TABLE V

SUMMARY OF ROTATORY DISPERSION CONSTANTS OF GELATIN IN PRESENCE OF SODIUM HALIDES

	Linear constants $k_{0.5°}$	 $k_{40°}$	Logarithmic constants k	 $\log 1/K$
NaCl	2.670	2.458	0.639	4.154
NaBr	4.847	4.415	1.33	2.002
NaI	6.760	6.220	2.66	0.998

Summary

The rotatory dispersion of gelatin in sodium chloride solutions at 0.5 and 40° has been investigated.

At 40° the dispersion constants bear a linear relationship to salt concentration, $k_{40°} = 44.517 - 2.458C_{NaCl}$.

The dispersion at 0.5° is the result of two effects, one a linear relation to salt concentration $k_{0.5°} = 99.541 - 2.670C_{NaCl}$, and the other a logarithmic function, $C_{NaCl} = \frac{1}{0.634}\log\left(\frac{a}{1-a}\right) - \log(1/K)$ in which $\log(1/K)$ equals 4.154.

The various dispersion constants so far found for gelatin-sodium halide systems are summarized,

GENEVA, N. Y. RECEIVED JULY 16, 1937

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE, AND THE UNIVERSITY OF MARYLAND]

Calcium Arsenates. An Investigation into the Three-Component System Calcium Oxide–Arsenic Oxide–Water

BY O. A. NELSON[1] AND M. M. HARING

Approximately 30 million pounds of commercial calcium arsenate is used annually in the United States for combating different types of insects. In spite of this extensive use, however, the knowledge of the chemical and physical characteristics of the basic arsenates of calcium, the only ones suitable for insecticidal purposes, is very limited.

Smith and Murray[2] first showed, by analysis of sixteen brands of commercial arsenates, that the chemical characteristics vary between wide limits. Later Cassil and the senior author,[3a] and also Goodhue,[3b] showed wide variations in both chemical and physical characteristics, from examination of twenty-two brands,

The purpose of the investigation described in this paper was to obtain additional knowledge of the arsenates of calcium through a systematic study of the three-component system calcium oxide–arsenic oxide–water. The plan followed was to make up arbitrary mixtures of the three components, determine the conditions after equilibrium had been reached, and then interpret these from the point of view of the phase rule, The temperature of 62° was chosen, because equilibrium conditions are generally reached in less time at high temperatures and also because most commercial processes for the manufacture of calcium arsenates are carried on at elevated temperatures.

Historical

There are five series of calcium arsenates, distinguished by their molar CaO/As_2O_5 ratio, or acidity. The members of each series differ only in their water content. In the interest of brevity only the formulas and references to original articles are recorded. The numbers in parentheses refer to the relative number of moles of CaO, As_2O_5, and H_2O in the compound, Thus, $Ca(AsO_3)_2$ becomes $1CaO \cdot 1As_2O_5 \cdot 0H_2O$ (1·1·0), while $CaH_4(AsO_4)_2$ becomes $1CaO \cdot 1As_2O_5 \cdot 2H_2O$ (1·1·2).

Compounds with CaO/As_2O_5 = 1,

$Ca(AsO_3)_2$ (1·1·0)[4,5,6]
$CaH_4(AsO_4)_2$ (1·1·2)[5,7]
$CaH_4(AsO_4)_2 \cdot H_2O$ (1·1·3)[8]

Compounds with CaO/As_2O_5 = 2,

$Ca_2As_2O_7$ (2·1·0)[4,9]
$CaHAsO_4$ or $Ca_2H_2(AsO_4)_2$ (2·1·1)[10]
$CaHAsO_4 \cdot H_2O$ (2·1·3)[5,7,10,11,12]
$CaHAsO_4 \cdot 2H_2O$ (2·1·5)[6,12-15]
$CaHAsO_4 \cdot 3H_2O$ (2·1·7)[6]

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(1) Abstracted from a dissertation presented by the senior author to the faculty of the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) C. M. Smith and C. W. Murray, *Ind. Eng. Chem.*, **23**, 207–208 (1931).

(3) (a) O. A. Nelson and C. C. Cassil, *J. Econ. Ent.*, **30**, 474–478 (1937); (b) L. D. Goodhue, *ibid.*, **30**, 466–474 (1937).

(4) C. L. Bloxam, *Chem. News*, **54**, 193–194 (1886).

(5) P. Kotschoubey, *J. prakt. Chem.*, **49**, 182–190 (1850).

(6) C. C. McDonnell and C. M. Smith, private communication.

(7) C. M. Smith, THIS JOURNAL, **42**, 259–266 (1920).

(8) O. Horman, Inaugural Dissertation, Erlangen, 1879.

(9) C. Lefèvre, *Ann. chim. phys.*, [6] **27**, 1–62 (1892).

(10) H. Debray, *ibid.*, [3] **61**, 419–455 (1861).

(11) H. Goguel, *Mem. soc. sci. phys. Nat. Bordeaux* [5] **1**, 85 (1896).

(12) W. Haidinger, *Edinburgh J. Sci.*, **3**, 302–306 (1825).

(13) E. Turner, *ibid.*, **3**, 306–310 (1825).

(14) H. Dufet, *Compt. rend.*, **106**, 1238–1240 (1888).

(15) A. de Schulten, *Bull. soc. franç. minéral.*, **26**, 18–24 (1903).

The 4, 6, 8, hydrates of this series have been claimed, but later observations have cast some doubt as to their identity.

