

CALCIUM ARSINATES

An investigation into the three component system: Calcium Oxide-Arsenic Oxide and Water.

By

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This dissertation is presented with the permission of the Chief of The Bureau of Entomology and Plant Quarantine.

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INTRODUCTION

The use of commercial calcium arsenates for the control of leaf eating insects has increased at an enormous rate during recent years. It is estimated that approximately thirty million pounds are used annually in the United States for the purpose of combating different types of insects. This insecticide has proven particularly effective against the boll weevil where perhaps it finds its greatest application, although it is rapidly coming into use against the codling moth, and other insects.

It often happens in the field of insecticides that a preparation is found to be effective and is widely used long before much is known about its chemical nature. In the case of pyrethrum powder, its usefulness as an insecticide can be traced back to ancient times while the chemical nature of its active principle was not discovered until about twelve years ago. Another example in the organic field is derris. The insecticidal value of this preparation has long been known, but it was not until comparatively recently that chemical and physical characteristics of rotenone, its active principle was discovered. In the inorganic field may be mentioned Bordeaux mixture and lime sulfur sprays, both of which have wide application but whose chemistry is not yet definitely known.

To this list of insecticides one must add calcium arsenate. Of the chemical and to a large extent the physical characteristics

of the more basic calcium arsenates very little is known with certainty. Most of the facts are of empirical nature, as for example it is known that by adding an excess of lime to the commercial preparation the effect is to lessen its injuriousness to tender foliage, the idea being that a more basic preparation is formed with the accompanying decrease in soluble arsenic. Against this empirical fact should be stated the results of recent systematic tests which prove beyond a doubt that the most basic calcium arsenate obtainable, even with the addition of some free lime, is much more injurious to foliage than is the more soluble tricalcium arsenate. From this it is apparent that the protective action of lime must be explained in some other way. It is also well known that the chemical and the physical characteristics of commercial calcium arsenates vary between wide limits. C. M. Smith and C. W. Murray¹ analyzed sixteen commercial calcium arsenates from as many different manufacturers and obtained widely different results as is indicated in the table below:

Average Analysis of Sixteen Calcium Arsenates			
	Maximum	Minimum	Average
	%	%	%
Moisture	3.22	0.74	1.94
Loss on ignition	12.72	6.94	9.30
Total CaO	47.70	40.42	43.91
CaCO ₃	11.73	1.21	6.37
Ca(OH) ₂	12.65	1.52	6.63
CaO as arsenate	40.59	31.49	35.34
Total As ₂ O ₅	44.39	40.32	42.42
H ₂ O soluble As ₂ O ₅	2.37	0.06	---

Such widely different products reflect an incomplete knowledge of the processes, and conditions under which different combinations take place.

The purpose of this investigation was to obtain additional knowledge of the arsenates of calcium, by means of a systematic study of the three component system: $\text{CaO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$. The temperature of 62°C . was chosen because as a general rule equilibrium conditions are reached in less time at higher temperature than at lower, and also because most commercial processes for the manufacture of calcium arsenates are carried on at elevated temperatures.

HISTORICAL

The literature concerning the arsenates of calcium is of considerable volume, and no attempt will be made to give a complete review of all papers and patent literature on this subject. Only such references will be considered that have a direct bearing on the investigation under consideration.

It has been found advisable to consider the different calcium arsenates from the point of view of their $\text{CaO}/\text{As}_2\text{O}_5$ ratios, and in compounds containing water, either in combination within the molecule or as hydrate, or both, to consider only the total number of mols present. By doing this one can greatly simplify the formulae by using numerals for the number of mols of each component present in the compound. Thus for example, tricalcium arsenate octa-hydrate, $(\text{Ca}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O})$ becomes 3.1.8 and calcium-hydro-arsenate-mono-hydrate, $(\text{CaHAsO}_4 \cdot \text{H}_2\text{O})$ becomes simply 2.1.3.

There are five distinct series of calcium arsenates, and these will be reviewed briefly, beginning with the most acidic, i.e., the 1.1.X series.

Calcium Arsenates with

Molecular Ratio $\text{CaO}/\text{As}_2\text{O}_5=1$.

Calcium metarsenate $\text{Ca}(\text{AsO}_3)_2$ (1. 1. 0.)

The preparation of calcium metarsenate was first described by Bloxan^{2/} although Kotschubey^{3/} claimed that a compound obtained by him by dissolving neutral calcium arsenate in arsenious acid lost water on heating leaving a product which was much less soluble in both water and acetic acid than was the hydrous form. Bloxan prepared the compound by treating a mixture of CaCO_3 and arsenious acid with nitric acid, then evaporating to dryness and igniting. Analysis of the resulting compound showed it to be the metarsenate. McDonnell and Smith^{4/} prepared the compound from KH_2AsO_4 , 93% As_2O_5 and $\text{CaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$. The crystals obtained belonged to the hexagonal system. The specific gravity at 35° C was 4.35. The crystalline material is very stable toward reagents. Boiling with water or strong hydrochloric or nitric acid dissolves practically no As_2O_5 . The compound must be decomposed with mixed alkali carbonates previous to analysis.

$\text{CaH}_4(\text{AsO}_4)_2$ (1. 1. 2.)

This compound (monocalcium tetrahydrogen arsenate) may be the product mentioned by Kotschubey (l.c.). Its preparation was later described by Smith^{5/} who also determined many of the

optical properties of the crystals obtained. The specific gravity of the crystalline material was found to be 3.20-3.24 at 35° C. The compound was obtained during the present investigation and will be discussed more fully later.

The monohydrate of this arsenate, the 1.1.3 compound, was prepared and described by Hermann⁶ but later investigators have been unable to duplicate his results. Hermann prepared the compound by the action of excess arsenious acid on calcium carbonate, and states that the compound occurs as colorless leaflets from which its water of crystallization may be removed by heating to 190° C. and its water of constitution at 360° C.

Calcium Arsenate with

Molecular ratio $\text{CaO}/\text{As}_2\text{O}_5 = 2$.

This series of calcium arsenates include the calcium pyro arsenate, and the dicalcium arsenates.

The calcium pyro arsenate was first prepared by Floxan by ignition of calcium ammonium arsenate, and later by Lefevre⁷ by dissolving lime or calcium carbonate in fused potassium metarsenate. The compound appeared as transparent colorless leaflets which on treatment with water changed slowly into a hydrated form. Later attempts to prepare this compound have not been very successful.



The claim is made by Debray⁸ that he obtained anhydrous dicalcium arsenate by heating the monohydrate with pure water at about 100° C. has recently been proven erroneous. McDonnell and

Smith (1.e.) found that the dicalcium arsenate mono or dihydrate hydrolyzed in hot water to yield a compound with a $\text{CaO}/\text{As}_2\text{O}_5$ ratio of 2-1/2, or a 5.2.5 compound. These observations have also been made by the author and will be discussed more fully later on. Goguel^{9/} prepared this compound from calcium carbonate and arsenic acid in a sealed tube at 150-200° C. and McDannell and Smith^{4/} produced it by dehydrating haidingerite in a concentrated solution of calcium chloride containing a small quantity of hydrochloric acid, at 150° C. Its preparation from lime and arsenic acid will be described under discussion of the results of this investigation.



(2.1.5)

This arsenate occurs in nature as the mineral Haidingerite (after Wm. Haidinger^{10/}). It has been prepared by Kotschubey^{3/} from calcium chloride and sodium arsenate, by Debray^{2/} from calcium carbonate and arsenic acid at room temperature, but Goguel^{9/} was the first to produce a well crystallized artificial haidingerite. This investigator added a solution of sodium arsenate to a solution of calcium chloride containing some arsenic acid. He also prepared it from arsenic acid and calcium acetate. McDannell and Smith experienced no difficulty in preparing this calcium arsenate in a pure and well crystallized form from calcium acetate and potassium dihydrogen arsenate. Smith^{5/} also obtained this compound in his investigation of the $\text{CaO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$ equilibrium at 35° C. The compound has a specific gravity of 2.99 at 35° C. (Smith), it is readily soluble in dilute acids, even in acetic and arsenic. In water it hydrolyzes and under certain conditions

yields a 5.2.5 compound.



While several investigators (Turner¹¹, ⁵/₃ and ⁸/₃) have described preparations which seem to agree with this formula, recent work has proven conclusively that this compound does not exist. McDonnell and Smith found that in every case where the water content dropped below the equivalent of two mols as water of hydration the microscope revealed a mixture of crystalline haidingerite and pharmacolite.



This calcium arsenate, occurring in nature as the mineral pharmacolite was first described by Haidinger¹⁰ and later analyzed by Turner¹¹. The formula assigned to the compound by Turner was $\text{CaHAsO}_4 \cdot 2-1/2\text{H}_2\text{O}$, and it remained for Dufet¹² to prepare this arsenate in the laboratory and to ascertain its correct formula. Dufet prepared the compound by slow diffusion of a solution of calcium nitrate and sodium arsenate and obtained large well formed crystals, and later DeSchnlten¹³ prepared it by adding a solution of disodium arsenate to a solution of calcium chloride containing a small amount of hydrochloric acid.

McDonnell and Smith (1.0.) prepared this arsenate by the same method as they prepared haidingerite, except the solutions were cooled to 7° or 8° C. before mixing. The mixture was kept at this temperature and after a day or so crystals of pharmacolite separated out. The author had occasion to prepare a small quantity of this salt and found that better yields

could be obtained by using the following proportions:

100 grams $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in 150 c.c. H_2O

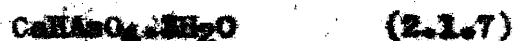
20 grams As_2O_5 as H_3AsO_4

40 grams $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ in 100 c.c. H_2O

The solutions were mixed cold, the mixture was left in the refrigerator for a day or two after which 32 grams of the compound separated out.



This compound was claimed by some of the early workers but as with the case of the 2.1.4 compound, later investigators have shown that the earlier results were in error either because of faulty analysis or impurities in the preparations.



There are no published accounts of the preparation and properties of the 2.1.7 compound, and McDonnell and Smith seem to be the only investigators who have succeeded in obtaining it. During their preparation of pharmacolite they observed under the microscope the existence of two kinds of crystals. These were separated mechanically and analysed, whence it was found that the 2.1.7 compound had formed along with the 2.1.5. The crystals soon became opaque due to efflorescence.



The mineral Wafflerite has been taken to be this calcium arsenate, but on analysis it has been shown that H_2O is a constituent of this mineral, so there seems to be no justification for considering it a simple calcium arsenate.

