a diazine, $C_{11}H_{14}N_2$, of undetermined structure were isolated.

This research will be concluded with an investigation now in progress on 18 fractions in the boiling range of 172.5–215°, in an effort to explain the abnormally high nitrogen content of these bases, coupled with a progressive exaltation of densities and refractivities from d^{25}_4 0.9514 and n^{25}_D 1.5025 to d^{25}_4 1.0189 and n^{25}_D 1.5375, respectively.

AUSTIN, TEXAS RECEIVED APRIL 13, 1936

[CONTRIBUTION FROM DIVISION OF CHEMISTRY, NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

A Phase Rule Study of the Calcium Arsenates[1]

BY G. W. PEARCE AND L. B. NORTON

Calcium arsenate is a product of uncertain composition and variable properties, both in the form of the commercial insecticide and of the so-called pure salt. Although commercial preparations are generally assumed to consist essentially of tricalcium arsenate and an excess of hydrated lime, recent work[2,3,4] has shown that this assumption is inadequate to account for the variations in properties among products of similar gross composition. These variations suggest that other arsenates of calcium are probably present in the products prepared by the usual methods. Since data concerning the identity and the ranges of stability of the calcium arsenates are at present incomplete, a study of the equilibrium conditions in the system $CaO–As_2O_5–H_2O$ has been carried out.

A number of calcium arsenates have been reported in the literature. Smith,[5] in a study of the equilibrium conditions in the more soluble portion of the system, established the existence of two acid salts: monocalcium arsenate, $CaH_4(AsO_4)_2$, and dicalcium arsenate, $CaHAsO_4$. The dicalcium salt has also been prepared and studied by a number of other workers, and is known in the form of the minerals Haidingerite and Pharmacolite. Robinson[6] has reported the preparation of pure tricalcium arsenate, $Ca_3(AsO_4)_2$, from calcium chloride and sodium arsenate. Tartar *et al.*[7] obtained a basic product having the composition $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$, by the repeated hydrolysis of calcium ammonium arsenate and of tricalcium arsenate prepared by Robinson's method.[6] Smith and Murray[8] concluded from complete analyses of a number of commercial preparations, that these products consist mostly of a compound more basic than tricalcium arsenate. Clifford and Cameron,[9] however, considered that some of the calcium arsenates reported were merely solid solutions of calcium oxide and arsenic oxide incidentally having the composition of possible compounds.

Experimental

The experiments were confined to the ranges of compounds more basic than dicalcium arsenate, since the work of Smith[5] on the acid compounds appears quite conclusive. Smith was unable to reach complete equilibrium in a reasonable time in the more basic region of the system at 35°, so a higher temperature was chosen for the present work. Preliminary experiments showed that changes in the system tend to occur more rapidly at higher temperatures, in spite of the decreased solubility of most of the compounds involved. Accordingly, a bath of petroleum oil maintained at 90 ± 0.1° was used for all of the work.

The calcium oxide was prepared by precipitating calcium carbonate from calcium chloride with ammonium carbonate, and igniting the product in an electric muffle furnace. It was found to be free from appreciable amounts of magnesium. Baker C. P. arsenic acid was used without further purification.

All analyses for calcium were made by the precipitation of calcium oxalate and titration with permanganate. Arsenic was determined by distillation as the trichloride and titration with bromate solution.[10] Application of these procedures to samples of pure calcite and of Bureau

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(1) Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 136, April 8, 1936.

(2) Pearce, Norton and Chapman, N. Y. Agr. Expt. Sta. Tech. Bull. 234 (1935).

(3) Chapman, Pearce, Dean and Hammer, *J. Econ. Entomol.*, **27**, No. 2, 421 (1934).

(4) Howard and Fletcher, U. S. Bur. Entomol. Paper E-304, mimeographed (1933).

(5) Smith, THIS JOURNAL, **42**, 259 (1920).

(6) Robinson, *J. Agr. Research*, **13**, 281 (1918).

(7) Tartar, Wood and Hiner, THIS JOURNAL, **46**, 809 (1924).

(8) Smith and Murray, *Ind. Eng. Chem.*, **23**, 207 (1931).

(9) Clifford and Cameron, *ibid.*, **21**, 69 (1929).

