a suspension in a 50% alcoholic solution, treated in a similar way. The results expressed in percentages of the opalescence of the 50% alcoholic solution are given in Table IX.

TABLE IX.—OPALESCENCE IN VARIOUS SOLVENTS.

Solvent.	Molar conc. × 10⁵. 6.2.	23.
50% alcohol	(100)	(100)
Water	115	115
50% acetic acid	101	102

The opalescence in 50% acetic acid is substantially the same as in 50% alcohol; that in water is somewhat greater, but no effect of concentration is evident.

Summary.

It has been shown that:

(1) In a 50% alcohol-water solution, heating silver chloride suspensions of widely differing concentrations to 40° for 30 minutes after precipitation, produces a more intense and constant opalescence than can be attained at room temperature; further heating for 30 minutes at 40°, or standing at room temperature for an hour produces no perceptible change in this opalescence.

(2) Using this technique, chlorides in such solutions can be estimated with an average deviation of about 3 to 4% over concentrations ranging between 4 and 300×10^{-6} M.

(3) Opalescence in such solutions decays more rapidly in diffuse daylight than in the dark.

(4) The opalescence of the same quantity of silver chloride in water is about 15% greater than in 50% alcohol or 50% acetic acid.

Certain phases of this problem are being studied further by Meldrum.

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[CONTRIBUTION FROM THE INSECTICIDE AND FUNGICIDE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE ARSENATES OF CALCIUM. I. EQUILIBRIUM IN THE SYSTEM ARSENIC PENTOXIDE, CALCIUM OXIDE, WATER AT 35° (ACID SECTION).

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Owing to the commercial importance which calcium arsenate has recently assumed as an agricultural spray material more detailed knowledge of its chemical and physical properties has become essential. One of the most important questions in relation to a spray for use on vegetation is its behavior with water, which may and often does result in the liberation of so called "soluble" arsenic—including in that term not only the arsenic which may be present as a soluble impurity but also that which comes from any decomposition or solution of the spray material by the water with which it is in contact.

It appeared that the best way to treat this question was by a study of the general equilibrium conditions in the system, and the application of the phase rule criteria to the interpretation of the results.

This system is one of 3 components, calcium oxide, arsenic oxide, and water. According to the phase rule, a 3-component system will always behave in such a way that the sum of the number of phases and the degrees of freedom will be 5. For the purpose of the investigation, only those conditions under which at least 3 phases—gas, solution, and solid—exist are of interest to us. By working at constant temperature the system may be reduced to one degree of freedom, in which state the existence of one solid phase will be indicated by variation of the solution, while the appearance of a second solid phase will render the system invariant and result in the production of a constant solution. Consequently, if various empirical mixtures are made up and allowed to come to equilibrium, analysis of the solutions and solid phases will serve to establish the limits within which the different compounds can exist.

Owing to the fact that arsenic acid is extremely soluble, while calcium oxide is only sparingly so, the entire range of experiments could not be covered in the same way. Consequently the subject was divided into two sections, which have been designated the acid and basic sections, and the two series of solutions arranged so they overlap. The acid region forms the subject of this paper, the basic region being covered in a paper to appear subsequently.

In order to obtain pure calcium oxide, that used was all prepared from calcium chloride by two precipitations with ammonium carbonate and subsequent ignition in an electric muffle. By this means a product was obtained containing only 0.04% of magnesium oxide and 0.08% of carbon dioxide, and no more than mere traces of any other impurities.

The arsenic acid was purified as follows: Ordinary commercial acid containing about 75% of ortho arsenic acid was concentrated by boiling until the boiling point rose to 150°. It was then cooled and "seeded' with a crystal or two of solid arsenic acid ($As_2O_5.4H_2O$). This caused the separation, in a short time, of the main bulk of arsenic acid as the above mentioned hydrate. (The "seeding" is absolutely necessary, for supersaturated solutions have been kept in the laboratory for 2 years without spontaneous separation having occurred. The first crop of crystals was obtained by cooling some supersaturated solution to about —10°.) If the solution is left undisturbed after "seeding," the crystals form large enough to be filtered on a Büchner funnel without the use of any filter medium. (Paper could not be used on account of the destructive action of the strong arsenic acid upon it.) Six such recrystallizations were carried out by the method of combining filtrates and residues which gave a product practically free from all common impurities. (It may be mentioned that the chief impurity in the commercial acid was an extremely finely divided suspension of oxide of iron, which readily passed through the Büchner funnel.) This crystallized product melts at about 36°. It is hygroscopic and is not suited for weighing definite amounts, but it is very readily soluble in water, and solutions of any desired strength up to about 74% of arsenic oxide may be prepared from it.

