the cells of Tables I and II. Addition of these two series of electromotive forces gives the values in the last line of Table III.

The relation between electromotive force and temperature can be expressed within 0.02 mv. by the equation $E_t = E_{25} + 0.000013(t - 25)$. However, the relation is not exactly linear and an additional term would improve the equation. The temperature coefficient, 0.000013, is less than one-third of the average temperature coefficient of the Weston cell between 20 and 30°.

The lag in adjustment to equilibrium after a decrease in temperature was about the same as has been observed in regular Weston cells. An exact comparison cannot be made, because no Weston cells were made of the same materials.

There is no apparent reason why the cell of Table III should be less constant or less reproducible than the saturated Weston cell. If experience shows this to be the case, the new cell should be superior to the unsaturated Weston cell as a practical standard for use at room temperature. Its temperature coefficient is small enough so that a change in temperature of 8° is required for 0.01% change in electromotive force,[6] and a temperature correction may be applied, if desired. Its electromotive force is within the customary range for unsaturated cells. It is planned to continue the study of this cell and also to construct some similar cells with other added salts in the hope of finding a cell still better adapted for use as a practical standard at room temperature.

Summary

Substitution of cadmium–bismuth amalgam for the cadmium amalgam of the Weston cell and saturation of the electrolyte with the double salt of sodium and cadmium sulfates as well as with cadmium sulfate gives a cell with an electromotive force of 1.0184 v. at 25° and a temperature coefficient of 0.000013 v. per degree.

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[6] An unsaturated cell may be expected to decrease 0.01% in electromotive force in the course of one to three years: (a) Vosburgh, *J. Optical Soc. Am.*, **11**, 59 (1925); (b) Smith, *Rev. Sci. Instruments*, **5**, 425 (1934).

DURHAM, N. C. RECEIVED MAY 5, 1937

[CONTRIBUTION FROM THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

Further Phase Rule Studies of the Calcium Arsenates[1]

BY G. W. PEARCE AND A. W. AVENS

In a previous paper[2] the equilibrium conditions in the system $CaO–As_2O_5–H_2O$ at 90° are described. Since the calcium arsenates exhibit a negative coefficient of solubility and most of them are hydrolyzed readily, it was believed that the system would be quite different at other temperatures. Accordingly the present paper deals with the equilibrium conditions in the system $CaO–As_2O_5–H_2O$ at 35°. The study has been confined to the more basic part of the system in which Smith[3] and others[4] apparently were unable to reach equilibrium.

Experimental

The methods of analysis and their limitations as well as the apparatus and reagents are the same as described in the report on the system at 90°.[2] In that study a technique was developed for rapid attainment of equilibrium. The same technique has been applied to the system at 35°.

Using the data obtained at 90°[2] as a basis for calculating the approximate concentrations required, preliminary experiments at 35° were carried out. Samples were prepared in one-liter, wide-mouthed, Pyrex Erlenmeyer flasks by adding a saturated solution of lime to a solution of arsenic acid partially saturated with lime and cooled to about 10°, until the first perceptible precipitation occurred. The samples were brought to a volume of about 600 cc., placed in a constant temperature bath maintained at 35 ± 0.1°, and connected to the multiple stirring device previously described.[2] After remaining in the bath with intermittent stirring for periods of five to ten days, the samples were removed and examined according to the procedure used for the study at 90°.[2]

The results of the preliminary runs were used in calculations for confirmatory experiments. In the latter instance the proportions of lime, arsenic acid and water were calculated so that known amounts of solids would precipitate at 35°. The samples were made up at room temperature because as a rule no precipitation occurred until they were brought to 35°. In the few cases where partial precipitation occurred before placing in the bath, the results indicated that no error was introduced, probably because there is no great difference in the system at room temperature

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[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 200, April 15, 1937.

[2] Pearce and Norton, THIS JOURNAL, **58**, 1104 (1936).

[3] Smith, *ibid.*, **42**, 259 (1920).