(10) The bromate method for arsenic in foods [*J. Assoc. Official Agr. Chem.*, **16**, 75 (1933)] was modified by using hydrazine sulfate instead of the ferrous sulfate–sodium bromide mixture as reducing agent.

of Standards arsenious oxide, respectively, showed that the maximum errors of the analysis were less than 0.1 mg. of calcium oxide and 0.05 mg. of arsenic oxide. In the analyses of the unknown samples, such quantities were taken that the analytical error was less than 1% except for the four most dilute solutions, in which it rose to about 3%.

Preliminary experiments, in which solid lime was shaken with arsenic acid of various concentrations, showed that equilibrium was not attained in six weeks, even at 90°. It appeared that penetration of the particles of lime by the dilute arsenic acid and the subsequent conversion to the proper compound is a process difficult to complete in a reasonable length of time. Further experiments in which the lime was added in solution showed more promise, but the solid in all cases showed a great reluctance to change, after once being precipitated, in contact with the extremely dilute solutions which characterize this portion of the system. These difficulties were finally avoided by precipitating the solid under such conditions that it had practically its final composition when it was first deposited. Both solution and solid then reached a constant and reproducible composition very quickly.

The procedure by which the final data were obtained was as follows. The solutions were made up in such proportions that small amounts of solid would precipitate at 90°, but the solutions would remain perfectly clear at room temperature. Such conditions were obtained when calculations from the preliminary data indicated that amounts of solid ranging from 50 mg. in the basic region to 500 mg. in the acid region should be deposited from 600 cc. of solution. Six hundred-cc. portions of the solutions were made up at room temperature in 1-liter wide-mouthed Pyrex Erlenmeyer flasks, using recently boiled distilled water and carefully standardized solutions of lime and of arsenic acid nearly saturated with lime. Each flask was closed with a rubber stopper through which extended a glass stirrer fitted with a mercury seal to protect the solution from evaporation and from contact with atmospheric carbon dioxide. The stopper also carried a small stoppered tube for withdrawal of samples for analysis during the course of the run. The flasks were immersed to the neck in the 90° bath, clamped in place, and the stirrers connected to a multiple stirring device which permitted the running of eight samples at one time. Most of the solids began to deposit only after the solutions had been held for some time at 90°. Under these conditions, equilibrium was established very quickly. Analyses of the solutions showed that no detectable changes occurred after the first few hours, but the samples were run for two to ten days before the final analysis. At the end of this period, most of the solids had begun to show a definite crystalline structure.

When the mixtures had reached a constant composition, they were removed from the bath and filtered rapidly by suction through a Büchner funnel. The filtration required about one minute, during which time the temperature of the solution dropped not more than 15–20°. No appreciable error was introduced by this procedure, since the composition of the filtered solutions checked within the

TABLE I

Expt.	Composition of solns. % by wt. As_2O_5	Composition of solns. % by wt. CaO	Composition of solns. Mol. ratio CaO/As_2O_5	Composition of solids ratio CaO/As_2O_5 Wt.	Composition of solids ratio CaO/As_2O_5 Mol.	Max. solid pptd., mg.	Compounds[a] in solid phases	Mol. ratio CaO/As_2O_5, calcd.
6	0.001	0.001	4.12	0.843	3.46	50	Basic + lime	
6	.003	.002	2.74	.814	3.34	50	Basic	3.33
5	.004	.002	2.05	.802	3.29	50	Basic	
6	.007	.003	1.76	.794	3.26	50	Basic	
2	.008	.004	2.05	.804	3.30	50	Basic	
4	.008	.003	1.54	.768	3.16	50	Basic + Tri	
6	.010	.004	1.64	.751	3.08	50	Tri	3.00
5	.012	.005	1.71	.746	3.06	50	Tri	
6	.013	.006	1.89	.743	3.05	50	Tri	
6	.018	.007	1.60	.731	3.00	100	Tri	
4	.021	.007	1.37	.717	2.94	100	Tri	
6	.025	.010	1.65	.731	3.00	100	Tri	
4	.031	.010	1.33	.729	2.99	100	Tri	
4	.038	.013	1.41	.704	2.89	100	Tri + Penta	
4	.042	.015	1.47	.604	2.48	100	Penta	2.50
3	.050	.018	1.48	.597	2.45	100	Penta	
4	.055	.018	1.34	.595	2.44	100	Penta	
4	.068	.022	1.33	.597	2.45	100	Penta	
3	.069	.022	1.31	.597	2.45	100	Penta	
3	.073	.023	1.29	.607	2.49	100	Penta	
1	.082	.026	1.30	.614	2.52	500	Penta	
1	.115	.034	1.22	.619	2.54	500	Penta	
1	.134	.038	1.17	.604	2.48	500	Penta	
1	.153	.044	1.18	.561	2.30	500	Penta + Di	
1	.156	.046	1.21	.497	2.04	500	Di	2.00
1	.177	.050	1.16	.492	2.02	500	Di	
1	.241	.065	1.11	.500	2.05	500	Di	

