NaOH^{**}$ (wt %) | dil. $NaOH^†$ (wt %) | |
| Expt. 11, Table 2 | 20.7 | 13.4 | trace | 4.53 | — | — |
| Expt. 13, Table 2 | 25.0 | 6.65 | trace | 5.21 (1 hr) 2.75 (2 hr) | 2.78 | — |
| Expt. 26, Table 4 | 18.5 | 10.9 | trace | 3.35 | 4.89 | 10.4 |

* 32% NH_3 solution in water.** 10% $NaOH$ solution.† 0.5% $NaOH$ solution.†† 0.001 molar HCl solution, 5 days of contact at room temperature,
plus 8 hours at 100° C with agitation.

Table 15

Material Balance Experiments in Fluidized Bed

| <u>Experiment No. 1 Time 10 minutes</u> | | | | | | | | | |
|--|-------------------------|-----------------------------------|-----------|--------------------|-----------|--------------------|-----------|--------------------|-----------|
| | Total solids (gm) | <u>P₂O₅</u> | | <u>Ca</u> | | <u>F</u> | | <u>S</u> | |
| | | Wt (gm) | Wt (%) | Wt (gm) | Wt (%) | Wt (gm) | Wt (%) | Wt (gm) | Wt (%) |
| a) Original Charge | 6.00 | 2.034 | 33.9 | 2.454 | 40.9 | 0.222 | 3.80 | 0.022 | 0.38 |
| b) Products | | | | | | | | | |
| Reacted charge | 4.711 | 1.262 | 26.8 | 1.499 | 31.8 | 0.127 | 2.70 | 0.476 | 10.1 |
| Disengager solid residue | 2.714 | 0.172 | 6.6 | 0.857 [†] | — | 0.019 [†] | — | 0.649 | — |
| Disengager filtrate | — | 0.441 | — | — | — | — | — | 0.784 | — |
| Absorption train | — | (trace) | — | — | — | — | — | — | — |
| Totals | <u>7.425</u> | <u>1.875</u> | | <u>2.356</u> | | <u>0.146</u> | | <u>1.973</u> | |
| <u>Experiment No. 2 Time 15 minutes</u> | | | | | | | | | |
| a) Original Charge | 6.00 | 2.034 | 33.9 | 2.454 | 40.9 | 0.222 | 3.80 | 0.222 | 0.38 |
| b) Products | | | | | | | | | |
| Reacted charge | 5.850 | 1.405 | 24.0 | 1.767 | 30.2 | 0.160 | 2.74 | 0.473 | 11.2 |
| Disengager solid residue | 1.837 | 0.162 | 8.8 | 0.588 [†] | — | 0.016 [†] | — | 0.355 [†] | — |
| Disengager filtrate | — | 0.241 | — | — | — | — | — | 1.200 | — |
| Absorption train | — | 0.020 | — | — | — | — | — | — | — |
| Totals | <u>7.674</u> | <u>1.828</u> | | <u>2.355</u> | | <u>0.176</u> | | <u>2.050</u> | |

[†] Figure obtained by assuming measured P₂O₅ in residue is due to unreacted rock, with remainder of sample weight due to calcium sulfate.

Table 16
X-Ray Diffraction Analysis of Phosphate Rock and Standard Product
(Cu K α radiation)

| Phosphate Rock (measured) | | Standard Product (measured) | | Fluorapatite (Ref. 67) | | Calcium Sulfate (anhydrite) (Ref. 67) | |
|------------------------------|-----------------------------|--------------------------------|-----------------------------|---------------------------|-----------------------------|--|-----------------------------|
| Spacing | Intensity Ratio, I/I_1 | Spacing | Intensity Ratio, I/I_1 | Spacing | Intensity Ratio, I/I_1 | Spacing | Intensity Ratio, I/I_1 |
| (Å) | | (Å) | | (Å) | | (Å) | |
| — | — | — | — | 8.21 | 16 | — | — |
| 3.4241 | 92.0 | 3.4241 | 100+ | — | — | 3.498 | 100 |
| — | — | 3.3115 | 41.5 | — | — | — | — |
| — | — | — | — | 3.09 | 18 | — | — |
| 3.0253 | 44 | — | — | — | — | — | — |
| — | — | 2.8376 | 93.0 | — | — | 2.849 | 33 |
| 2.7783 | 100+ | 2.7859 | 83.7 | 2.816 | 100 | — | — |
| 2.6727 | 100+ | 2.6804 | 42.8 | 2.722 | 100+ | — | — |
| 2.6159 | 63.5 | — | — | — | — | — | — |
| 2.2254 | 44.0 | 2.3189 | 58.0 | 2.264 | 35 | 2.208 | 20 |
| 1.9278 | 56.7 | 2.1994 | 55.5 | 1.913 | 16 | — | — |
| 1.8294 | 66.2 | 1.8610 | 46.2 | 1.729 | 25 | 1.869 | 15 |
| — | — | — | — | — | — | — | 14 |