Compounds with CaO/As_2O_5 = 2,5,

$Ca_5H_2(AsO_4)_4 \cdot H_2O$ (5·2·2)[16]
$Ca_5H_2(AsO_4)_4 \cdot 4H_2O$ (5·2·5)[6]
$Ca_5H_2(AsO_4)_4 \cdot 5H_2O$ (5·2·6)
(described in this paper)
$Ca_5H_2(AsO_4)_4 \cdot 6H_2O$ (5·2·7)[6]

Compounds with CaO/As_2O_5 = 3.

$Ca_3(AsO_4)_2$ (3·1·0)[4,16]

The hydrated tricalcium arsenates corresponding to 3·1·1, 3·1·2, 3·1·3, 3·1·4 1/2 (?), and 3·1·8 usually can be prepared from calcium hydroxide and arsenic acid by careful control of concentration of reactants and temperature.

Compounds with CaO/As_2O_5 = 4.

The existence of a basic calcium arsenate having a molar CaO/As_2O_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 discussed later. Whether or not this compound forms with water of hydration has not yet been ascertained.

Only one other compound remains to be mentioned in this historical sketch, the basic arsenate claimed by Tartar and co-workers.[17] These investigators hydrolyzed tricalcium arsenate in distilled water with gentle heating until the arsenic concentration in solution became constant. (The concentration decreased with successive changes of water.) Analysis of the product gave figures that indicated the compound $Ca(OH)_2 \cdot 3Ca_3(AsO_4)_2$. They found that 100 g. of water dissolved 0.0048 g. of the salt.

Pearce and Norton[16] have also reported the existence of the compound $10CaO \cdot 3As_2O_5 \cdot xH_2O$. A critical examination of their published results for the basic range throws some doubt on their claims, however. In Table I[16a] (p. 1105) we find the following figures.

	Composition of Solutions			Molar ratio CaO/As_2O_5 in solid phase	
Expt.	% by wt, As_2O_5	CaO	Molar ratio, CaO/As_2O_5		Compounds in solid phase
6	0.001	0.001	4.12	3.46	Basic + lime
6	.003	.002	2.74	3.34	Basic
2	.008	.004	2.05	3.30	Basic
5	.004	.002	2.05	3.29	Basic
6	.007	.003	1.76	3.26	Basic

It is seen from this table that as the molar ratio of the components in solution decreases the molar ratio of the components in the solid phase changes in the same direction, indicating a solid solution rather than a definite compound. Furthermore the solubility of calcium oxide in water at 90° is of the order of 0.061% according to chemical handbooks. It would therefore be impossible for lime to remain in the solid phase in solutions in which the lime concentration was 0.001%.

Purification of Materials

Arsenic Acid ($H_3AsO_4 \cdot 0.5H_2O$).—Commercial arsenic acid was filtered through glass wool and concentrated by boiling until the boiling point was 150°. It was then cooled to about 20° and seeded with a crystal of $H_3AsO_4 \cdot 0.5H_2O$. Seeding is absolutely necessary; attempts to induce crystallization by "scratching," local chilling, further supercooling, and seeding with crystals of other arsenic acids were unsuccessful. The crystals were then melted and recrystallized until the melted material was practically colorless. The specific gravity of the melted acid was 2.325 (15°/4°), which corresponded to 74.5% As_2O_5 (theoretical for $H_3AsO_4 \cdot 0.5H_2O$ = 76.1%).

Calcium Oxide and Calcium Hydroxide.—The calcium oxide was prepared from pure precipitated calcium carbonate by ignition in an electric furnace. The loss in weight observed after ignition agreed with theory, and subsequent analysis of the oxide gave 99.9% CaO. For some experiments pure calcium hydroxide was prepared from calcium chloride and carbonate-free sodium hydroxide. After the precipitate had been washed out of contact with carbon dioxide until the filtrate showed no test for chlorides, the lime obtained analyzed about 98.0% $Ca(OH)_2$, the remainder probably being water.

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

Experimental Procedure

In each of thirty-three 4-ounce (112-g.) bottles was placed 50 cc. of arsenic acid solution of successively increased concentrations, followed by calcium oxide in such quantities as to produce sufficient precipitates for analysis, that is, from 1.25 to 5.5 g. The arsenic pentoxide left in solution after this treatment ranged from a trace to 71.5%. The bottles were then placed in a rotating machine in a water thermostat kept at 62 ± 0.05°. The samples were rotated day and night for nearly four months to ensure the attainment of equilibrium.

The question of equilibrium in investigations such as this is of utmost importance. In discussing real and apparent equilibrium Findlay 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. Another method of determining equilibrium is to remove and analyze samples of the reaction mixture from time to time and in this way ascertain when no further changes are taking place. This latter criterion was used in this in-

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(16) G. W. Pearce and co-workers [(a) THIS JOURNAL, **58**, 1704 (1936); (b) *ibid.*, **59**, 1258 (1937)] obtained 5·2·*x* compounds.

(17) H. V. Tartar, L. Wood, and E. Hiner, *ibid.*, **46**, 809–814 (1924).

vestigation. Stirring of the samples was continued for long periods of time, after analysis of portions of the mixtures indicated equilibrium condition had been reached.

After the first series had been completed, it was found that no conclusive evidence for the formation of the compounds 5·2·*x*, 3·1·*x*, and 4·1·*x* had been obtained, although the existence of these compounds had been strongly indicated in previous investigations.[6] Also the crystals from this series were small, and for this reason difficult to analyze under the microscope. Accordingly another series was set up, chiefly with the idea of covering this range of concentration more carefully and, if possible, of growing crystals that could be studied under the microscope. Calcium hydroxide was used instead of calcium oxide, and larger quantities were taken.