The experiments which form the immediate subject of this paper were planned as follows: The arsenic acid was prepared in the form of a thick sirupy solution, d 2.31 and containing 74.8% of arsenic oxide. To a series of 2-ounce bottles, numbered from 1 to 15 inclusive, were added successively increasing amounts of the strong acid, the amounts being so arranged that on dilution of each with water to a volume of 40 cc. there was obtained a series of arsenic acid solutions ranging from 5% to 75% of arsenic oxide in steps of 5%. Both strong acid and water were measured from a buret, and rather crudely, for an exact knowledge of the composition was not necessary. To these solutions was now added powdered calcium oxide in small quantities until the acid was saturated, and then about one g. additional. This insured the presence of 2 or 3 g. of solid residue. The bottles were then securely stoppered and attached to a rotating machine which was immersed in a water bath maintained at 35°. The machine was run continuously day and night, and tests of one solution at the end of 10 days and 17 days showed that it had reached equilibrium. Since the machine contained at the same time the basic experiments, which were much slower in reaching equilibrium, the whole lot was not removed for about 3 months. In that time the maximum variation of temperature was about 2°, with an average daily variation of less than 0.5°.

When the samples were removed from the shaking machine they were filtered as quickly as possible, using a Gooch crucible containing a disc of hardened filter paper. When the liquid had drained out, it was recovered while the wet residue was transferred to a weighing bottle, weighed, and dissolved in a known amount of dil. hydrochloric acid The amount of the latter used was figured to give a solution of a strength suitable for analysis. The densities of all the filtrates were determined at 35°, correction being made for buoyancy of air. All analyses were made on weighed samples, but the density data of the filtrates permitted recalculation to volume figures, which has been done.

The methods of analysis used were as follows: For calcium oxide a suitable aliquot was taken, the acidity reduced if necessary with ammonia, the solution heated to boiling, and 50 cc. of boiling ammonium oxalate solution (40 g. per liter) run in very slowly from a pipet. This procedure quantitatively separates the lime from the arsenic, and produces a precipitate so granular that it settles almost immediately and may be filtered after half an hour or so. After filtration and washing, the precipitate was titrated with standard permanganate solution. For arsenic, a suitable weight of sample was evaporated to about 10 cc. on the steam bath, cooled, 25 cc. of conc. hydrochloric acid added, then 10 cc. of water containing one g. of potassium iodide, then 25 cc. of ammonium chloride solution (200 g. per liter), and the liberated iodine finally titrated with standard thiosulfate solution. The results of these analyses are given in Table I.

TABLE I.

	Composition of wet residue % by wt.		Composition of solution % by wt.			Composition of solution. G. per liter.		
Expt.	CaO.	As_2O_5.	CaO_5.	As_2O_5.	Density of solution.	CaO.	As_2O_5.	Molecular ratio in solution. CaO/As_2O_5.
1	18.24	31.10	0.096	0.198	0.996	0.956	1.372	1.99
2	22.49	45.93	0.702	2.711	1.025	7.20	27.79	1.06
3	22.16	46.14	1.903	7.98	1.09	20.74	87.0	0.98
4	21.12	44.89	3.206	12.97	1.157	37.09	150.1	1.01
5	21.66	46.42	4.59	18.70	1.242	57.0	232.3	1.01
6	20.96	45.31	4.64	19.99	1.261	58.5	252.1	0.95
7	22.31	48.09	5.34	21.97	1.300	69.4	285.6	1.00
8	15.56	62.91	6.54	28.78	1.413	92.5	405.4	0.94
9	14.44	62.02	5.34	35.03	1.48	79.0	518.4	0.62
10	12.42	60.77	4.07	43.43	1.590	64.7	690.5	0.38
11	11.66	63.00	2.95	50.30	1.697	50.1	853.6	0.24
12	6.56	59.98	1.87	55.43	1.795	33.6	995.0	0.14
13	7.64	66.39	0.822	62.66	1.975	16.2	1237.0	0.05
14	7.36	70.92	0.135	71.04	2.167	2.93	1539.0	0.008
15	4.21	77.92	0.114	72.14	2.217	2.53	1599.0	0.006