APPENDIX B

CALCULATION OF STANDARD FREE ENERGY
FOR VARIOUS REACTION MECHANISMSA. Sources of Data

The following sources of data have been used for enthalpy and entropy of the compounds involved:

Fluorapatite. $(\Delta H_F^O)_{298}$ from Jacques (1963).⁷² $(H_T^O - H^O)_{298}$ and $(S_T^O - S^O)_{298}$ from Egan, Wakefield, and Elmore (1951).⁷³

Sulfur trioxide. $(\Delta H_F^O)_{298}$, $(H_r^O - H^O)_{298}$, and S_T^O from JANAF tables (1960).⁷⁴ Data agree well with those of Lovejoy et al. (1962).⁷⁵

Phosphorus pentoxide. $(\Delta H_F^O)_{298}$ from Hartley et al. (1963).⁷⁶ $(H_T^O - H^O)_{298}$ and S_T^O from JANAF tables (1960).⁷⁴

Calcium metaphosphate. $(\Delta H_F^O)_{298}$ calculated from Hartley et al. (1963).⁷⁶ $(H_T^O - H^O)_{298}$ and $(S_T^O - S^O)_{298}$ from Egan and Wakefield (1956).⁷⁷

Calcium pyrophosphate. $(\Delta H_F^O)_{298}$ calculated from Hartley et al. (1963).⁷⁶ $(H_T^O - H^O)_{298}$ and $(S_T^O - S^O)_{298}$ from Egan and Wakefield (1957).⁷⁸

Tricalcium phosphate. $(\Delta H_F^O)_{298}$ from Hartley et al. (1963).⁷⁶ $(H_T^O - H^O)_{298}$ and $(S_T^O - S^O)_{298}$ from Kelley (1960).⁷⁹

Monocalcium phosphate. $(\Delta H_F^O)_{298}$ and S^O_{298} from Egan, Wakefield, and Elmore (1956).⁸⁰

Calcium sulfate. $(\Delta H_F^O)_{298}$ from NBS Circular 500 (1952).⁸¹

$(H_T^O - H^O)_{298}$ and $(S_T^O - S^O)_{298}$ from Kelley (1960).⁷⁹

Calcium sulfite. $(\Delta H_F^O)_{298}$ from Maslov (1959).⁸² S^O_{298} from NBS Circular 500 (1952).⁸¹

Calcium fluoride. $(\Delta H_F^O)_{298}$ from NBS Circular 500 (1952).⁸¹

$(H_T^O - H^O)_{298}$ and $(S_T^O - S^O)_{298}$ from Kelley (1960).⁷⁹

Phosphorus oxyfluoride. (ΔH_F^O) , $(H_T^O - H^O)_{298}$, and S_T^O from JANAF tables (1963).⁷⁴

Sulfuryl fluoride. (ΔH_F^O) , $(H_T^O - H^O)_{298}$, and S_T^O from JANAF tables (1960).⁷⁴

Water. (ΔH_F^O) , $(H_T^O - H^O)_{298}$, and S_T^O from JANAF tables (1960).⁷⁴

Oxygen. $(H_T^O - H^O)_{298}$ and S_T^O from JANAF tables (1960).⁷⁴

Sulfur. $(H_T^O - H^O)_{298}$ and S_T^O from JANAF tables (1960).⁷⁴

B. Method of Calculation

The general method of calculation of values of ΔF_T^O for a particular reaction mechanism is as follows:

$$\Delta F_T^O = \sum (\Delta H_F^O)_{298} + \sum (H_T^O - H^O)_{298} - T \sum (S_T^O - S^O)_{298} - T \sum S^O_{298}.$$

At 298.15° K (25° C), this reduces to

$$\Delta F^O_{298} = \sum (\Delta H_F^O)_{298} - (298.15) \sum S^O_{298}$$

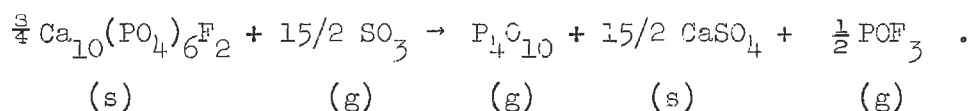
where a subscript 298 refers to 298.15° K or 25° C.* The symbol \sum is used

* Older references use 298.16° K.

here to denote the sum of the values for the reaction products, minus the sum of the values for the reactants.