[4] Clifford and Cameron, *Ind. Eng. Chem.*, **21**, 69 (1929).

and at 35°. The amounts of solids precipitated varied from 50 mg. in the more insoluble portion of the system to 3000 mg. in the more soluble portion. The precipitation of the larger amounts of solid was necessary because of supersaturation. As the solutions became more concentrated, supersaturation became more evident, but it was found that critical concentration points could be reached above which no supersaturation would take place. These points were roughly estimated for that part of the system which gave difficulties, and the samples were then prepared so that supersaturation would be avoided. Determination of arsenic in the solutions at intervals during the course of a run showed that equilibrium was established immediately or soon after precipitation occurred.

In general, the solids obtained were well crystallized, but no data will be presented in this paper to show the amount of water associated with any of the compounds. The data at hand in this respect are limited to the more acidic compounds obtained and do not differentiate between water of crystallization and water of constitution. Efforts are being made to gain complete information on all the compounds.

Results and Discussion

The data obtained by the procedures described are presented in Table I, and are shown graphically in Figs. 1 and 2. The reproducibility of the results is shown by the fact that the ranges of each of the compounds are determined by points obtained from at least three different experiments.

As in the case of the study at 90°[2] it was impractical to plot the composition of both solids and solutions to the same scale because of the high dilution of the solutions. Accordingly, Fig. 1 is

TABLE I

Expt.	Sample	Composition of solutions % by weight As_2O_5	CaO	Mol. ratio CaO/As_2O_5	Composition of solids Ratio CaO/As_2O_5 Wt.	Mol.	Amt. of solid pptd., mg.	Compounds[a] in solid phases	Mol. ratio CaO/As_2O_5 Calcd.
6	1	0.0005	0.009	73.90	0.838	3.44	50	Tri + lime	
1	6	.001	.006	24.65	.729	2.99	..	Tri	3.00
3	1	.001	.005	20.54	.726	2.98	50	Tri	
3	2	.002	.005	10.27	.733	3.01	50	Tri	
3	3	.008	.005	2.57	.746	3.06	50	Tri	
1	7	.022	.012	2.24	.743	3.05	..	Tri	
3	4	.029	.015	2.12	.733	3.01	100	Tri	
3	5	.046	.023	2.05	.731	3.00	100	Tri	
1	8	.050	.025	2.05	.719	2.95	..	Tri	
3	6	.058	.027	1.91	.724	2.97	100	Tri	
4	1	.058	.027	1.91	.750	3.08	..	Tri	
6	2	.068	.032	1.93	.738	3.03	100	Tri	
3	7	.078	.036	1.89	.719	2.95	150	Tri	
1	5	.076	.038	2.05	.687	2.82	..	Tri + penta	
3	8	.075	.035	1.92	.609	2.50	150	Penta	2.50
1	4	.084	.039	1.91	.612	2.51	..	Penta	
1	3	.111	.050	1.85	.616	2.53	..	Penta	
4	3	.116	.050	1.77	.621	2.55	200	Penta	
4	5	.129	.055	1.75	.609	2.50	..	Penta	
4	4	.137	.056	1.68	.624	2.56	200	Penta	
4	6	.139	.059	1.74	.600	2.46	..	Penta	
1	2	.140	.059	1.73	.616	2.53	..	Penta	
4	7	.152	.063	1.70	.590	2.42	..	Penta	
6	5	.166	.066	1.63	.600	2.46	2400	Penta	
5	1	.168	.068	1.66	.595	2.44	..	Penta	
6	4	.182	.072	1.62	.600	2.46	1800	Penta	
6	3	.184	.073	1.63	.595	2.44	1200	Penta	
7	1	.195	.076	1.60	.590	2.42	800	Penta	
5	2	.217	.080	1.51	.602	2.47	..	Penta	
7	2	.218	.084	1.58	.590	2.42	1200	Penta	
7	4	.236	.084	1.46	.478	1.96	1600	Di	2.00
7	3	.236	.087	1.51	.500	2.05	1600	Di	
7	5	.264	.090	1.40	.504	2.07	1800	Di	
5	4	.270	.095	1.45	.495	2.03	..	Di	
6	8	.289	.096	1.36	.504	2.07	3000	Di	
6	6	.290	.096	1.36	.504	2.07	2000	Di	
6	7	.291	.097	1.37	.497	2.04	2500	Di	
7	6	.333	.105	1.29	.483	1.98	2500	Di	
7	7	.389	.118	1.25	.487	2.00	2500	Di	

[a] Empirical formulas: tri = $Ca_3(AsO_4)_2$; penta = $Ca_5H_2(AsO_4)_4$; di = $CaHAsO_4$.

employed for identification of the compounds, while Fig. 2 shows in greater detail the equilibrium conditions of the system. The points marked A, B and C in both diagrams correspond.