The data obtained in these two series show that the most basic preparations were represented by a CaO/As_2O_5 ratio of 3.84. In earlier experiments on the preparation of calcium arsenates it was found that a compound corresponding to tetracalcium arsenate ($4CaO \cdot As_2O_5 \cdot xH_2O$), or 4·1·*x*, can be prepared readily at room temperature by adding 2 moles of arsenic acid to a little more than 4 moles of calcium hydroxide suspended in a large excess of water. Sufficient lime must be used so that the supernatant liquid is about half saturated with calcium hydroxide after the reaction is completed. On analysis such a product shows a CaO/As_2O_5 ratio of 4, no free lime, and of course no free arsenic acid. The supernatant liquid contains a trace of arsenic pentoxide and a calcium hydroxide content depending on the excess lime originally taken.

In a third series of experiments a quantity of saturated lime water was prepared and kept in a well-stoppered paraffined bottle, and portions of this stock solution were withdrawn and diluted with distilled water that recently had been boiled free from carbon dioxide and cooled. The concentration of the diluted lime solution was determined by titrating with standard 0.01 *N* hydrochloric acid, using phenolphthalein as indicator. To the standard calcium hydroxide solution a definite quantity of standard arsenic acid solution was added at room temperature, and the mixture was heated to 62° and shaken in a platinum Erlenmeyer flask for five to six hours. The precipitate was then filtered off and the calcium hydroxide concentration in the supernatant liquid again determined by titrating with 0.01 *N* hydrochloric acid. Only the merest trace of arsenic pentoxide could be detected in the filtrate. From the data thus obtained the CaO/As_2O_5 ratio in the precipitate was calculated readily.

After equilibrium had been established in the first two series, the contents of the bottles were filtered through Gooch crucibles fitted with a double thickness of fairly tight filter paper. Both the precipitates and the filtrates were kept in stoppered bottles until analyses could be made.

The arsenic was determined by the thiosulfate method and in some cases by the Gooch–Browning method, and the calcium oxide was determined by precipitating the calcium as oxalate and titrating with standard potassium permanganate.

The data and results are shown in Tables I, II, and III, and Figs. 1 and 2. In Table I the molar CaO/As_2O_5 ratios in the solutions in the basic range are omitted for the reason that here both the CaO and the As_2O_5 concentrations are so low that any slight error in analysis would cause such variation in the CaO/As_2O_5 ratios as to render them meaningless.

TABLE I

ANALYSES OF CALCIUM OXIDE–ARSENIC OXIDE–WATER MIXTURES. FIRST SERIES

Expt.	Analysis of precipitate CaO, %	As_2O_5, %	Molar ratio CaO/As_2O_5	Analysis of solution CaO, %	As_2O_5, %	Molar rat io CaO/As_2O
1	16.44	22.19	3.04	0.056	0.15	...
2	14.58	20.14	2.97	.068	.16	...
3	18.00	23.18	3.18	.028	.023	...
4	21.72	26.18	3.40	.057	.016	...
5	20.50	24.35	3.44	.035	.013	...
6	17.65	19.56	3.64	.030	.015	...
7	16.75	18.65	3.54	.020	.018	...
8	18.60	20.47	3.70	...	..	...
9	16.00	33.62	2.24	.440	1.84	...
10	18.45	38.50	1.97	...	..	...
11	17.00	36.10	1.94	1.04	4.23	1.01
12	17.85	38.70	1.89	1.66	7.04	0.97
13	15.80	34.80	1.86	1.66	6.91	.99
14	16.45	36.60	1.84	2.43	10.20	.98
16	18.55	41.20	1.85	2.98	12.60	.97
18	28.13	58.90	1.95	4.01	16.92	.97
19	27.40	58.00	1.94	4.66	21.20	.91
21	22.90	53.00	1.78	5.42	24.20	.92
22	17.80	44.20	1.65	...	34.10	.98
24	20.21	63.60	1.31	6.54	30.60	.88
25	16.60	69.00	0.98	6.53	30.65	.88
26	16.48	67.80	.99	6.25	31.60	.82
27	16.15	67.80	.97	5.02	38.10	.54
28	17.05	71.60	.97	4.35	41.10	.43
29	15.40	68.15	.93	3.36	48.00	.28
30	15.25	69.00	.91	2.37	54.30	.18
31	13.75	69.15	.82	1.48	61.30	.10
32	11.32	69.80	.66	0.50	67.65	.03
33	8.05	71.50	.46	.11	71.75	.006

TABLE II

ANALYSES OF CALCIUM OXIDE–ARSENIC OXIDE–WATER MIXTURES, "A" SERIES

Expt.	Analysis of precipitate CaO, %	As_2O_5, %	Molar Ratio CaO/As_2O_5	Analysis of solution CaO, %	As_2O_5, %
1-A	41.79	44.68	3.84	0.013	Trace
2-A	42.50	47.10	3.70	.006	Trace
3-A	41.75	49.15	3.48	.005	Trace
4-A	42.35	50.58	3.42	.003	Trace
5-A	41.75	53.10	3.23	.016	0.030
6-A[a]	40.10	51.10	3.22	.032	.089
7-A[a]	38.10	52.78	2.96	.043	.171
8-A[a]	36.40	52.50	2.84	.051	.216
9-A[b]	33.00	54.28	2.49	.065	.210
	33.00	55.10	2.46	.068	.208

[a] Crystals of 3·1·2 compound formed. [b] Crystals of 5·2·6 compound formed.

Discussion of Results

In order to be better able to interpret the results obtained from the foregoing experiments, the detailed graph (Fig. 1) was redrawn to show, instead of the individual tie lines, the regions wherein compounds, solutions, or mixtures could be formed (Fig. 3). The point representing $4CaO \cdot As_2O_5 \cdot xH_2O$ is included in this graph, even though this compound was not obtained in the first and "A" series. Tetracalcium arsenate appears to be unstable at elevated temperatures, although the results tabulated in Table III give evidence that it will form by indirect method at 62°. With this figure as reference these regions will be discussed from the point of view of the phase rule.