Calcium Arsenates with

Molecular Ratio $\text{CaO}/\text{As}_2\text{O}_5 = 2.5$.

This Series of calcium arsenates has not been described in the literature. Field¹⁴ obtained a product the analysis of which approached $5\text{CaO} \cdot 2\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ by precipitating ammonium arsenate containing a slight excess ammonium hydroxide with calcium chloride, washing and drying at 300°C . He regarded the product as a mixture of tricalcium arsenate and calcium ammonium arsenate, the ammonia having been driven off during the heating.

That such a series of calcium arsenate does exist cannot longer be questioned. McDonnell and Smith obtained well defined crystals of the 5.2.5. compound by the hydrolysis of haidingerite. The author has repeated these experiments and obtained crystals whose analysis and optical properties could be determined with accuracy. Smith⁵ also succeeded in obtaining the 5.2.7 compound in his equilibrium experiments, and finally the author has produced the 5.2.6 compound in the course of this investigation. The range of concentrations in which this series of compounds forms is very narrow, which perhaps accounts for the fact that it has not been described by earlier workers. More will be said about this series under discussion of the results of this investigation.

Calcium Arsenates with

Molecular Ratio $\text{CaO}/\text{As}_2\text{O}_5 = 3$

This series of calcium arsenates include the anhydrous tricalcium arsenate and a number of hydrated forms corresponding to 3.1.1; 3.1.2; 3.1.3; 3.1.4-1/2 (7) and 3.1.8.



Blom^{2/} claimed to have found some anhydrous calcium arsenate while analysing calcium arsenium arsenate and observed that his product was a white powder insoluble in aqua regia. His efforts to reproduce his experiments were unsuccessful, the resulting products being the meta arsenate. The author has prepared considerable quantities of this compound by simply heating 3.1.3 compound at about 450°-500° C.



The tricalcium arsenate monohydrate is readily prepared by heating the 3.1.3 compound at 110° C. in an oven. In nature Collophanite - a phosphate of calcium, and Hopeite - a phosphate of zinc have analogous compositions.



This compound was obtained in this investigation and will be described later.



The existence of this compound has not been definitely proven. P. Koschubeg^{3/} is the only investigator who has claimed its existence and some of his claims may be subject to doubt.



No reference was found in the literature to this compound or its preparation. Apparently the only method known is that of McDonnell and Smith who treated haidingerite with lime and agitated the mixture for nearly a month. Careful analysis together with phase rule evidence strongly points to a definite compound.



McDonnell and Smith prepared this compound by treating artificial haidingerite with lime water until the supernatant liquid showed a permanent alkaline reaction to phenolphthalein. The compound crystallized in thin rhombohedral plates, on which complete optical data was obtained. Analysis further confirmed the composition of the compound.

Calcium Arsenate with

Molecular Ratio $\text{CaO}/\text{As}_2\text{O}_5 = 4$

The existence of a basic calcium arsenate having a molecular $\text{CaO}/\text{As}_2\text{O}_5$ ratio of 4 has been established in the course of this investigation, and in recent work on the preparation of commercial calcium arsenates, and will be more fully discussed later on. It has been impossible to ascertain whether or not the basic calcium arsenate forms with water of hydration. This question must be left unanswered until opportunity presents itself to determine its vapor pressure curve of some definite temperature.

Only one other compound remains to be mentioned in this historical sketch, and this is the basic arsenate claimed by H. V. Zarter and co-workers^{15/}. These investigators hydrolyzed tricalcium arsenate in distilled water with gentle heating until the percent arsenate ion in solution became constant. (The percent of arsenic ion decreased with successive changes of water.) Analysis of the resulting product gave figures which indicated the compound $\text{Ca}(\text{OH})_2 \cdot 3\text{Ca}_3(\text{AsO}_4)_2$. While the evidence for the

existence of such a compound is not conclusive, nevertheless their observations carry considerable weight. They found that 100 grams of water dissolved 0.0048 gram of the salt.

Outline of Investigation

As stated above the purpose of this undertaking was to investigate the equilibrium conditions for the system: calcium oxide - arsenic oxide and water at a certain temperature, and in this way ascertain under what conditions the different arsenates of calcium could be formed, then if possible determine some of the properties of these compounds.

It is evident that a complete survey of the equilibrium conditions of a three component system requires an enormous amount of experimental work. That this is so can readily be seen from a consideration of the Phase Rule applied to such a system. The relation $P + F = C + 2$ (P = number of phases; F = degrees of freedom and C = number of components) tells us that for an invariant system no less than five phases are required, in other words the system is invariant only at a quintuple point. In an investigation such as this however the only conditions which are of interest are those under which at least three phases exist, - gas, solution and solid, and of these, the gas or vapor phase may be left out of consideration for the reason that when working at constant temperature the changes in vapor pressure due to changes in concentration exert only an insignificant effect on the compositions of the solid and liquid phases. The phase rule also tells us that as the number of phases diminishes the degrees of freedom increase, from which it follows that by working

at constant temperature the system may become univariant. In such a system the existence of one solid phase is indicated by a variation of the solution, while with two solid phases the system becomes invariant - that is - the solution has constant composition. This reduces the complexity of the system very materially, and in order to ascertain the limits within which the different calcium arsenates can exist one need only prepare a series of mixtures of calcium oxide (or hydroxide) and arsenic acid of different concentrations in water and to analyze both the solutions and the solid phases after equilibrium has been established.

One of the questions always confronting the investigator of problems involving the phase rule is that of equilibrium. In discussing real and apparent equilibria Findley states: "the chief criterion for the former is that the same condition of equilibrium is reached from whichever side it is approached". The difficulty in applying this criterion becomes apparent when working with very insoluble solid phases which interact with one another to form other solid phases. The time required for such a system to reach equilibrium would often be greater than could be allowed, and the difficulties involved in maintaining constant conditions for long periods of time are often considerable. Another method of determining equilibrium is to remove and analyze samples of the reaction mixtures from time to time, and in this way ascertain when no further changes are taking place, that is the equilibrium condition. This latter criterion was used in this investigation.

Purification of Material

Arsenic acid ($\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$)

Commercial arsenic acid was filtered through glass wool and concentrated by boiling until the boiling point was 150°C . after which it was cooled to about 20°C . and seeded with a crystal of $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. It may be mentioned here that seeding is absolutely necessary. The author tried to induce crystallization by "scratching", local chilling, further supercooling and seeding with crystals of other arsenic acids without success. Crystallization can be started with a crystal of the corresponding phosphoric acid, in fact this method had to be resorted to in order to obtain the first crop of crystals. The crystals were then melted and recrystallized until the melted material was practically colorless. The specific gravity $15/4$ of the melted acid was 2.325 which corresponded to 74.5% As_2O_5 . (Theoretical for $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O} = 76.1\%$).

Calcium Oxide

The calcium oxide used in the first series of equilibrium experiments was prepared from pure precipitated calcium carbonate by careful ignition in an electric furnace. The loss in weight observed after ignition agreed with theory and subsequent analysis of the oxide proved it to be of the order of 99.9% CaO . For later experiments pure calcium hydroxide was prepared from calcium chloride and carbonate-free sodium hydroxide. After washing the precipitate out of contact with CO_2 until the filtrate showed no test for chlorides, the lime obtained analysed about 98.0% Ca(OH)_2 the remainder being water.

Distilled water boiled to drive off any dissolved carbon dioxide was used in all experiments.

EXPERIMENTAL.

In a series of thirty three four ounce bottles were added successively increased amounts of arsenic acid and 100 cc. water, then calcium oxide in such quantities as would produce sufficient precipitate for analysis. The amounts of CaO added ranged from 1.25 to 5.5 grams. The percent of As_2O_5 left in solution after this treatment varied from a trace to 71.5. The bottles were then placed in the rotating machine shown in Figs. 1 and 2, which in turn was placed in a water thermostat kept at $52.0 \pm 0.05^\circ C.$ by means of an 'Aminco High Precision Thermo Regulator'. The samples were agitated day and night for nearly four months to insure equilibrium. On some of the mixtures duplicate runs were made lasting only a short time and these were found to give analysis which checked with those of the main series, from which it was concluded that equilibrium had been reached in all runs.

Analysis of Calcium Arsenates.

After equilibrium had been established the contents of the bottles were filtered through a Gooch filter fitted with a double thickness of fairly tight filter paper. Both the precipitates and filtrates were kept in stoppered bottles until analysis could be made. The precipitates were analysed wet because it was feared that changes might take place during washing and drying.