[a] Empirical formulas: basic = $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$; tri = $Ca_3(AsO_4)_2$; penta = $Ca_5H_2(AsO_4)_4$; di = $CaHAsO_4$.

analytical error with samples of the same solutions previously pipetted directly from the flasks during the course of the run. Following the filtration, portions of the solution were cooled, weighed, and analyzed for calcium and arsenic. The solid was washed on the filter paper with small amounts of hot water, dissolved in 1:1 hydrochloric acid, made to volume, and suitable aliquots of this solution analyzed for calcium and arsenic. Because of the small quantity of the solid, no attempt was made to weigh it before analysis, but only the ratio of calcium oxide to arsenic oxide was determined.

Results and Discussion

The data obtained by the final procedure are presented in Table I, and plotted in Figs. 1 and 2.

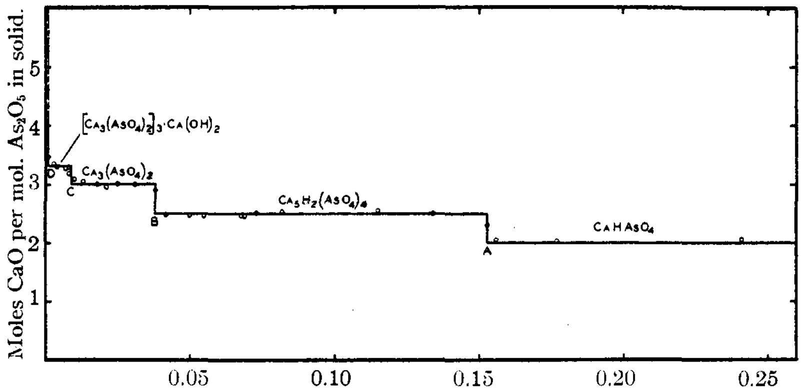

Fig. 1.

As shown in the table, the data are taken from the results of six different runs, only those samples being selected from each run which fulfilled the conditions of precipitating at 90° and not at room temperature. The reproducibility of the results is shown by the fact that the ranges of each of the three more basic compounds contain points from three different experiments.

The method of plotting used in Fig. 1 was employed for the identification of the compounds because the high dilution of all of the solutions made it impossible to plot the compositions of both solids and solutions to the same scale on a diagram such as that of Fig. 2.

The flat portion of the curve in Fig. 1 from the extreme right to the point A shows the existence of a compound $2CaO:As_2O_5$. Although the data do not show the amount of water associated with any of the solid compounds, this composition corresponds to the dicalcium arsenate, $CaHAsO_4$. The curve as plotted shows only the extreme lower end of the range of this compound, which is stable in contact with solutions containing up to 27.5% arsenic oxide at 35°, according to Smith.[5] All of the solids in this group showed a definitely crystalline structure under the microscope.

The flat portion AB corresponds to a pentacalcium compound $5CaO:2As_2O_5$, which is another acid compound, the simplest empirical formula for which would be $Ca_5H_2(AsO_4)_4$. So far as the writers are aware, this compound has not previously been reported. An analogous compound is known among the calcium phosphates, however, in the form of the mineral Martinite, $Ca_5H_2(PO_4)_4$. The arsenate came out readily in the form of long, pointed needles, quite different in form from the crystals of dicalcium arsenate. The solid obtained in the sample, which falls on the vertical portion of the curve at A (Fig. 1), showed distinct crystals of both types.