At constant temperature, and with gas and liquid phases always present, the existence of one solid compound would be indicated by a variation in the solution, and of two solid compounds by a constant solution. Since the effect of moderate changes in pressure on the equilibrium conditions is negligible, in systems involving equilibria between liquids and solids the effects of the gas phase and air as an additional component may be ignored. The system can therefore be treated as a "condensed system."[18] With these requirements established the different regions in Fig. 3 are interpreted readily.

The line O–A–B–C–D represents solutions in equilibrium with all compounds less acid than monocalcium arsenate (F), and line D–E represents solutions in equilibrium with monocalcium 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 $CaH_4(AsO_4)_2$) 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 dicalcium arsenates.

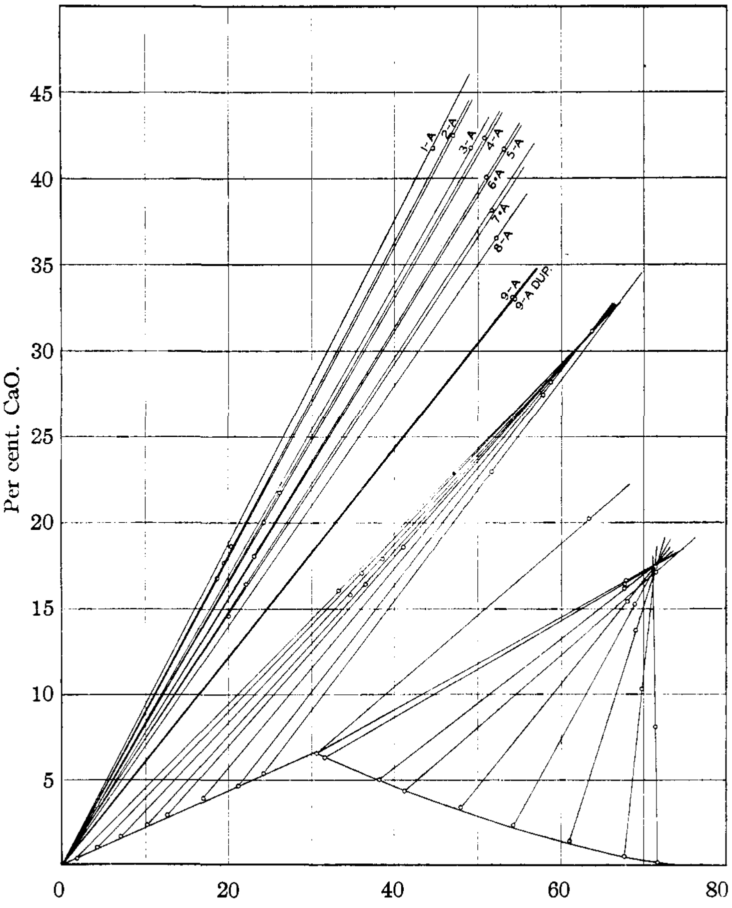

Fig. 1.—Equilibrium in the system calcium oxide–arsenic oxide–water.

Similarly the remaining regions may be shown to contain the following compounds and solution:

Region	Compound
C–G–D–C	(G) $CaHAsO_4$
C–H–G–C	(H) $Ca_5H_2(AsO_4)_4 \cdot 5H_2O$ + (G)
B–H–C–B	(H) $Ca_5H_2(AsO_4)_4 \cdot 5H_2O$
B–I–H–B	(I) $Ca_3(AsO_4)_2 \cdot 2H_2O$ + (H)
A–I–B–A	(I) $Ca_3(AsO_4)_2 \cdot 2H_2O$
A–K–I–A	(K) $4CaO \cdot As_2O_5 \cdot xH_2O$ + (I)
O–K–A–O	(K) $4CaO \cdot As_2O_5 \cdot xH_2O$

TABLE III

ANALYSES OF CALCIUM OXIDE–ARSENIC OXIDE–WATER MIXTURES, "B" SERIES

Expt.	CaO/As_2O_5 ratio at start	CaO/As_2O_5 ratio in ppt. (calcd.)	0.01 *N* HCl per 10 cc. of filtrate, cc.	CaO in filtrate, g./l.
7-B	10.30	4.55	11.6	0.3475
1-B	9.50	4.28	11.4	.3412
2-B	8.95	4.07	10.2	.3075
3-B	8.65	4.02	9.7	.2900
8-B	8.35	4.01	8.8	.275
4-B	7.50	4.01	7.4	.221
5-B	6.47	3.95	5.3	.159
	6.50	4.00	5.2	.159
6-B	5.75	3.86	3.9	.115
	5.80	3.90	4.0	.118

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[18] H. S. Taylor, "A Treatise on Physical Chemistry," 2d ed., Vol. I, D. Van Nostrand Co., New York, 1931, p. 515.

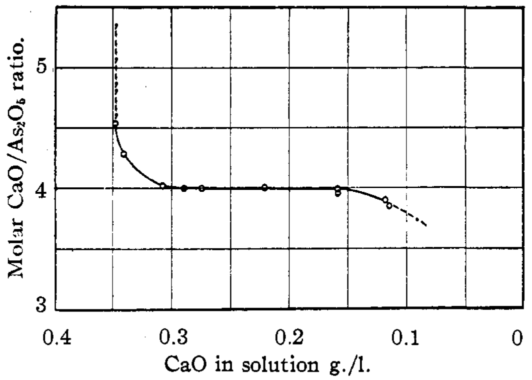

Fig. 2.—Effect of concentration of lime on composition of calcium arsenate.