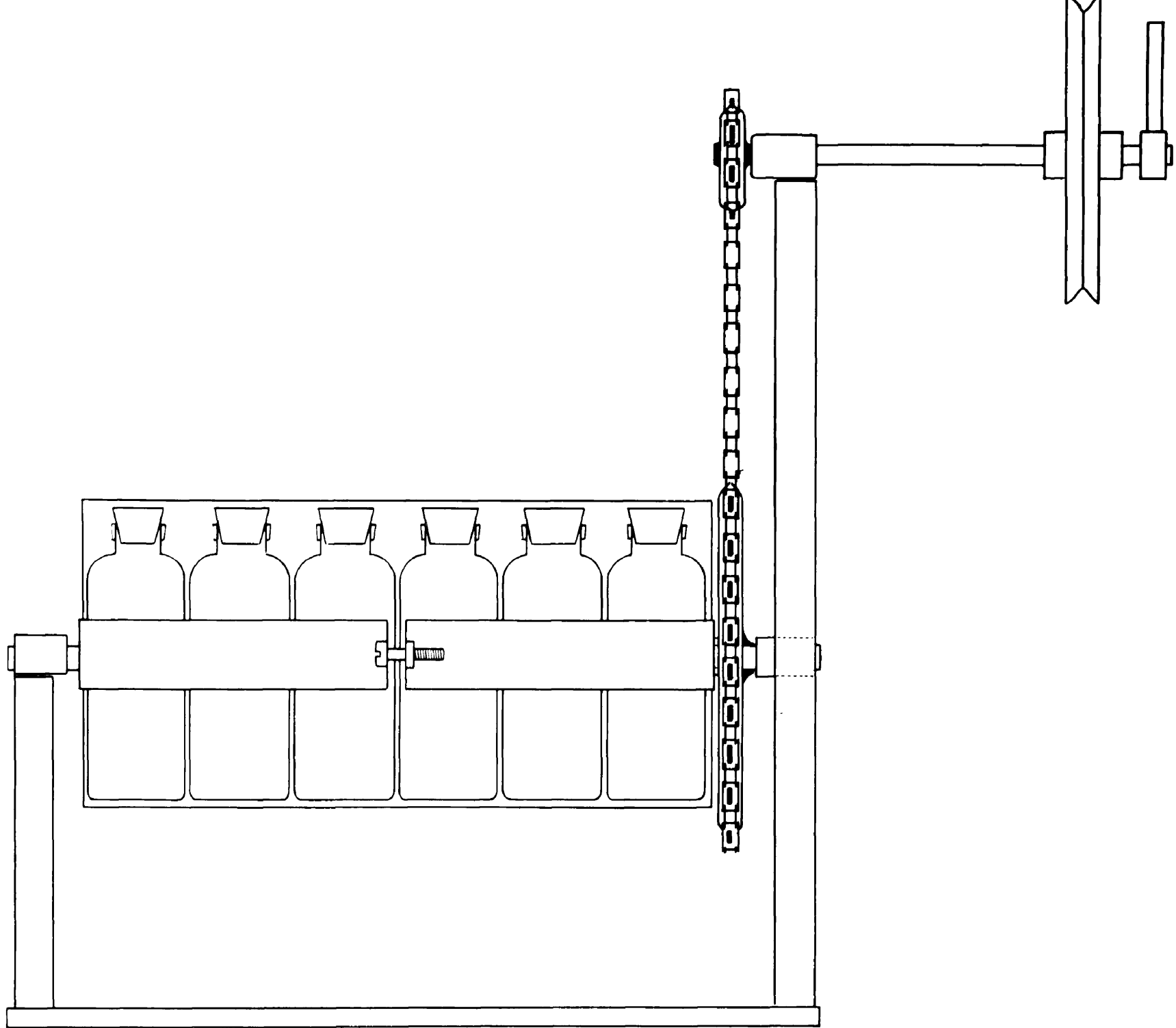


FIG. I
SIDE ELEVATION OF ROTATING MACHINE

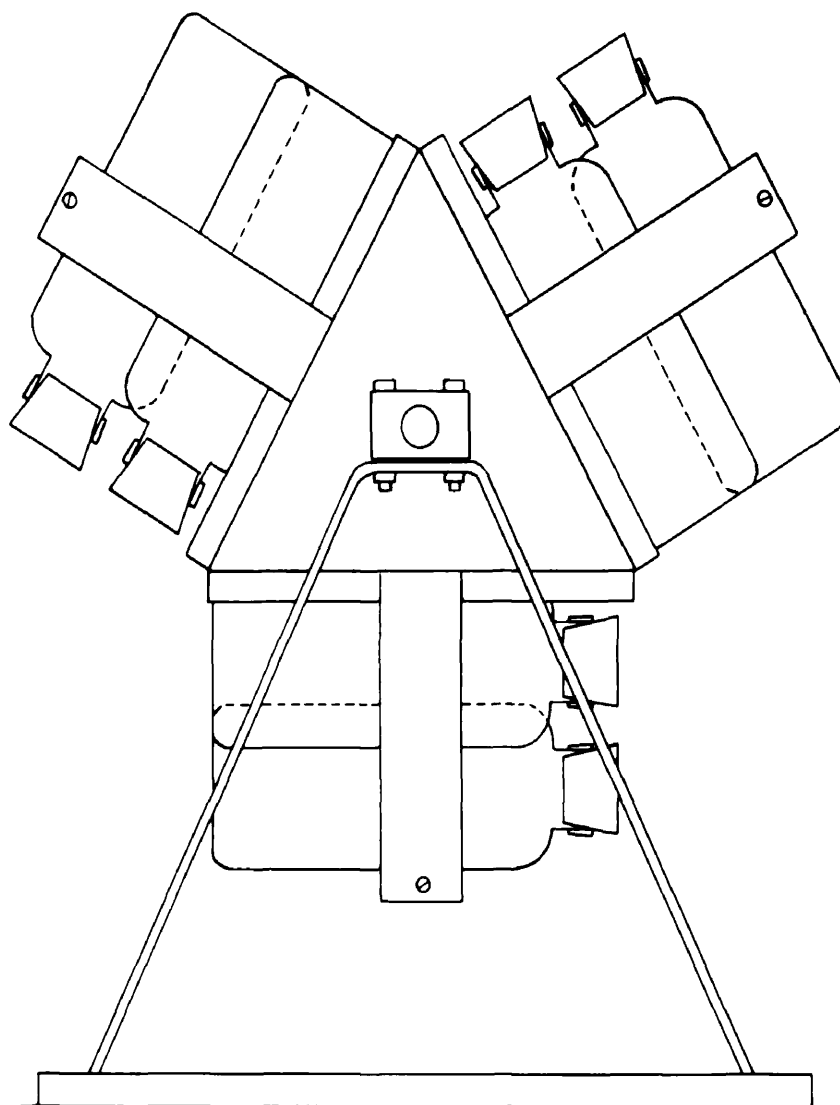


FIG. II
END ELEVATION OF ROTATING MACHINE
(LEFT END OF FIG. I)

The weighed precipitates were dissolved in 1-4 (by volume) acetic acid, and the solution made to 500 c.c. Suitable aliquots were then taken for arsenic and lime determinations.

The arsenic was determined by adding a volume of concentrated hydrochloric acid equal to the volume of the aliquot, then 10 cc. potassium iodide solution (2 grams KI) and the liberated iodine titrated with standard thiosulfate solution. The arsenic in the most dilute solutions were determined by the Goech-Browning method or the Gutzzeit method. The former of these methods are recommended by A.O.A.C. methods for determining soluble arsenic in commercial calcium arsenates, and the latter is widely used in determining arsenic in spray residues.

The calcium oxide was determined by precipitating as oxalate from boiling solutions of arsenates in dilute acetic acid. After filtering and washing the precipitate it was dissolved in dilute sulfuric acid and titrated hot with standard permanganate. It may be of interest to mention here that calcium oxalate precipitated in this way is very readily filtered and washed, a condition not often met with when precipitating from basic or neutral solutions.

Analytical Results

The results of the analysis of the precipitates and solutions obtained from the first series are given in Table 1.

TABLE I

Analytical Results of the "D" Series

Expt.	Analysis of Precipitates			:	Analysis of Solutions		
	Percent CaO	Per cent As ₂ O ₅	Molar CaO/As ₂ O ₅		Percent CaO	Per cent As ₂ O ₅	Molar CaO/As ₂ O ₅
D-1	16.44	22.19	3.04		00.056	00.15	---
D-2	14.48	20.14	2.97		00.068	00.16	---
D-3	18.00	23.18	3.18		00.028	00.025	---
D-4	21.72	26.18	3.40		00.057	00.016	---
D-5	20.50	24.35	3.44		00.035	00.013	---
D-6	17.65	19.56	3.64		00.030	00.015	---
D-7	16.75	18.85	3.64		00.020	00.018	---
D-8	18.60	20.47	3.70		---	---	---
D-9	16.00	33.62	2.24		01.440	1.82	---
D-10	18.45	33.50	1.97		---	---	---
D-11	17.00	36.10	1.94		1.04	4.23	1.01
D-12	17.55	38.70	---		1.64	7.04	0.97
D-13	15.80	34.80	---		1.56	6.91	0.99
D-14	16.45	36.60	---		2.43	10.20	0.93
D-15	18.55	41.20	---		2.98	12.60	0.97
D-16	23.13	53.90	---		4.01	16.92	0.97
D-17	27.40	58.00	---		4.66	21.20	0.91
D-18	22.90	53.00	---		5.42	24.20	0.92
D-19	17.80	44.20	---		3.15	34.10	0.93
D-20	20.21	63.80	---		6.54	30.80	0.88
D-21	16.80	62.00	---		6.53	30.65	0.86
D-22	14.48	67.80	---		6.25	31.60	0.82
D-23	23.13	67.80	---		5.02	38.10	0.54
D-24	17.05	71.60	---		4.35	41.10	0.43
D-25	15.40	66.15	---		3.36	43.00	0.28
D-26	18.25	69.00	---		2.37	54.30	0.18
D-27	13.75	69.15	---		1.42	61.30	0.10
D-28	11.32	69.30	---		0.505	67.55	0.05
D-29	8.05	71.50	---		0.11	71.75	0.006

It will be seen from the table that the results are divided into two sections, those for precipitates and those for solutions. The $\text{CaO}/\text{As}_2\text{O}_5$ ratios for the precipitates are given only for the basic arsenates, for the reason that over this range there is practically no arsenic acid adhering to the precipitate, and the ratios have some meaning. On the acid side however, where more and more concentrated solutions are left with the crystals the $\text{CaO}/\text{As}_2\text{O}_5$ ratios as found by direct analysis would have no significance and are omitted. The $\text{CaO}/\text{As}_2\text{O}_5$ ratios in the solutions for the basic side are omitted for the reason that here both the CaO and the As_2O_5 content of the solution are so low that any slight error in analysis would cause such a variation in the $\text{CaO}/\text{As}_2\text{O}_5$ ratios as to render them meaningless. From experiments D-12 to D-33 these ratios are stated, and while only the ratios for experiments D-12 to D-24 have any real significance, as will be shown later the entire series are included.

Graphical Representation of Results.

Perhaps the most common method of representing results of phase rule studies of three component systems is by the use of the equilateral triangular graph. Such representation is most suitable in cases where the behavior of the three components toward one another is similar, but is quite unsuitable for systems wherein the behavior of two components to one another is very different from their behavior toward the third.

In such systems the results can be shown with greater clearness on rectangular coordinate paper by plotting the percentages of two components along coordinates at right angles to each other. On such graphs overstepping in some areas may be avoided, or the bringing out of certain relationships more clearly, may be accomplished by the proper choice of scales of plotting. In Figure 3 the results obtained in two series of experiments are so plotted.

After the first series had been completed and plotted it was seen that there was evidence of at least one, and possibly three compounds to the left of disodium arsenate. It was felt that it should be possible to demonstrate the existence of the 4.1.X and 3.1.X compounds and possibly a 5.2.X compound. The crystals from the first series were small and for this reason difficult to analyze under the microscope. The reason for the smallness of the crystals might have been due to the high rate of speed at which the rotating machine was revolving. Accordingly another series of experiments was set up, chiefly with the idea of covering this range of concentration more carefully, and if possible grow crystals that could be analyzed under the microscope. Calcium hydroxide was used instead of calcium oxide, and larger quantities were taken. The results obtained from these runs are plotted in Figure 3, marked (E-1) to (E-9) and the numerical results obtained are recorded in Table 2.