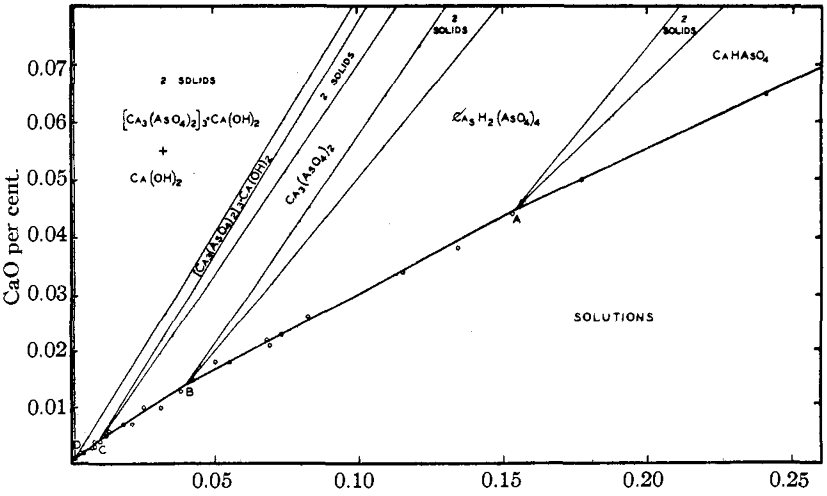

Fig. 2.

The flat portion BC indicates the compound $3CaO:As_2O_5$, or tricalcium arsenate, $Ca_3(AsO_4)_2$. The very narrow range of this compound accounts for the difficulty experienced by other workers in preparing pure samples. The solids in this group were largely amorphous, although several showed a few crystals which were quite definitely not similar to those of either of the acid compounds.

The portion CD is somewhat more uncertain than the other three, being extremely short. There is very little question, however, from these results and from the results of preparations which are discussed later, that this portion represents a definite basic compound, $10CaO:3As_2O_5$, which is the same as the compound $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$ reported by Tartar *et al.*[7] These solids appeared almost entirely amorphous, with a slight indication in one or two cases of the incipient formation of crystals.

The curve becomes vertical again at the point D, representing most probably a mixture of the basic compound with free lime. The points were not carried any farther up this curve, because the limitations of the analysis would not permit the identification of any further compounds if they existed, and because the etching of the flasks, which occurred in this region, would in any case make the results uncertain.

Figure 2 shows in more detail the general equilibrium conditions in the system. The curve ABCD represents the compositions of solutions in equilibrium with the various solid compounds. The letters A, B, C, and D represent the same points as in Fig. 1.

The diagram in Fig. 2 was used as the basis for a number of preparations of the different compounds, which were made in order to check the validity of the curve, and to furnish larger quantities of the pure compounds for a study of their properties. Small amounts of each of these preparations were made at 90°, but it was found more convenient for the larger amounts to be prepared at 100°, assuming that the curve would not be widely different at that temperature. Samples of two or three grams were prepared by making up solutions having a composition on the curve ABCD at about the center of the range of the compound sought, heating to boiling, and simultaneously adding lime and arsenic acid solutions in the proper proportions to form the compound, regulating the boiling and the rate of addition of the solutions so that the total volume of the mixture was kept constant. Little difficulty was experienced in obtaining products having the proper CaO/As_2O_5 ratios. Products were obtained having the following molecular ratios: basic, 3.30, 3.26; tri, 3.01, 3.00; penta, 2.49, 2.52; di, 2.00, 1.98. The actual percentages of the constituents varied somewhat, due to the fact that the products were rather amorphous in most cases, making it difficult to remove all of the mechanically combined water. Further attempts are being made to prepare completely crystalline samples of the compounds, on which accurate chemical and physical data can be obtained.

Figure 2 also furnishes an explanation of the fact that preparations made by adding concentrated arsenic acid to a suspension of lime are not consistent in properties. Even though the final composition of the mixture may lie in the region corresponding to a mixture of the basic compound with free lime, temporary local concentrations of the acid may make possible the formation of appreciable amounts of the other compounds. The conversion of these compounds being very slow, considerable amounts of them may be left unchanged in the final product. Thus commercial calcium arsenates probably contain a mixture of several compounds depending on the conditions of precipitation.

It is apparent from the fourth column in Table I that the basic compound is the only one which can dissolve in water at 90° without hydrolysis. All of the solutions in equilibrium with the other compounds have a lower ratio of lime to arsenic than the compounds themselves, as was noted by Smith[5] in the case of dicalcium arsenate. The data are in agreement with Tartar's[7] observation that the basic salt is formed by hydrolysis of the tricalcium salt, but is unchanged by further treatment with water. The di and penta salt should also be convertible to the basic by the same treatment.

Acknowledgment.—The authors wish to express their appreciation to Dr. A. W. Avens for his assistance in much of the analytical work.