Although the analytical evidence is not entirely conclusive from the point of view of the phase rule, X-ray data to be presented later indicate that the solid phase in region A–K–I–A is actually a solid solution of compounds K and I. Since no calcium arsenate more basic than $4CaO \cdot As_2O_5 \cdot xH_2O$ has been found or prepared, the region to the left of line O–K must consist of free lime, compound K, and solution. The region above and to the right of the line K–I–H–G–F represents the region of no solution. This line could be extended to the composition of $3As_2O_5 \cdot 5H_2O$, which is known to exist, although in these experiments the solution was not sufficiently concentrated to precipitate this arsenic acid.

The analyses of the solid phases in experiments 25 to 33, inclusive, proved the presence of monocalcium arsenate (1·1·2). This compound was obtained and described by Smith.[7]

Point G in Fig. 3 represents the composition of anhydrous dicalcium arsenate (2·1·1). That the anhydrous compound formed instead of one of the hydrated compounds is evidenced by the direction and intersection of the tie lines connecting the solutions and solid phases within the region C–G–D–C. The optical characteristics of crystals obtained in the region are as follows: values for two true indices, about 1.625 and 1.655; extinction unsymmetric; habit, elongated parallelogrammic plates. Fig. 4 is a photomicrograph of these crystals.

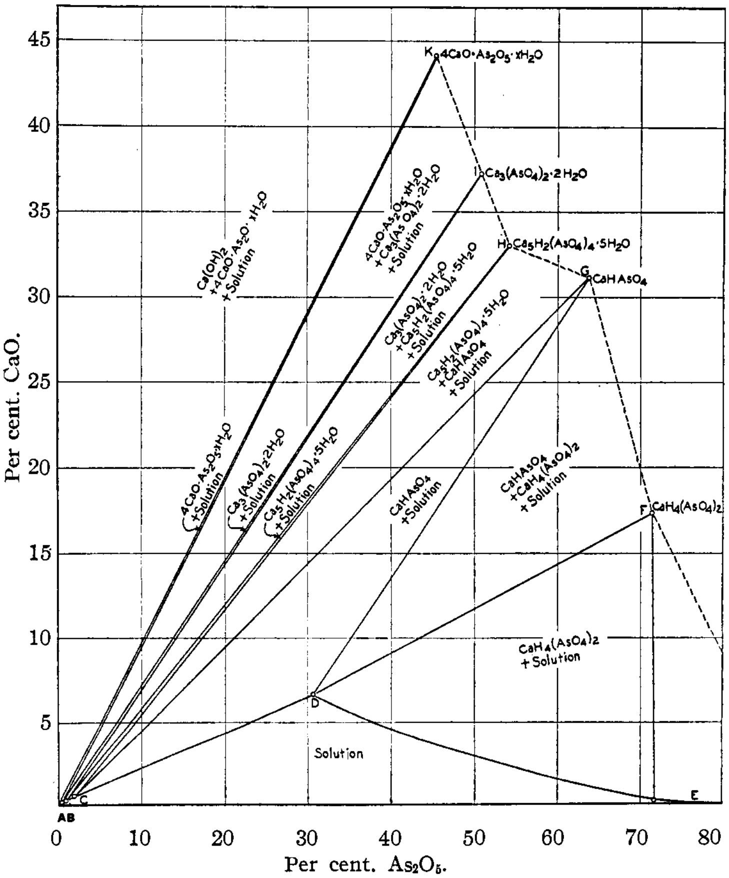

Fig. 3.—Figure 1 redrawn to show regions wherein compounds, solutions or mixtures could exist.

Point C, which represents a solution of constant composition where the solid phase would consist of the two compounds G and H, was not located accurately. Its position lies somewhere between 0.22 and 1.84% As_2O_5, probably near the lower concentration. Pearce and co-workers[16] have lately established this point at about 0.23% As_2O_5 at 35° and 0.153% As_2O_5 at 90°.

Point B, representing the solution of constant composition where compounds H and I could coexist, was located at about 0.21% As_2O_5 and 0.06% CaO (Table II, Expts. 8-A and 9-A).

The compound represented by H, namely, $Ca_5H_2(AsO_4)_4 \cdot 5H_2O$ or 5·2·6 compound, forms within a very narrow range of concentrations. It was discovered by analysis of the solid phase after all extraneous water had been removed, and then by obtaining well-defined crystals on which optical data could be determined. The chemical analysis of this compound gave 33.00% CaO and 54.28% As_2O_5, which agrees very well with the theoretical composition of the 5·2·6 compound, namely, 33.05% CaO, 54.21% As_2O_5, and 12.75%

H_2O. **Optical data:** indices, thought to be beta and gamma, were 1.60 and 1.64, respectively; optical character probably negative; elongation commonly positive; extinction approximately parallel; habit, rectangular plates nearly square. A photomicrograph of the crystals is shown in Fig. 5.