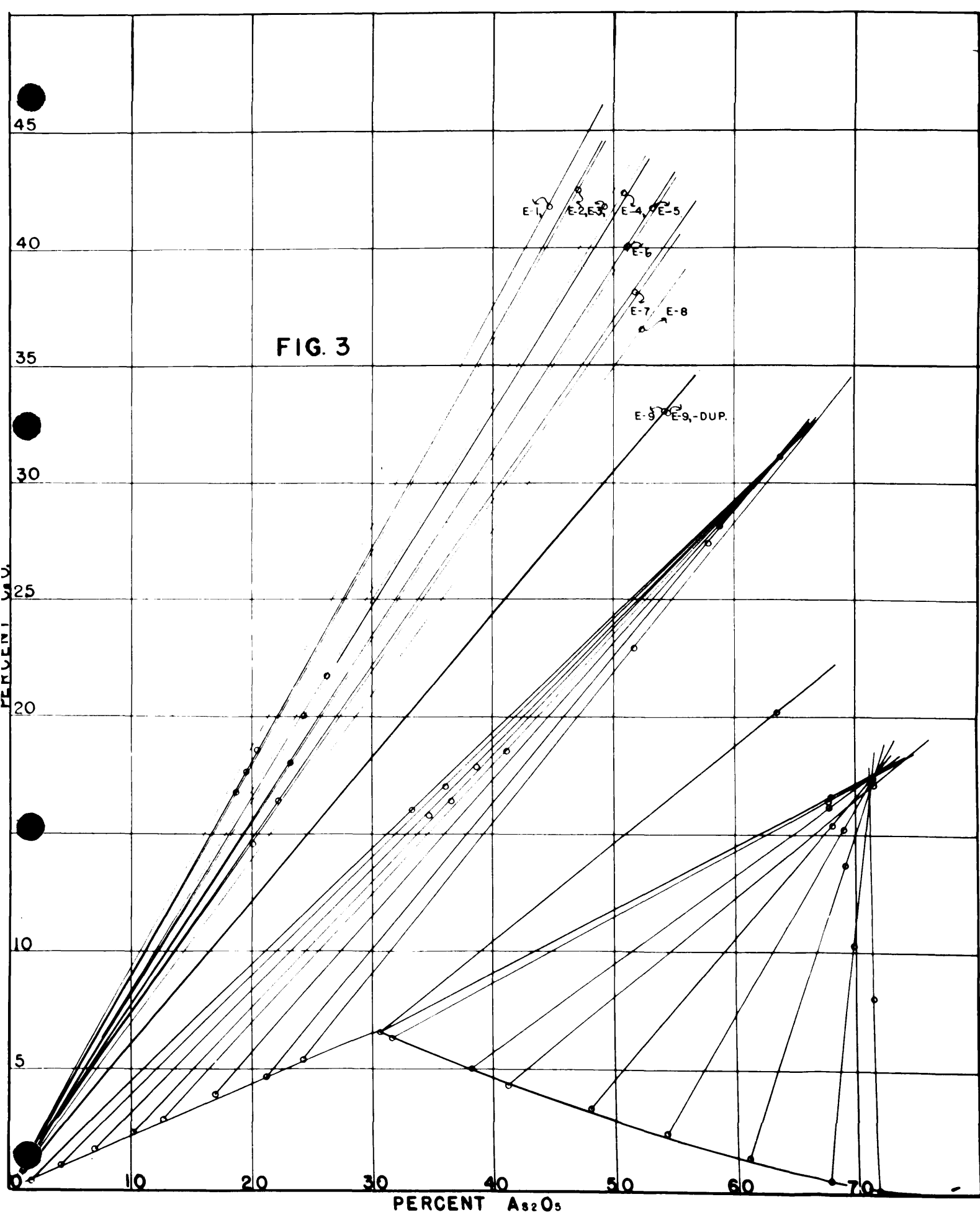
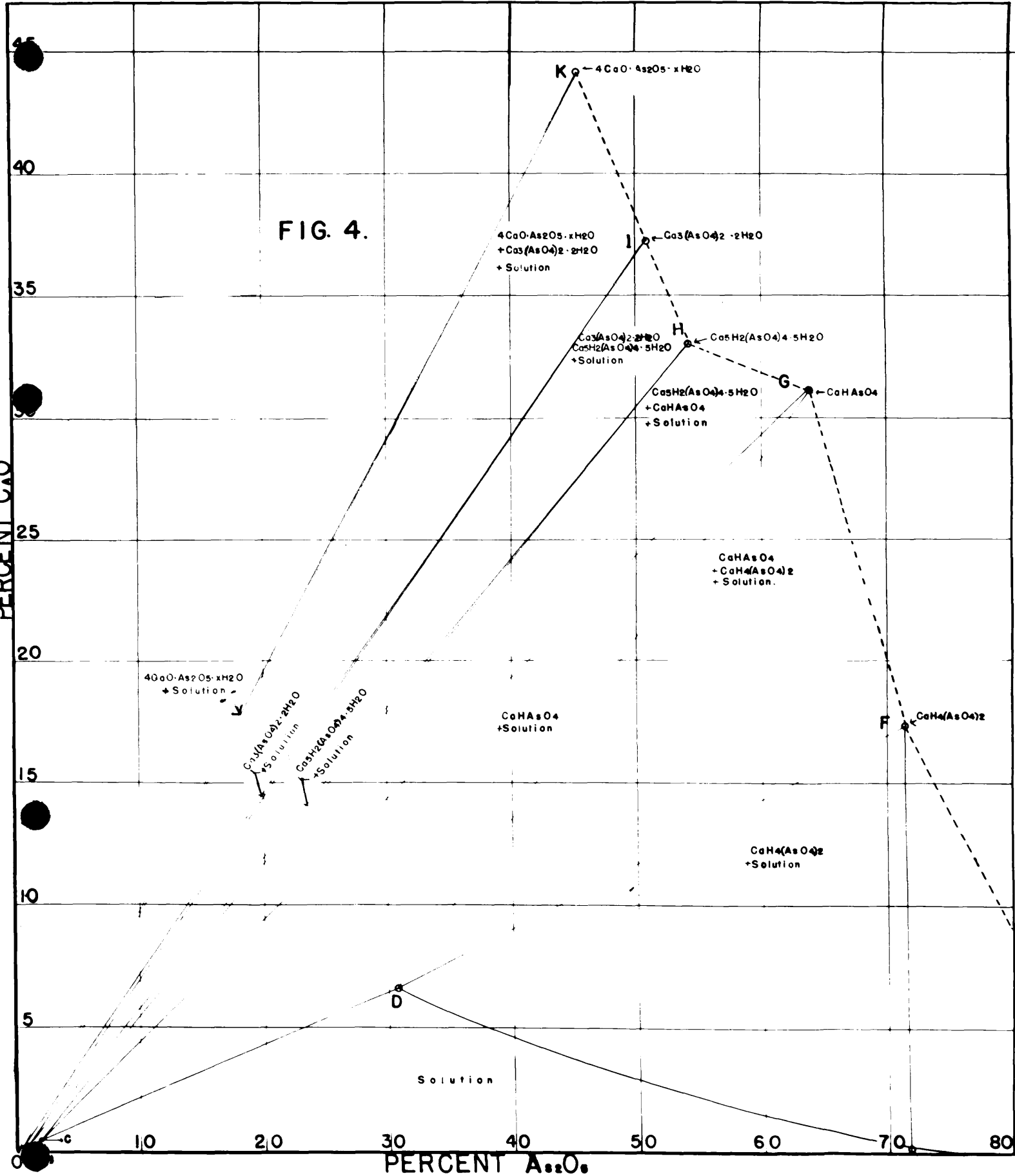


TABLE 2

Analytical Results of the "B" Series

Expt. No.	Analysis of Precipitates			Analysis of Solution		Remarks
	Percent CaO	Percent As ₂ O ₅	Molar CaO/As ₂ O ₅	Percent CaO	Percent As ₂ O ₅	
E-1	41.79	44.83	3.84	0.015	Trace	
E-2	42.30	47.10	3.70	0.006	"	
E-3	41.75	49.15	3.48	0.005	"	
E-4	42.35	50.58	3.42	0.003	"	
E-5	41.75	53.10	5.23	0.016	0.050	
E-6	40.10	51.10	3.22	0.032	0.099	Crystals of 3.1.2
E-7	38.10	52.78	2.96	0.043	0.171	" " 3.1.2
E-8	35.40	52.50	2.74	0.051	0.216	" " 3.1.2
E-9	33.00	54.23	1.493	0.065	0.210	" " 5.2.6
E-9 Dup.	33.00	55.10	2.46	0.093	0.208	" " 5.2.6
E-1 Dup.	36.10	38.70	3.65	0.100	Trace	In Pt. Flask 1.67% free CaO.
E-2 Dup.	40.00	45.50	3.84	0.080	"	In Pt. Flask 2.98% free CaO.

FIG. 4.



Discussion of Results

In order to be better able to analyze the results obtained from the foregoing experiments, the detailed graph (Figure 3) was redrawn leaving out the individual tie lines and showing instead the regions wherein compounds, solutions or mixtures could be formed. These regions will be discussed from the point of view of the phase rule using Fig. 4 as reference.

In discussing the requirements of the phase rule as applied to three component systems it was stated that with the three phases present (solid, gas and solution) and working at constant temperature the system could become univariant. Under such conditions the existence of a compound would be indicated by a variation in the solution, or the existence of two compounds by a constant solution. With these requirements established the different regions in Figure 4 are readily interpreted.

The line O-D represents solutions in equilibrium with all compounds less acid than mono calcium arsenate (F) and line D-E represents solutions in equilibrium with mono-calcium arsenate. The area bounded by the lines O-D-E-O represents the region of solution, while region D-F-E-D contains the compound (F), $(CaH_4(AsO_4)_2)$, and solution. The solution being variable the phase rule requires the existence of but one compound in this region. At point (D) the solution is constant and compounds (F) and (G) may co-exist (two solid phases)

therefore the region D-G-F-D would contain compounds (G) and (F) (CaHAsO_4 and $\text{CaH}_2(\text{AsO}_4)_2$) and solution. Experiment 24 shows such a condition. The composition of the solution at (D) was found to be 6.54% CaO and 30.60% As_2O_5 , and both chemical and optical examination of the solid phase proved that it was a mixture of mono and di calcium arsenates.