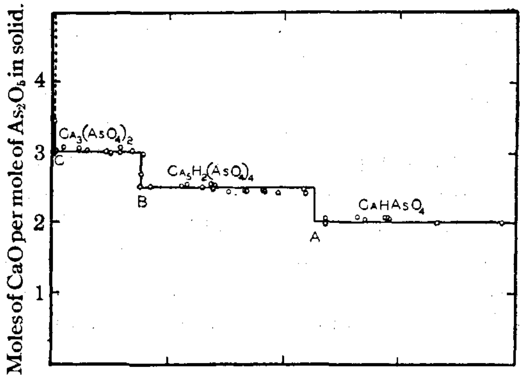

Fig. 1.

A study of the data presented shows the existence of three compounds as indicated by the three horizontal portions of the curve in Fig. 1. The portion from the extreme right to the point A represents $2CaO:As_2O_5$ or dicalcium arsenate, $CaHAsO_4$. Smith's data show that this compound is stable in contact with solutions containing up to 27.5% As_2O_5 at 35°. It is to be noted that the lower end of the range of dicalcium arsenate is at approximately 0.230% As_2O_5 at 35°, while it goes down to 0.153% As_2O_5 at 90°.[2]

Pentacalcium arsenate, $5CaO:2As_2O_5$, is shown by the flat portion AB in Fig. 1. This compound was first demonstrated at 90° and may be represented by the empirical formula $Ca_5H_2(AsO_4)_4$. There is an appreciable difference in the ranges of solution concentrations with which it can be stable at the different temperatures. At 35° it occurs throughout the range 0.076 to 0.230% As_2O_5, while at 90°[2] it occurs in the range 0.038 to 0.153% As_2O_5.

The flat portion, BC, Fig. 1, represents the compound $3CaO:As_2O_5$, or tricalcium arsenate, $Ca_3(AsO_4)_2$. Again as in the case of the other compounds the range of solution concentrations with respect to arsenic acid is extended, being 0.008 to 0.038% As_2O_5 at 90°[2] and 0.001 to 0.076% As_2O_5 at 35°.

One of the most important observations to be made from the present study is the fact that no basic calcium arsenate has been obtained whereas it was present in the system at 90°.[2] This suggests that commercial preparations made by adding a concentrated arsenic acid solution to a slurry of lime should be prepared at temperatures in the neighborhood of 90° if a product containing basic calcium arsenate is desired. In reality this is usually the rule because the lime slurry frequently is prepared by adding water to unslaked lime, and the heat thus generated persists in more or less degree during the addition of the arsenic acid. Obviously, even though a high temperature be employed large amounts of the more acid salts are liable to be formed on account of impoverishment of the slurry with respect to lime in the immediate vicinity of contact with the arsenic acid solution.

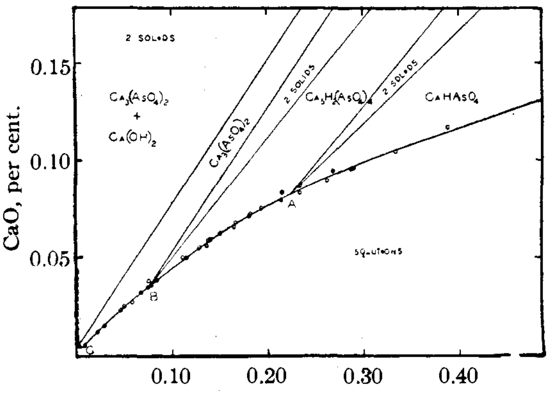

Fig. 2.