Since it was impossible to remove all adhering mother liquor from the solid precipitates, the following well known graphical scheme was used for finding the composition of these solids. If the points representing any solution and its corresponding wet residue are connected by a line, this line produced passes also through the point representing the dry residue. Two such lines will converge at this latter point, provided the solid material remains the same. However, to establish definitely that it is a fixed compound it is necessary that a third line converge at this point. This method has been followed in Fig. 1 In the presentation of the results rectangular coördinates are used instead of the possibly more common triangular ones because of greater ease of interpretation. The percentage of calcium oxide has been plotted against the percentage of arsenic oxide, the ordinate scale being given a relative magnification of 2.5 in order to bring out the relationship more clearly.

Now consider the results of Expts. 2 to 7 inclusive. It is seen that the solution results fall upon a straight line, AB, while the lines drawn through solutions and residues actually converge to a more or less definite point. Owing to the fact that the lines are not very convergent, it is difficult to pick the point of convergence from the graph. However, by applying the method of least squares, the most probable position of this point was found to correspond to 27.1% of calcium oxide and 55.3 % of arsenic oxide.[1]

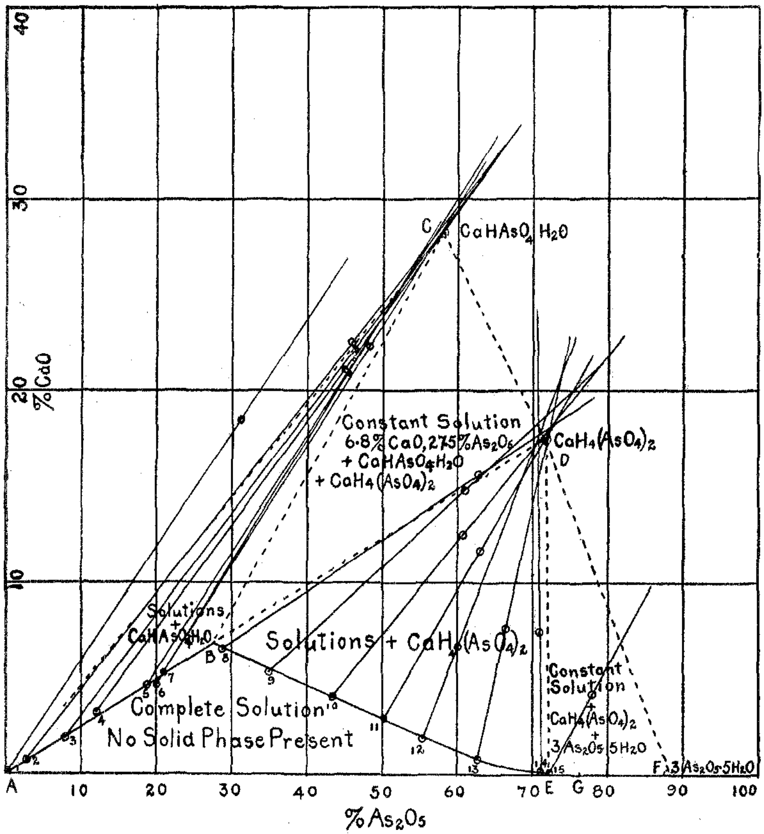

Fig. 1.—Equilibrium in the system As_2O_5–CaO–H_2O at 35°

These figures are almost exactly those corresponding to the formula, $CaHAsO_4.1.5H_2O$. Such a formula has been ascribed to products obtained by Turner,[2] Kotschubey,[3] and Debray,[4] but De Schulten's experiments,[5]

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[1] This calculation was based on the following assumptions that all the individual analyses were of equal weight; that the lines should be given weight proportional to the length between their determining points; and finally that the most probable point of convergence should be taken as the point where the sum of the squares of the weighted perpendicular distances from the various lines is a minimum.

[2] *Edinburgh J. Sci.*, 3, 306 (1825).

[3] *J. prakt. Chem.*, 49, 182 (1850).

[4] *Ann. chim. phys.*, [3] 61, 427 (1861).

[5] *Bull. soc. franc. min.*, 26, 22 (1903).

as well as our own[1] have not confirmed it. The two well defined natural hydrates have the formulas $CaHAsO_4.H_2O$ and $CaHAsO_4.2H_2O$ (haidingerite and pharmacolite). The probable error in the point of convergence is great enough to include both of these compounds, but examination by the petrographic microscope shows that the former is the compound actually present. Consequently the compound of the formula $CaHAsO_4.H_2O$ can be in equilibrium only with solutions along the line AB.