Similarly the remaining regions may be shown to have the following compositions:

Region C-G-D-C	Compound (G) (CaHAsO_4) and	Solution
" C-H-G-C	" (H) ($\text{Ca}_2\text{H}_2(\text{AsO}_4)_4 \cdot 5\text{H}_2\text{O}$) + (G) + Soln.	
" D-H-C-B	" (H) (" " " " + Soln.	
" E-I-H-B	" (I) ($\text{Ca}_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$) + (H) + Soln.	
" A-I-B-A	" (I) (" " " " + Soln.	
" A-K-I-A	" (K) ($4\text{CaO} \cdot \text{As}_2\text{O}_5 \cdot \text{XH}_2\text{O}$) + (Y) + Soln.	
" O-K-A-O	" (K) (" " " ") + Soln.	

Since no calcium arsenate more basic than $4\text{CaO} \cdot \text{As}_2\text{O}_5 \cdot \text{XH}_2\text{O}$ has been found or prepared, the region to the left of line O-K must consist of free lime and compound (K) and solution. The region above and to the right of line K-I-H-G-F represents the region of no solution. This line could be extended to the composition of $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ which is known to exist, although in these experiments the solution was not concentrated to a sufficient extent to precipitate this arsenic acid.

From this preliminary discussion it will be seen that no less than four new compounds have been indicated as forming

under conditions prevailing in this investigation. In what follows more detailed or specific evidence will be presented for the existence of the compounds indicated in Figure 4.

In the case of the monocalcium arsenate (2.1.2 opd) not much need be said. The analysis of the solid phases in Experiments D-25 to D-33 inclusive showed that not very much mother liquor adhered to the crystals, thus the tie lines connecting the solids and the solutions did not have to be projected far beyond the composition of the solid phase. It was also observed that all the tie lines intersected so near the point representing the theoretical composition of $\text{CaH}_2(\text{AsO}_4)_2$ as to leave no doubt as to the composition of the solid phases in these experiments. Furthermore this compound was obtained by Batch 5 at 25° C., and it would be impossible for any other compound to form in this range of concentrations at a temperature only 25° C. higher.

Point (G), Figure 4, represents the composition of anhydrous dicalcium arsenate, or CaH_2AsO_4 or (2.1.1 opd). That the anhydrous compound formed instead of one of the hydrated forms is shown by the directions and intersection of the tie lines connecting the solutions with the solid phases within the region C-G-D-C. If a line be drawn from O to G it will lie above the line C-G, Figure 4. Dicalcium arsenate monohydrate (2.1.2 opd) has the compositions CaO 28.31% and As_2O_5 58.04%. It will be seen from Figure 3 that the intersection of all the tie lines in

this region lies well above and to the right of a point representing the composition of the 2.1.2 compound. The optical characteristics of crystals obtained in this region are as follows: tentative values for two true indices are 1.525 and 1.555 resp. Extinction unsymetric. Habit: elongated parallelogrammatic plates. Figure 5 is a photograph of the 2.1.1. compound crystals.

Point (G) which represents a solution of constant composition, where the solid phase would consist of the two compounds (G) and (H) was not located with accuracy. All that is known about its position is that it lies somewhere between 0.22% As_2O_3 and 1.84% As_2O_3 , and the probability is that it is nearer to the former concentration.

The next compound to be considered is that represented by (H). It is obvious that the exact location of this compound could not be definitely ascertained by the intersection of the lines, since these are so nearly parallel as to make such a determination impossible. It was stated above that the range of concentration in which this compound can form is very narrow. The method by which this compound was discovered was by analysis of the solid phase after all extraneous water had been removed, and then by obtaining well defined crystals on which reliable optical data could be determined. Point (H), Figure 4, represents a compound having the formula $\text{Ca}_3\text{H}_2(\text{AsO}_4)_4 \cdot 5\text{H}_2\text{O}$, or the 5.2.6 compound. The chemical analysis of the compound, after removing adsorbed water by washing with 95% alcohol and gentle warming, to remove the alcohol was: CaO , 33.00%,

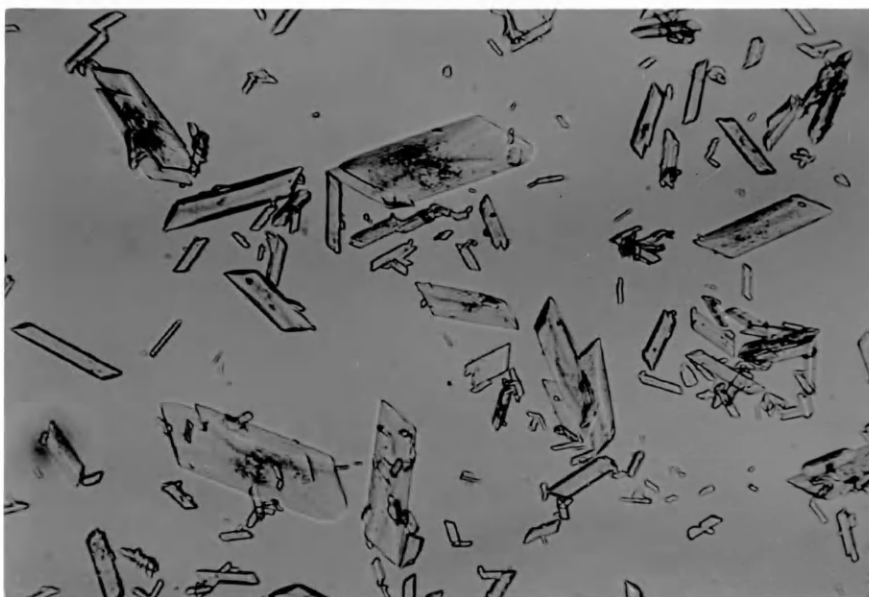


Figure 5
Photomicrograph of crystals
of CaHAsO_4 or Zeolite.

As_2O_5 54.28%. The theoretical values for the 5.2.6 spd. is CaO 33.05%; As_2O_5 54.21%, H_2O 12.72%. The almost perfect agreement of the analysis with the theoretical values is very strong evidence for the existence of the arsenate. As additional data on the properties of this compound the following optical characteristics are recorded: Two true indices thought to be β and γ are 1.60 and 1.64 respectively, the optical character probably negative and the elongation commonly positive. Extinction approximately parallel. Habit: Plates nearly square, usually somewhat elongated. A photomicrograph of the crystals is shown in Figure 6.

McDonnell and Smith succeeded in obtaining a compound of the composition $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 6\text{H}_2\text{O}$ in one of their experiments at 35° C. and compound was crystalline from which definite optical data was obtained, nevertheless they were unable to reproduce their results. Smith later prepared the 5.2.5 compound by hydrolysis of haidingerite. This experiment is readily reproduced and photomicrographs of the two compounds are shown in Figure 7 and Figure 8 for comparison with that of the new compound shown in Figure 6. Evidence for the order of formation of the 5.3.6 compound was gained from following the changes taking place in one experiment (E-9 duplicate) under the microscope (See Figure 9). It was noted that in the early stages crystals of the 5.2.5 compound were very numerous while relative few 5.2.6 could be seen. As time went on, however the

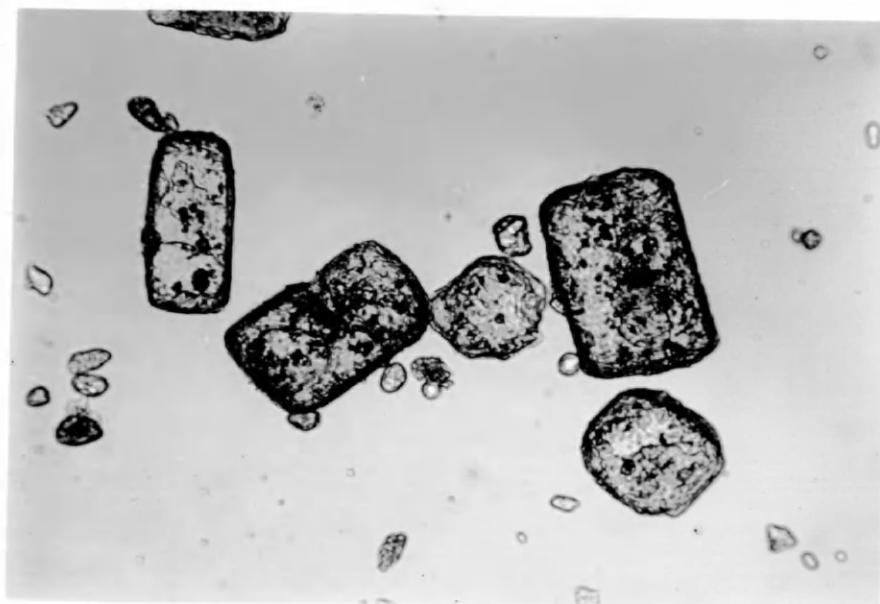


Figure 6
Photomicrograph of crystals
of $(AgH_2(AsO_4)_4 \cdot 5H_2O)$ or
S.2.6 compound.

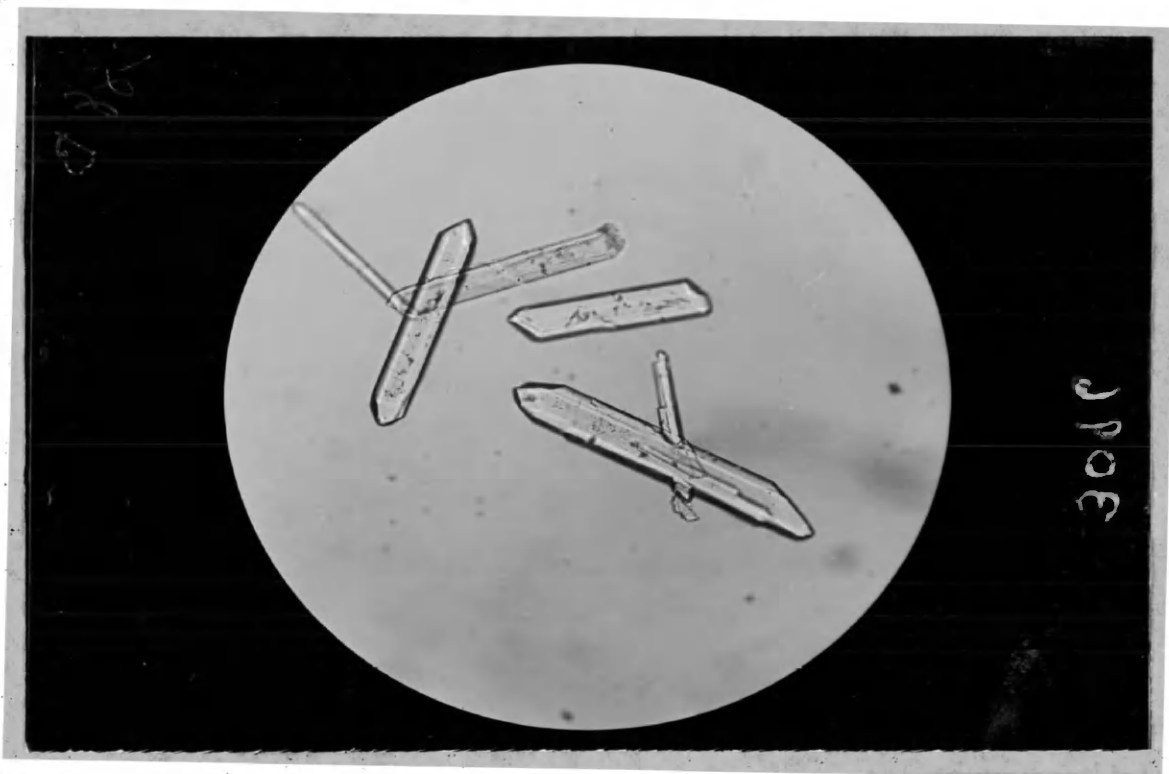


Figure 7.
Photomicrograph of Crystals
of $\text{CaH}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$ or
6.2.5 compound. (From C.M. Smith)