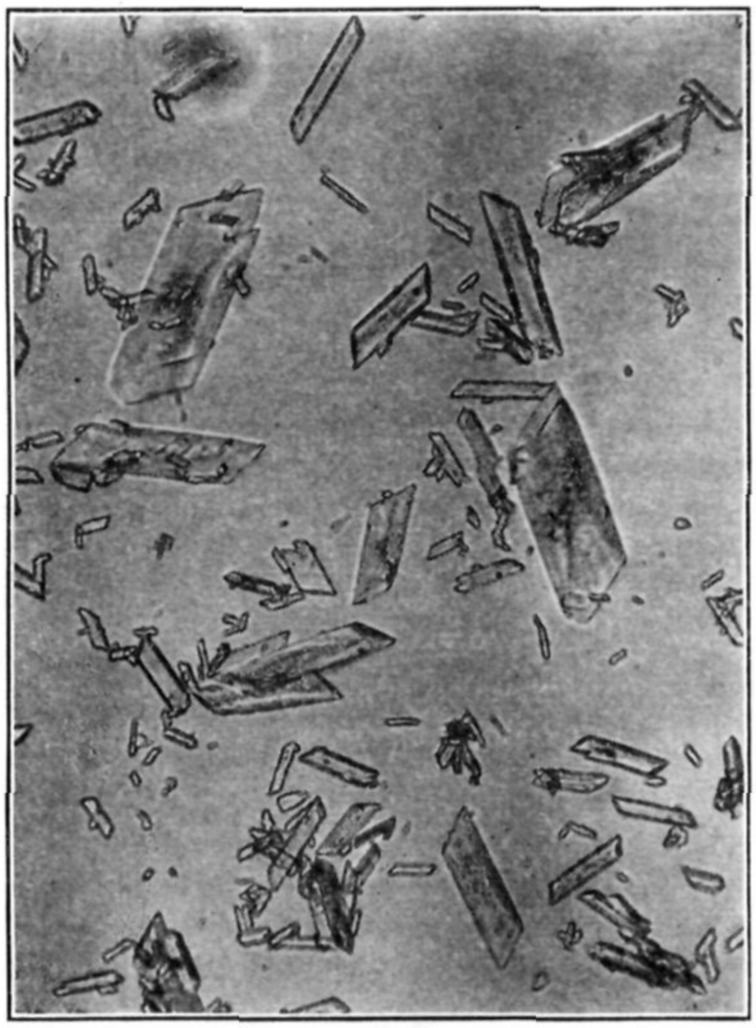

Fig. 4.—Photomicrographs of $CaHAsO_4$ crystals.

The identity of the compound represented by I (Fig. 3) had to be determined from the analysis and optical characteristics of the solid phase, for the tricalcium arsenates are so insoluble as to make the tie lines between solids and solutions run almost parallel. That $Ca_3(AsO_4)_2{\cdot}2H_2O$, or 3·1·2 compound, was obtained was ascertained readily from chemical analysis of the solid phase after the adsorbed water had been removed by washing with alcohol and gentle drying. Analysis of the solid from experiment 7-A gave CaO, 38.10%; As_2O_5, 52.78%. The theoretical composition for 3·1·2 compound is CaO, 38.74%; As_2O_5, 52.96%; H_2O, 8.30%. This analysis, therefore, indicates that about 0.72% of water or alcohol was adhering to the solid. The optical data of the crystals of this compound are as follows: two true indices, thought to be beta and gamma, 1.615 and 1.62, respectively; optical character probably negative, and the elongation usually negative; extinction usually about 18° from the long edge of the crystals, which probably belong to the monoclinic system; habit, long irregular slabs terminating in small parallel projections, surface and edges rough; birefringence evidently quite low. Figure 6 is a photomicrograph of these crystals.

On account of the fineness of the crystals of the tetracalcium arsenate ($4CaO{\cdot}As_2O_5{\cdot}xH_2O$), no optical data could be obtained. X-ray examinations showed, however, that the compound was crystalline and not amorphous.

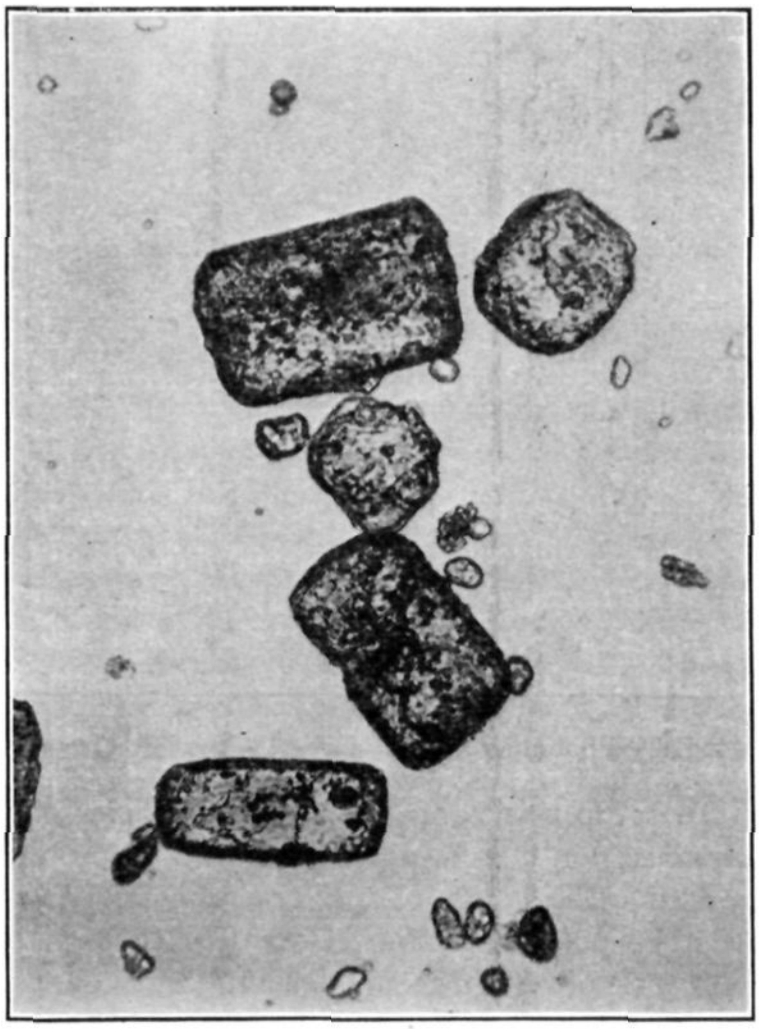

Fig. 5.—Photomicrographs of $Ca_5H_2(AsO_4)_4{\cdot}5H_2O$ crystals.