Passing now to Expts. 8 to 14 inclusive, it is found that the solutions range along another approximately straight line BE, while the solution-residue lines converge to a point the most probable location of which has been calculated to be that corresponding to 17.7% of calcium oxide and 71.4% of arsenic oxide. These are quite close to the theoretical values, 17.4 and 71.4, for the compound of the formula $CaH_4(AsO_4)_2$, monocalcium orthoarsenate.[2] Because of the wider divergence of these lines, the calculated values have much greater weight than in the former case, and furthermore since we have been able to produce a compound of this formula by other means, its existence here is definitely established.

The point B at which the two solution curves AB and BE intersect, represents the constant solution which exists in the presence of both solid phases. It is unfortunate that none of the experiments happened to fall at this point, but the graph shows it to be located at a position approximately corresponding to 6.8% of calcium oxide and 27.5% of arsenic oxide. Had any experiment fallen here its representative line would have traversed the region BCD and cut the dotted line CD at a point representing the composition of the mixture of solids present.

Expt. 15 was made by putting some calcium oxide into a mushy mixture of crystalline arsenic acid ($As_2O_5.4H_2O$) and its saturated solution, in an attempt to determine the constant solution in contact with both calcium arsenate and arsenic acid. The line representing this experiment does not converge to the point D, showing that a new phase has appeared, and furthermore the position of the wet residue point shows that the second phase is not the arsenic acid started with ($As_2O_5.4H_2O$). Menzies and Potter[3] state that they were able to prepare only two hydrates of arsenic pentoxide, the 1,4-hydrate just mentioned and a 3,5-hydrate ($3As_2O_5.5H_2O$). They also state that the latter compound is the more stable above 29.5°. This explains the transposition of the arsenic acid originally taken into the other hydrate. The point E, therefore, represents the constant solution in contact with monocalcium orthoarsenate

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[1] A subsequent paper will describe the various compounds of CaO, As_2O_5 and H_2O, the methods of their preparation in crystalline form and a study of their properties.

[2] This compound has not previously been reported, although Hoermann (Inaugural-Dissertation, "Beitrage zur Kenntniss der Pyro-und-Meta-Arsensäure." Erlangen, 1879) has described its monohydrate.

[3] THIS JOURNAL, 34, 1469 (1912).

and the 3,5-hydrate. It contains 0.114% of calcium oxide and 72.14% of arsenic oxide, the latter figure being in close agreement with the figure 73.0 given by Menzies and Potter for the solubility of the 3,5-hydrate at 35°.

It may be seen from the graph that the points representing solid phases and constant solutions have been connected by dotted lines. These lines divide the entire chart into various regions, which permit of predicting the behavior of any empirical mixture of calcium oxide, arsenic oxide, and water when kept at 35°. For instance any empirical mixture whose representative point falls within the area BDE will separate into the solid monocalcium orthoarsenate and a solution represented by some point on the line BE. Likewise, any empirical mixture whose representative point falls within the region ABE will form a solution with no residue.

There remains to be considered one line, that representing Expt. 1. This does not pass near the point C, showing that there must be present some compound more basic than dicalcium orthoarsenate monohydrate. The equilibrium conditions in this system covering the basic region will be presented in a subsequent paper.

It appears worthy of note that the line AB, representing solutions in equilibrium with dicalcium orthoarsenate monohydrate, if extended, passes very close to the point D representing monocalcium orthoarsenate. In other words, dicalcium orthoarsenate monohydrate is stable only (apparently) in solutions of monocalcium orthoarsenate. This is brought out plainly in the last column of Table I, where it is seen that the average value of the molecular ratio of the solutions from Expts. 2 to 7 inclusive is 0.99.

Summary.

1. The general equilibrium relations in the 3-component system arsenic pentoxide, calcium oxide, and water have been investigated for the acid region at 35° and the phase rule criteria applied to the interpretation of the results.

2. Two compounds have been found to be stable under the conditions of the experiment, dicalcium orthoarsenate monohydrate, $CaHAsO_4.H_2O$, identical with the natural mineral haidingerite, and monocalcium orthoarsenate $CaH_4(AsO_4)_2$, existing below and above, respectively, an acid concentration corresponding to 27.5% arsenic pentoxide.

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