Summary

1. A study of the system $CaO-As_2O_5-H_2O$ at 90° has been carried out.

2. A technique has been developed which permitted rapid attainment of equilibrium in the system.

3. Four compounds have been identified: dicalcium arsenate $CaHAsO_4$, pentacalcium arsenate $Ca_5H_2(AsO_4)_4$, tricalcium arsenate $Ca_3(AsO_4)_2$, basic calcium arsenate $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$.

4. Application of the data to the preparation of pure and commercial calcium arsenates has been discussed.

GENEVA, N. Y. RECEIVED APRIL 11, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

The Action of Light on Beta-Bromobenzalpyruvic Acid

BY MARIE REIMER

The action of sunlight on the methyl ester of benzalpyruvic acid results in polymerization of the ester to cyclobutane derivatives[1] as is the case with the cinnamic acids and many other ethylenic compounds. In a study of other unsaturated α-ketonic acids, in this Laboratory, it has been found[2] that benzalpyruvic acids in which methoxyl groups are substituted in the nucleus are less affected by light than the unsubstituted ester. The most active substance encountered is β-bromobenzalpyruvic acid which is extraordinarily sensitive to light. The present paper describes results so far obtained in the study of this light reaction.

When a colorless solution of β-bromobenzalpyruvic acid in benzene is allowed to stand in the diffused light of the laboratory it takes on a yellow color and, after two to three days, has become a brilliant lemon yellow. This color change does not take place in the dark.

On exposure of this yellow solution in thin layers to the direct sunlight the color fades quickly and the solution remains colorless for hours if kept in the direct rays of the sun. As soon as it is removed from the sunlight the yellow color reappears. The change from a yellow to a colorless solution in direct sunlight and from colorless to yellow in diffused light is rapid and can be repeated many times. The solution is so sensitive to the difference in intensity of the light that moving it a few cm. out of the direct rays is sufficient to bring back the yellow color and even the passing of a cloud over the sun has the same effect. After several hours of exposure a white crystalline substance begins to separate on the walls of the containing vessel. This is a dimeric form of β-bromobenzalpyruvic acid. The filtered solution, colorless after a day of exposure to the sunlight, becomes brilliantly yellow overnight. This yellow intermediate compound is, in all probability, a geometrical isomer of the original acid which forms an equilibrium mixture with that acid in diffused light. The effect of light on β-bromobenzalpyruvic acid is then, in part, as follows

$$\begin{tikzcd} \underset{\text{(colorless)}}{C_6H_5CH{=}CBrCOCOOH} \arrow[r, shift left] \arrow[rr, bend left, "\text{In diffused light}"] & \underset{\text{(yellow)}}{\text{intermediate compound}} \arrow[l, shift left] \arrow[r, shift left] & \underset{\text{(colorless)}}{\text{polymer}} \arrow[l, shift left] \arrow[ll, bend left, "\text{In bright light}"] \end{tikzcd}$$

The cause of the rapid change in color of the solution as it is moved into and out of the direct rays of the sun is evidently the difference in rate of polymerization in bright and in diffused light, the speed of polymerization outstripping that of isomerization in bright light but falling far behind it in diffused light, a sensitivity to difference of light intensity recalling that of lactoflavine, recently described.[3]

If the tubes used for exposure are tightly stoppered another effect of light becomes apparent in the formation of a volatile substance which, as soon as it has saturated the benzene solution, changes the course of the reaction. This substance was found to be hydrogen bromide formed evidently by photodecomposition of some of the bromine compounds present. In its presence there is no appearance of the yellow compound, the polymer is formed in but small quantity, much of the original acid being recovered unchanged. The solution slowly takes on a brown color due to formation of decomposition products. When the tubes are left open to the air, so that the hydrogen bromide escapes, there is no evidence of such products until the solution has been exposed for several weeks. The containers used were at first loosely stoppered to allow the escape of this gas but, as it was found that the solutions were sensitive to the oxygen of the air, later experiments were conducted in an atmosphere of nitrogen. The best yields of polymer were obtained in this way.

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(1) Reimer, THIS JOURNAL, **46**, 783 (1924).

(2) Reimer and Kamerling, *ibid.*, **55**, 4643 (1933); Reimer, Tobin and Schaffner, *ibid.*, **57**, 211 (1935).

(3) Karrer, Köbner, Salomon and Zehender, *Helv. Chim. Acta*, **18**, 270 (1935).