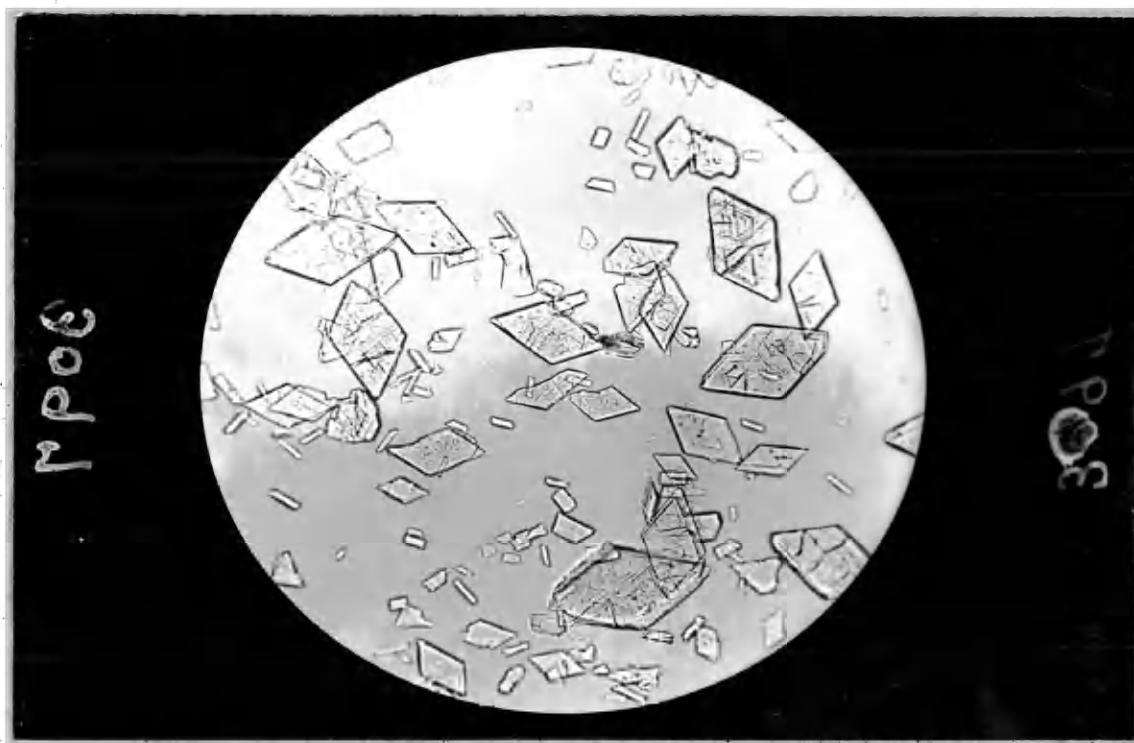


Figure 3
Photomicrograph of Crystals
of $\text{CaH}_2(\text{AsO}_4)_4 \cdot 6\text{H}_2\text{O}$ or
5.2.7 compound
(From C.M. Smith)

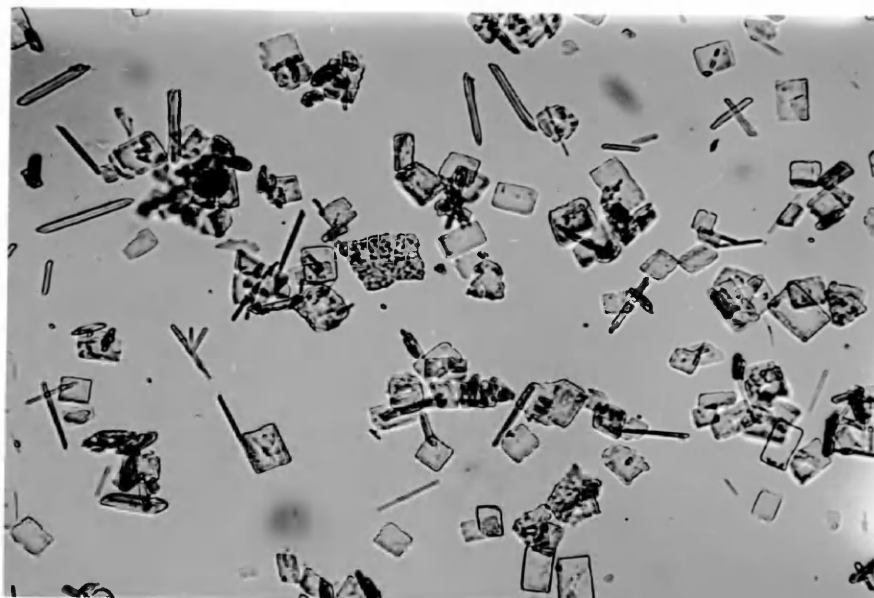


Figure 9
Photomicrograph of Mixture
of 5.2.6 and 5.2.5 showing
formation of the former
from the latter.

5.2.5 crystals decreased in number and size and the 5.2.6 increased. From such an observation one may postulate that at the temperature or concentration of the experiment the 5.2.5 compound is unstable and gradually changes over into the 5.2.6. From this it would follow that the 5.2.5 compound formed by hydrolysis of heddingerite might transform into the 5.2.6 compound if such a preparation were seeded with a crystal of 5.2.6 compound. This latter experiment has not been attempted.

The length and slope of the solubility curve B-C for this compound has not been definitely determined. It will be seen from Figure 3 and Figure 4 and from the tables that the solubilities of the compounds, H, I, and K (Figure 4), are of the order of 0.20% As_2O_5 or less and the accuracy of the determinations was not high enough to show the directions of the curves from O to C.

The identity of the compound represented by (I) Figure 4 had to be determined from the analysis and optical characteristics of the solid phase, for the reason that the trichlorum arsenates are so insoluble as to make the the lines between solids and solutions run almost parallel. That $\text{Ce}_2(\text{AsO}_4)_3 \cdot 2\text{H}_2\text{O}$ or 5.1.2 compound was obtained was readily ascertained from chemical analysis of the solid phase after the adsorbed water had been removed by washing with alcohol and gentle drying.

The solid from Experiment K-7 gave the following analysis:

CeO 39.10%; As_2O_5 52.78%. (Theoretical composition for

3.1.2 compound is CaO 38.74%; As_2O_5 52.96%; H_2O 8.30%.)

This indicates that about 0.72% H_2O or alcohol was adhering to the solid. The optical data of the crystals of this compound follows: two true indices thought to be β and γ are 1.615 and 1.602 respectively. The optical character is probably negative, and the elongation usually negative. The extinction is usually near 18° and the crystal probably belongs to the monoclinic system. Habit: Long irregular slabs terminating in small parallel projections, surface and edges rough. Birefringence evidently quite low. Figure 10 is a photomicrograph of crystals of 3.1.2 compound.

It was pointed out above (under Historical discussion) that tricalcium octa hydrate could be prepared with ease at room temperature, and also that by heating to 100°C . this hydrate loses $7/8$ of its water to form the monohydrate. From these observations it is quite reasonable to expect some intermediate hydrate to form at a temperature of 62°C .

This brings us to the last of the definite compounds identified in this investigation, the tetra-calcium-arsenate, $4\text{CaO} \cdot \text{As}_2\text{O}_5 \cdot x \text{H}_2\text{O}$ or 4.1.X compound. The formula for such a compound may be $\text{Ca}_2(\text{CaOH})_2(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$ or $\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ or $\text{Ca} \cdot \text{CaOH} \cdot \text{AsO}_4 \cdot x\text{H}_2\text{O}$. This compound is more readily prepared at room temperature and the most basic preparations obtained in either the B or E series of experiments were

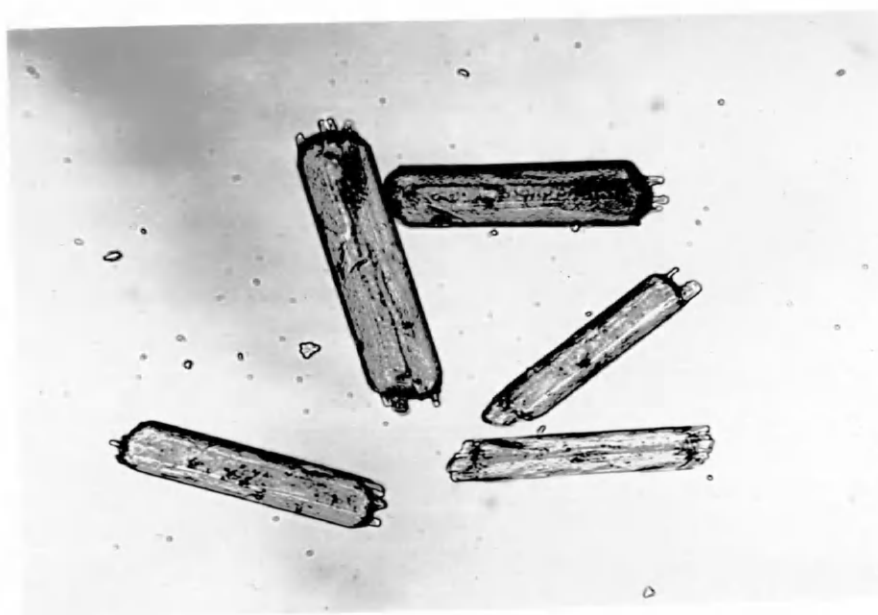


Figure 10
Photomicrograph of Crystals
of $\text{Ca}_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ or
5.1.2 compound

represented by a $\text{CaO}/\text{As}_2\text{O}_5$ ratio of 3.35. However in an Earlier series of experiments the evidence seems conclusive that the compound can be prepared at elevated temperatures as well. At room temperature the compound is readily prepared by adding two mols H_3AsO_4 to a little more than four mols $\text{Ca}(\text{OH})_2$ suspended in a large excess of water. Sufficient lime must be taken so that the supernatant liquid is about half saturated with $\text{Ca}(\text{OH})_2$ after the reaction is completed. If the concentration of the lime suspension is such as to produce a 7-8% suspension of the 4.1.X compound the reaction mixture takes the form of a fairly rigid jelly. This indicates an extremely fine state of subdivision of the basic arsenate formed. On analysis such a product shows a $\text{CaO}/\text{As}_2\text{O}_5$ ratio of 4, no free lime and of course no free arsenic acid. The supernatant liquid contains a trace of As_2O_5 and a $\text{Ca}(\text{OH})_2$ content depending on the excess lime taken originally.