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 that have not been described previously. According to the phase rule, region A–K–I–A, Fig. 3, should contain a mixture of 4·1·x and 3·1·2 compounds. Owing to the experimental difficulty of ascertaining whether or not the solution was constant in composition, it was not possible to determine whether two solid phases or a solid solution was present in this region. 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.

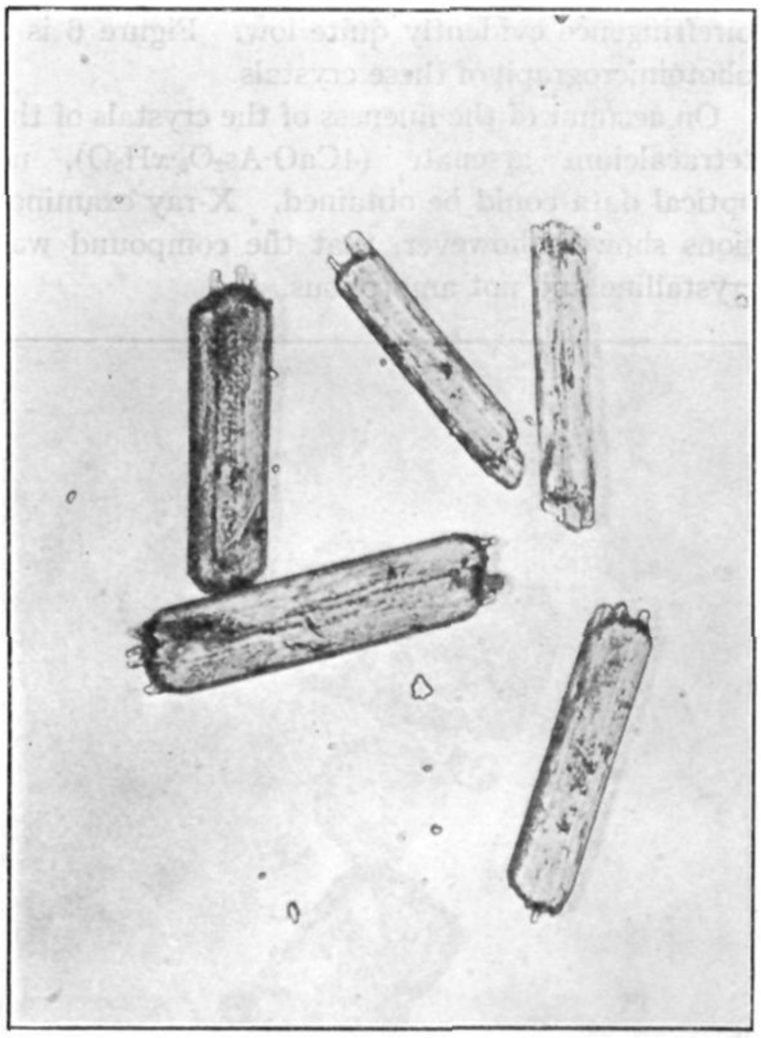

Fig. 6.—Photomicrographs of $Ca_3(AsO_4)_2 \cdot 2H_2O$ crystals.

To settle this point, X-ray photographs were obtained for a number of preparations in this region. Diffraction patterns were obtained for $3CaO \cdot As_2O_5 \cdot 2H_2O$ (expt. 7-A), $3.44CaO \cdot As_2O_5 \cdot xH_2O$ (expt. 4-A), equivalent mixture of tri- and tetracalcium arsenates, $3.84CaO \cdot As_2O_5 \cdot xH_2O$ (expt. 1-A), and $4CaO \cdot As_2O_5 \cdot xH_2O$. (Fig. 7.) Photographs were also obtained for pure calcium hydroxide, 3·1·8, 5·2·6, and 2·1·1 compounds, each of which showed patterns distinctly different from the ones shown herewith.

The photographs were taken with Cu Kα radiation in cylindrical cameras with radii of 3.16 cm. The minimum of one phase detectable by this method is 5%.

Examination of these photographs reveals that the pattern for $4CaO \cdot As_2O_5 \cdot xH_2O$ is quite different from the others, and also from that obtained for pure calcium hydroxide.

This observation, in addition to the data presented in Table III and Fig. 2, provides very strong evidence for the existence of tetracalcium arsenate.

The products from expts. 1-A, 4-A, and 7-A show identical diffraction patterns, which indicate solid solution. Now experiment 7-A gave $Ca_3(AsO_4)_2 \cdot 2H_2O$, and since there is no displacement of lines in patterns from expts. 4-A and 1-A, the interpretation is that the solid solutions are formed without altering the size of the lattice. Experiment 1-A represents a solid solution in which the CaO/As_2O_5 ratio is 3.84. This is the most basic solid solution obtained in any of the experiments, and may represent the limit of solubility of tetracalcium arsenate, or calcium oxide, in tricalcium arsenate at this temperature. The pattern obtained from a mixture of equal parts of tri- and tetracalcium arsenates provides evidence that the products in this region are not physical mixtures of calcium arsenates and lime.