C. Sample Calculation

As an example of the method used for calculating ΔF_T^O , consider the following postulated reaction mechanism (equation (19), Chapter I):



Calculations will be performed for 298.15° K and 500° K.

298.15° K

$$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2: (\Delta H_F^O)_{298} = -\frac{3}{4}(-3296) = +2472.0$$

$$\text{SO}_3: = -15/2(-94.450) = +708.4$$

$$\text{P}_4\text{O}_{10}: = +(-688.0) = -688.0$$

$$\text{CaSO}_4: = +15/2(-342.42) = -2568.2$$

$$\text{POF}_3: = \frac{1}{2}(-282.0) = -141.0$$

$$\sum (\Delta H_F^O)_{298} = (\Delta H_R^C)_{298} = -216.8 \text{ kcal/mole}$$

$$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2: -TS_{298}^O = +\frac{3}{4}(298.15)(185.5)/1000 = +41.48$$

$$\text{SO}_3: = +15/2(298.15)(61.342)/1000 = +137.17$$

$$\text{P}_4\text{O}_{10}: = -(298.15)(92.441)/1000 = -27.56$$

$$\text{CaSO}_4: = -15/2(298.15)(25.5)/1000 = -57.02$$

$$\text{POF}_3: = -\frac{1}{2}(298.15)(68.222)/1000 = -10.17$$

$$- \sum TS_{298}^O = +83.90 \text{ kcal/mole}$$

$$\Delta F_{298}^O = -216.8 + 83.90 = -132.9 \text{ kcal/mole}$$

500° K

$$\begin{array}{lcl}
& \frac{H_T^C - H_{298}^C}{T} - \frac{T(S_T^O - S_{298}^O)}{T^2} - \frac{TS_{298}^O}{T^2} - \frac{TS_T^C}{T^2} & \\
\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2: & -\frac{1}{4}[41,500 - 500(185.5 + 104.9)]/1000 & = +77.63 \\
\text{SiO}_2: & -15/2 [2,836 & -500(68.524)]/1000 = +235.71 \\
\text{P}_4\text{O}_{10}: & + [10,431 & -500(118.79)]/1000 = -48.96 \\
\text{CaSO}_4: & +15/2[5,200 - 500(25.5 + 13.28)]/1000 & = -106.50 \\
\text{POF}_3: & + \frac{1}{2}[3,801 & -500(77.864)]/1000 = -17.57 \\
& \sum (H_T^O - H_{298}^O) - T \sum S_T^O = +140.31 & \text{kcal/mole}
\end{array}$$

$$\Delta F_{500}^O = (\Delta H_R^O)_{298} + \sum (H_T^O - H_{298}^O) - T \sum S_T^O = -216.8 + 140.3 = -76.5 \text{ kcal/mole}$$

D. Interpolation and Consistency of Data

In the course of the investigation, it was desired to determine the inversion temperatures (i.e., temperatures at which $\Delta F_T^C = 0$) of various mechanisms as closely as possible. This was made difficult by the fact that all tabulations of thermodynamic properties are arranged with intervals of 100° K between individual listed values. A method of interpolation was therefore necessary.

An interpolation routine programmed for use with the Burroughs E220 digital computer of the Georgia Institute of Technology, was applied. However, the routine did not converge, which indicated that the differences between values at various temperatures exceeded the requirements for convergence, i.e., did not permit the nth difference to approach zero. This implied that the various sets of thermodynamic data, even though they were smoothed values, were not consistent.

An orthogonal polynomial method of fitting the data to a power series of the type

$$f(T) = a + bT + cT^2 + dT^3 + eT^4$$

was then adopted. Two procedures were employed:

(1) data from tabulations were individually fitted to polynomials of this type, and enthalpies, free energies, etc. calculated for each substance, then combined to obtain ΔF_T^0 ;

(2) complete functions (e.g., ΔF_T^0) were calculated for each T, and the functions fitted to a polynomial.

Interestingly, the results of (1) and (2) diverged by as much as five per cent in certain regions of the data. Tables were generated at 25° intervals, since this proved to be about the limit within which an inversion temperature could be reliably calculated. The Burroughs B220 computer was used for the computations.

Since the mechanisms studied were entirely hypothetical, and since the temperature criterion that was ultimately applied to the process was not thermodynamic, the data were not intensively studied for consistency and improvement of interpolation.

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VITA

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