A series of experiments were carried out at 62° C. as follows: A quantity of saturated lime water was prepared and kept in a paraffined bottle well stoppered. Portions of this stock solution were withdrawn and diluted with distilled water which had recently been boiled free from CO_2 and cooled. The concentration of the diluted lime solution was determined by titrating with standard N/100 HCl , using phenolphthalein as indicator. To the standard $\text{Ca}(\text{OH})_2$ solution was then added at room temperature a definite quantity of standard arsenic

acid solution, and the mixture heated to 62° C. and shaken in a platinum Erlenmeyer flask for 5 - 6 hours after which the precipitate was filtered off and the $\text{Ca}(\text{OH})_2$ concentration in the supernatant liquid again determined by titrating with N/100 HCl. Only the merest trace of As_2O_5 could be detected in the filtrate. From the data thus obtained the $\text{CaO}/\text{As}_2\text{O}_5$ ratio in the precipitate was readily calculated. The experimental data is given in Table 3 and shown graphically in Figure 11.

X-ray Examination of Calcium Arsenates:

In the preceding paragraphs evidence has been presented, from the point of view of the phase rule and chemical analysis, for the existence of a number of calcium arsenates, not previously described. According to the phase rule, region A-K-I-A, Figure 4, should contain a mixture of 4.1.X and 3.1.2 compounds. Due to the experimental difficulty of ascertaining whether or not the solution was constant in composition, it was not possible to definitely ascertain whether or not there was present in this region two solid phases or a solid solution. The phase rule requires that if the solid phase is a solid solution the solubility must change, as the ratio of the components of the solid solution changes, while if two solid phases are present the solution must be constant.

In order to settle this point X-ray photographs were obtained for a number of preparations in this region. Photographs were also made of the 3.1.8; 5.2.6 and 2.1.1 compounds,

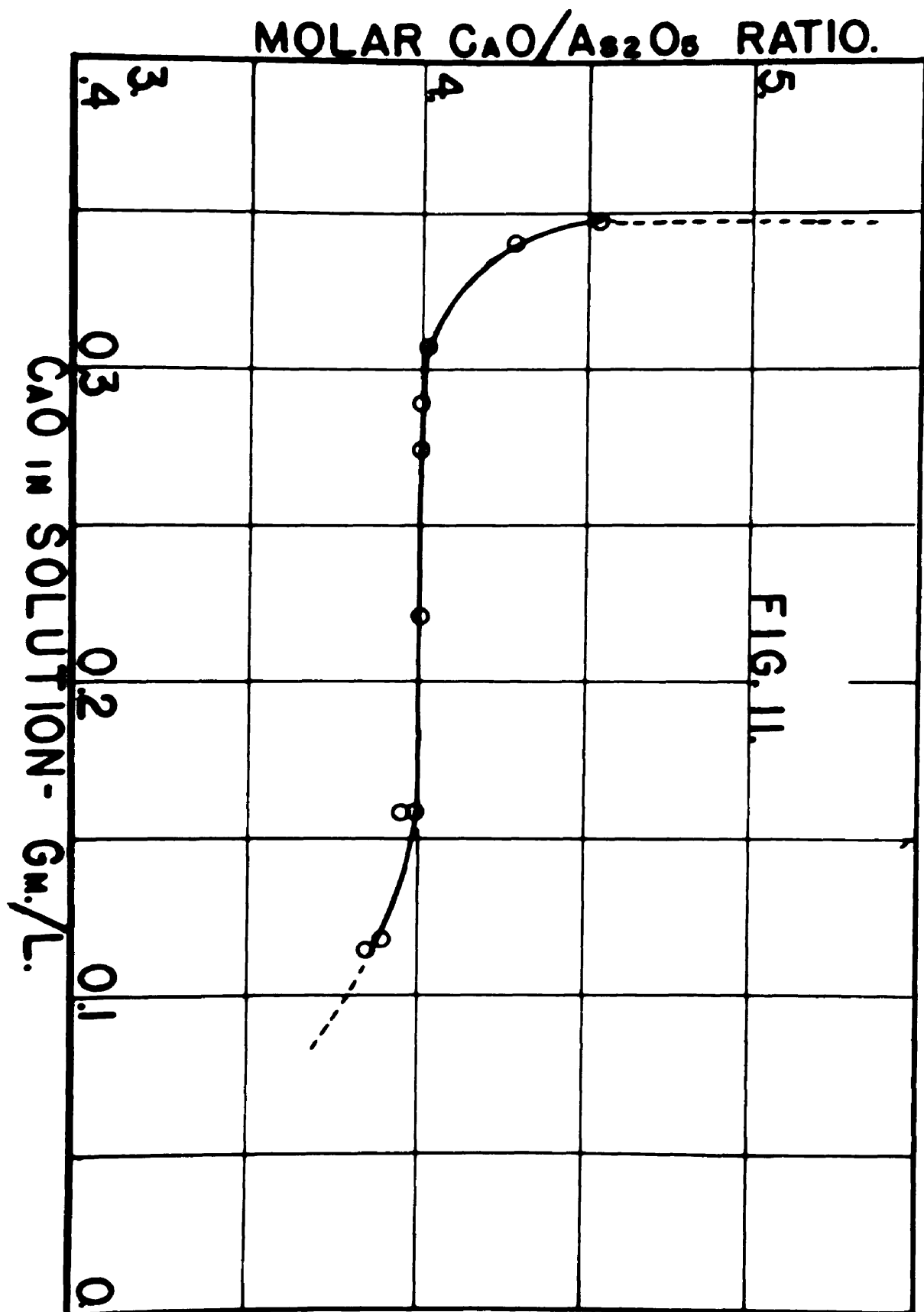
Table 3

Analytical Results of the "B" Series

Temperature = 30°C.

Expt. 1000/1000 : 1000/1000 : 1000/1000 : 1000 in
No. 1000 at : ratio in : 1000 per 1.0 : 1000
: 1000 : 1000 : 1000 : 1000

1-0	10.30	4.85	11.6	0.3475
1-0	9.50	4.20	11.4	0.3412
2-0	8.95	4.37	10.8	0.3375
3-0	8.65	4.12	9.7	0.2950
3-0	8.35	4.01	8.8	0.275
4-0	7.80	4.01	7.4	0.221
5-0	6.47	3.95	6.3	0.188
6-0	6.20	4.12	5.8	0.155
6-0	5.75	3.90	5.65	0.135
6-0	5.80	3.80	4.50	0.115



chiefly for the purpose of obtaining additional data on these compounds.

The preparations of which X-ray photographs were made were the following:

No. 1 - $\text{Ca}(\text{OH})_2$

No. 5 - Expt. E-7

No. 2 - $4\text{CaO} \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$

No. 6 - $\text{Ca}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$

No. 3 - Expt. E-2

No. 7 - Expt. E-9 (5.2.6)

No. 4 - Expt. E-4

No. 8 - Expt. D-12 (2.1.1)

The photographs were taken with $\text{Cu K}\alpha$ radiation in cylindrical cameras with radii of 3.46 cm. The minimum amount of one phase detectable by this method is 5.0%. The photographs obtained is shown in Figure 12.

Examination of these photographs reveal the following: No. 1 shows the usual diffraction pattern for hexagonal $\text{Ca}(\text{OH})_2$. No. 2 shows the diffraction pattern for the tetra calcium arsenate (4.1.X) and since this pattern differs from any of the others, it provides additional positive evidence for the existence of this basic compound. Nos. 3, 4, and 5 show identical diffraction patterns which indicates solid solutions. Now No. 5 is $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, and since there is no displacement of the lines in Nos. 3 and 4, the interpretation is that the solid solutions are formed without altering the size of the lattice. No. 2 is a solid solution in which the molar $\text{CaO}/\text{As}_2\text{O}_5$ ratio is 3.70. However examination of more basic preparations would be necessary