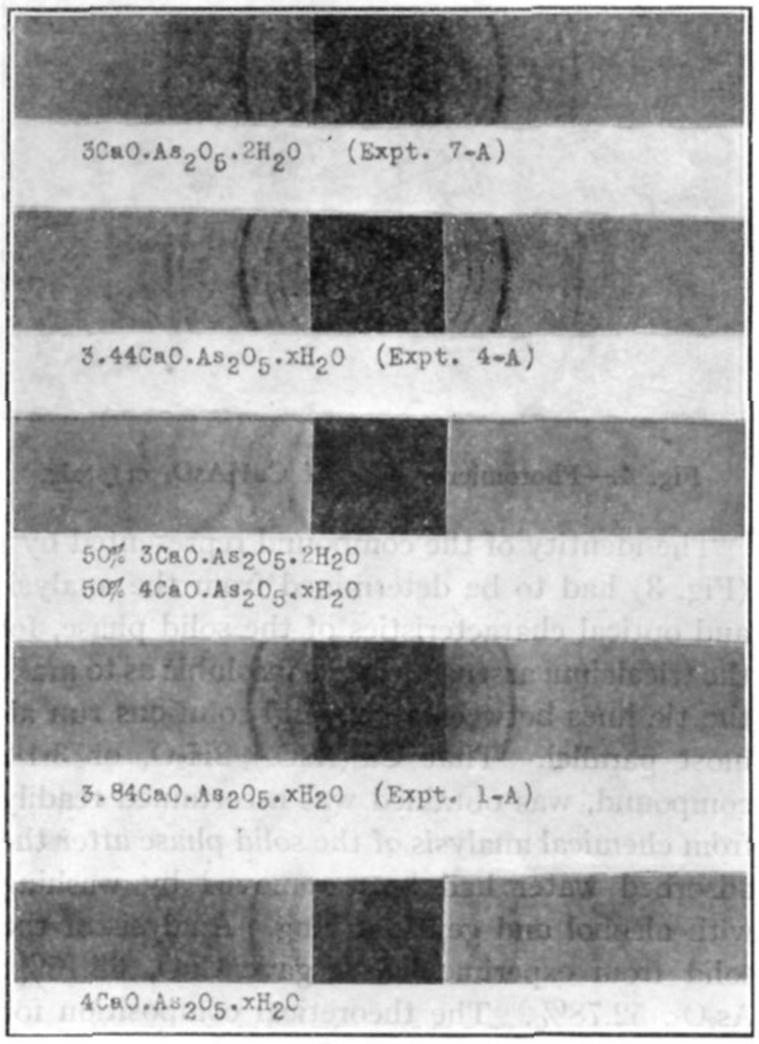

Fig. 7.—Photographs of diffraction patterns of calcium arsenates.

The X-ray examinations of the products in the basic range show, 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 tetracalcium arsenate. This must be taken to mean that tricalcium arsenate dihydrate is capable of dissolving a large quantity of tetracalcium arsenate, but that the 4·1·x compound can dissolve only a very small quantity of the 3·1·2 compound, or arsenic oxide.

Hydrolysis of Calcium Arsenates

The experimental data 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 CaO/As_2O_5 ratio is 0.964, it follows that there must be only slight hydrolysis in the case of the monocalcium arsenate (F, Fig. 3). This observation is confirmed by solubility determinations of this compound. The results also show that the dicalcium arsenate is stable only in solutions having a CaO/As_2O_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 $CaHAsO_4 \cdot H_2O$ to form the 5·2·5 compound.

Whether or not the compounds of the 5·2·x series are acted on by water has not been demonstrated definitely. Since the slopes of the solution equilibrium curves for these compounds are not known, at this temperature one cannot determine from an equilibrium diagram whether or not hydrolysis takes place. These slopes have later been determined at 90 and 35°.[16]

In the case of the tricalcium arsenate Tartar, Wood, and Hiner[17] observed that, when digested with water, the compound showed a continuous decrease in arsenic content for twelve days and no further change thereafter. The water was siphoned off from the solid matter each day and replaced with fresh water. The composition of the product was represented by the formula $3Ca_3(AsO_4)_2 \cdot Ca(OH)_2$. These investigators claim that this is a true compound, because upon standing in contact with calcium hydroxide its composition does not change. They also state that tricalcium arsenate undergoes slow chemical change when in contact with carbon dioxide-free sodium ammonium hydroxide solution, while the product of hydrolysis did not show such changes. There was no indication of such a compound in this investigation, and X-ray examination verified the data obtained from the phase-rule consideration.

"Solubilities" of Calcium Arsenates

From the foregoing discussion it is seen that probably all the acid arsenates and the tricalcium salt react with water to form more basic solid phases while the tetracalcium arsenate hydrolyzes in the opposite direction. It is evident, therefore, that the solubility of an arsenate of calcium depends on the conditions under which the determinations are made. The ordinary usage of the term "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 the composition of the solid material after equilibrium is attained depends on the quantity of water used, that is, the extent to which the salt has hydrolyzed.

Acknowledgment.—The authors wish to express their appreciation to Dr. R. C. Roark and Mr. Charles M. Smith, under whose supervision a large portion of this work was done, to Mr. E. L. Gooden for photomicrographs and optical properties of crystals, and to Dr. S. B. Hendricks for X-ray examinations.

Summary

1. The three-component system calcium oxide–arsenic oxide–water has been investigated from the point of view of the phase rule.

2. The existence of the following compounds has been determined: $CaHAsO_4$, $Ca_5H_2(AsO_4)_4 \cdot 5H_2O$, $Ca_3(AsO_4)_2 \cdot 2H_2O$, and $4CaO \cdot As_2O_5 \cdot xH_2O$. The evidence presented for the existence of these compounds includes, in addition to equilibrium data, information gained from microscopic and X-ray examinations.

3. The existence of the compound $10CaO \cdot 3As_2O_5 \cdot 4H_2O$ was not verified. All the data obtained pointed instead to a region of solid solutions between the conditions for tri- and tetracalcium arsenate.

4. A brief discussion of hydrolysis and solubility of calcium arsenates is included.

WASHINGTON, D. C. RECEIVED AUGUST 5, 1937