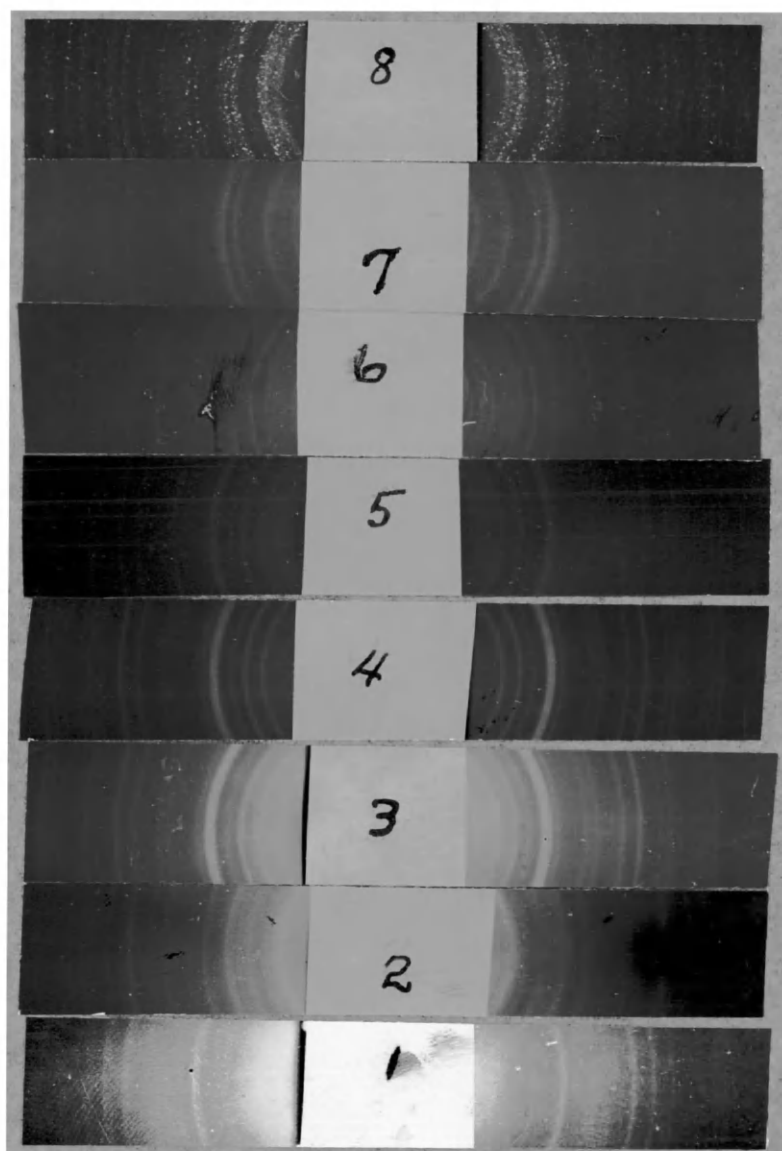


Figure 12. Photographs of Diffraction Patterns of $\text{Ca}(\text{OH})_2$ and Calcium Arsenates.

- | | |
|--|--|
| 1. $\text{Ca}(\text{OH})_2$ | 8. 3.1.2 (8-7) |
| 2. $4\text{CaO} \cdot \text{As}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ | 9. $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$ |
| 3. 5.7.1.1 (1-2) | 7. 5.2.6 (1-9) |
| 4. 3.44.1.1 (1-4) | 8. 2.1.1 (1-19) |

in order to definitely define the region of solid solution. There is also an indication that Nos. 3, 4, and 5 have apatite lattice, although measurements, and intensity calculations would be necessary before this can be stated with certainty. It should be of interest, however, to note that if it should develop that the lattice for the solid solutions is that of apatite, the claims made by Barber and co-workers for the existence of a 3-1/3.1.1 compound would be strengthened very materially.

The X-ray examination of the products in the basic range shows then, that a solid solution forms in which the pattern is the same as that of tricalcium arsenate dihydrate and that this solution may reach a basicity approaching that of tetra calcium arsenate. The examination also shows that the 4.1.1 compound is definitely present. This must be taken to mean that tricalcium arsenate dihydrate is capable of dissolving a large quantity of tetra calcium arsenate, but that the 4.1.1 can dissolve only a very small quantity of the 3.1.2.

Photographs Nos. 6, 7, and 8 show the patterns for 3.1.3; 5.2.6 and 2.1.1 compounds respectively. These preparations all show different patterns as was expected. The 3.1.3 compound was not obtained in this investigation, but its X-ray pattern is included here in order to provide additional evidence for the existence of the 3.1.2 compound.

The information recorded in the discussion of X-ray data, suggests other problems for investigation. Experimental data on the relative solubilities of different solid solutions would be valuable, and if it should be found that a solid solution of a certain composition has a minimum solubility then methods of preparing such a product should be investigated. Another problem that suggests itself is that of determining the water of hydration in tetra calcium arsenate.

Hydrolysis of Calcium Arsenates.

The experimental data recorded in the preceding pages provide considerable information regarding the behavior of the different calcium arsenates in aqueous solutions.

Since the concentrations of the solution along line C-D are such that the average $\text{CaO}/\text{As}_2\text{O}_5$ ratio is 0.964 it follows that there must be only slight hydrolysis in the case of the monocalcium arsenate. (F) Figure 4. This observation is confirmed by solubility determinations of this compound. The results also show that the di calcium arsenate is stable only in solutions having a $\text{CaO}/\text{As}_2\text{O}_5$ ratio of 0.964, from which it follows that in aqueous solutions this salt liberates arsenic acid, and thus itself becomes more basic. That such a reaction takes place was demonstrated in the hydrolysis of haldingerite to form the 5.2.5 compound.

Whether or not the 5.2.X series of compounds are acted on by water has not been definitely demonstrated. Smith obtained the 6.2.7 compound by hydrolysing 2.1.3 in the presence of insufficient lime to form 3.1.X compounds, for 28 days. He states that the product was apparently uniform and crystalline. From these observations one would be inclined to believe this series of compounds either do not hydrolyse or if they do the rate of reaction is very low. Since the slopes of the solution equilibrium curves for these compounds are not known one cannot determine from an equilibrium diagram whether or not hydrolysis takes place.

In the case of the tricalcium arsenate Tarter, Wood and Miner¹⁵ observed that if the compound was digested with water the compound showed a continuous decrease in arsenic content until after twelve days there was no further change. The water was siphoned off from the solid matter each day and replaced with fresh water. The composition of the resulting product was represented by the formula: $3\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2$. These investigators make the claim that this is a true compound because letting it stand in contact with $\text{Ca}(\text{OH})_2$ does not change its composition. They also state that tricalcium arsenate undergoes slow chemical change when in contact with CO_2 -free NaOH or NH_4OH solutions, while the product of hydrolysis did not show such changes. There was no indication of such a compound in this investigation, but since the preparations in the region between tri and tetra calcium arsenates are difficult of identification these results do not necessarily preclude the existence of the compound claimed by Tarter and his co-workers.

Hydrolysis of tetra calcium arsenate is shown from the results recorded in Table 3. From this table it is seen that unless the supernatant liquid contains some calcium hydroxide in solution the $\text{CaO}/\text{As}_2\text{O}_5$ ratio in the precipitate falls below 4, from which it follows that the hydrolysis here is in the opposite direction from that of the other calcium arsenates, that is this compound loses some of its base and thus becomes more acid.

Solubilities of Calcium Arsenates

From the considerations recorded above it is seen that probably all the acid arsenates and the tricalcium salt react with water to form more basic compounds, while the tetra calcium arsenate hydrolyses in the opposite direction. It is evident from these results that the solubilities of the arsenates of calcium depend on the conditions under which the determinations are made. The solubility of a compound implies an equilibrium condition between the solid and the solution, and also that the dissolved portion has the same chemical composition as the solid phase. With most calcium arsenates equilibrium conditions between solid and solution can be obtained without much difficulty, but the composition of the solid material after equilibrium depends on the quantity of water used, that is, the extent to which the salt has hydrolysed.

Commercial Calcium Arsenates and General Considerations.

In the introduction to this paper a table was given showing the analysis of a number of commercial calcium arsenates. These analyses show considerable variation in the composition of this important insecticide, and reflect incomplete information as to the reactions that take place during manufacture. In a recent publication Pearce, Norton and Chapman^{16/} have made the statement that commercial calcium arsenate probably contains some dicalcium salt together with more basic compounds. While their reasoning for reaching this conclusion may be open to

question, nevertheless it is not impossible for this rather soluble arsenate to be formed during the process of manufacture. Calcium arsenate is usually manufactured commercially by adding the required quantity of arsenic acid to a suspension of lime contained in a large wooden vat. During the addition of the acid the mixture is stirred and sometimes heated either by blowing live steam into the mixture, or by steam coils. The temperature at which the mixing is done varies with different manufacturers. After the reaction is considered completed the precipitate is separated from the solution by one of several methods available, then dried and pulverized. It is evident from such a process that unless special precautions are taken, as regards concentration of arsenic acid used, rate of addition and very efficient stirring localized conditions are set up for the production of di-calcium arsenate. The reaction between calcium hydroxide and arsenic acid to form di-calcium arsenate is very rapid, while the rate of hydrolysis of this salt is relatively low, from which it would follow that some di-calcium salt might very well be present in the finished product. This rate of hydrolysis is more rapid at elevated temperature, and of course in the presence of free lime, and Pearce, Norton and Chapman make use of these facts in explaining the effects of autoclaving calcium arsenates as observed by Howard and Davidson.^{17/}

Howard and Davidson found that if a calcium arsenate that was injurious to foliage was autoclaved at 150 pounds

steam pressure for a short period of time it was rendered safe. The chemical and/or physical changes taking place during such a process are not definitely known. Pearce and his co-workers have offered what may be a partial explanation, but that other changes are taking place must be concluded from applying this process to pure tetra calcium arsenate, which also is rendered safe by this means. Here the presence and hydrolysis of di-calcium arsenate is ruled out. It was noticed however that the finely divided powder became more granular during the treatment, so in addition to possible chemical changes there are strong indications that physical changes take place as well.

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SUMMARY

In the introduction to this paper, it was stated that the purpose of this investigation was to obtain additional knowledge regarding the arsenates of calcium of means of a Phase Rule Study of the System $\text{CaO} \cdot \text{As}_2\text{O}_5 - \text{H}_2\text{O}$.

A brief resume of the preparation and properties of five series of calcium arsenate was given, followed by a discussion of the Phase Rule as applied to a three component system.

Experimental data shown in form of tables and graphs has been recorded and evidence presented for the formation of the following compounds: $4\text{CaO} \cdot \text{As}_2\text{O}_5 \cdot x\text{H}_2\text{O}$; $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$; $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 5\text{H}_2\text{O}$ and CaHAsO_4 . CaHAsO_4 has been described by other workers, but never before obtained in equilibrium studies. The evidence presented included information obtained from equilibrium determinations, chemical analysis, microscopic and X-ray data, and leaves no doubt as to the existence of the new compounds claimed.

Very interesting and valuable results were obtained in the region of so-called basic arsenates of calcium. The evidence obtained from the point of view of the Phase Rule and chemical analysis strongly pointed to a region of solid solution between the tri and the tetra calcium arsenates. This conclusion was definitely verified by the diffraction patterns obtained by X-ray analysis of preparations in this field.

With this information in our possession, it may be stated with considerable certainty that commercial calcium arsenates very probably contain solid solutions of tri and tetra calcium arsenates together with definite compounds. It is also possible that their toxicity to foliage is due in part at least to the ratio of the components in the solid solution.

A brief discussion of solubility and hydrolysis of calcium arsenates has been included. These characteristics were considered from the point of view of the Phase Rule.