Waters and Witman[5] recently have studied some of the factors involved in the commercial preparation of the so-called "safe" calcium arsenates, which are generally believed to consist essentially of basic calcium arsenate. They found that procedures which would promote formation of a precipitate at temperatures between 75–100° under conditions which would suppress local impoverishment to a minimum in the lime slurry result in a product having a low water-soluble arsenic as determined by the Geneva method[6] and a corresponding high degree of "safeness" toward plant foliage.

The data on the system at either 35 or 90°[2] are not complete for that part of the system represented by the vertical lines at the extreme left of the diagrams. Thus the equilibrium conditions in that part of the system where the solutions have an excess of lime relative to the arsenic acid

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(5) Waters and Witman, *J. Econ. Entomol.*, **30**, 204 (1937).

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

should be studied. Such an investigation requires containers which are not attacked by lime. In the present study, four points have been obtained (Samples 1 and 2, Expt. 3; Sample No. 1, Expt. 6; Sample No. 6, Expt. 1 in Table I) which have an excess of lime with respect to the arsenic acid in solution. These samples showed no detectable etching of the flasks nor any significant amount of silica in either solids or solutions. The points were purposely grouped in the range of solution concentrations found for them in order to be sure that the basic salt is not formed.

An examination of the molecular ratios of lime to arsenic oxide in the solutions (Table 1, column 5) shows that tricalcium arsenate is the only one that can dissolve in water at 35° without hydrolysis. Robinson[7] has reported solubilities for tricalcium and dicalcium arsenates at 25° and that solution of these compounds takes place without hydrolysis. Assuming that there is little difference in the system at 25 and 35° one must infer that Robinson's data on the solubility of dicalcium arsenate represent a false equilibrium. Such an explanation appears logical in view of the difficulties encountered in obtaining equilibrium in the system as experienced by the writers[2] and others.[3,4]

It is also of importance to note that all the compounds are stable in solutions more basic at 35 than at 90°.[2] This observation is in accord with some unpublished data which indicate that the compounds are fairly stable at room temperature in the presence of a lime solution but are changed rapidly to more basic compounds at temperatures in the neighborhood of 90°.

Summary

1. A study of the system $CaO-As_2O_5-H_2O$ at 35° has been carried out.

2. Three compounds have been identified: dicalcium arsenate, $CaHAsO_4$; pentacalcium arsenate, $Ca_5H_2(AsO_4)_4$; and tricalcium arsenate, $Ca_3(AsO_4)_2$. No basic calcium arsenate was found.

3. Importance of the data from theoretical and practical standpoints has been discussed.

GENEVA, N. Y. RECEIVED APRIL 22, 1937

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Purines in the Plant Kingdom: The Discovery of a New Purine in Tea[1]

BY TREAT B. JOHNSON[2]

The recent discoveries in the field of vitamins and hormones, and their vital importance to the normal development and control of life processes, have stimulated a renewed interest today in the search for new organic constructions occurring in nature. The refined methods of analysis and the newer techniques which have been developed have made possible the separation and identification of many new organic compounds occurring in microchemical quantities only, which hitherto were not conceived as playing any part in nature's processes. There is no doubt that the occurrence of many new organic combinations will be revealed to us in the future, for the study of natural products has received a new impetus as a result of the application of the improved methods of experimentation.

The known purines occurring in the plant kingdom are the three methylated derivatives of xanthine, namely: caffeine, $C_8H_{10}O_2N_4$; theobromine, $C_7H_8O_2N_4$; and theophylline, $C_7H_8O_2N_4$. These may be considered, according to our present knowledge, as end-products of purine metabolism in plants. In addition to these there have also been found adenine, $C_5H_5N_5$,[3] and guanine, $C_5H_5ON_5$, in the form of glucosides, adenylic acid and vernine or guanosine, respectively, and the two corresponding deaminized or secondary purines xanthine, $C_5H_4O_2N_4$, and hypoxanthine, $C_5H_5ON_4$. This second group of non-methylated purines may be considered as degradation products of plant nucleic acids. When introduced into the animal organism, the methyl-

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(1) Preliminary notice published in *Science*, Vol. 85, pp. 431 (1937).

(2) I desire to express here my thanks to the following men for their kind help and coöperation in securing data for preparing this paper for publication: William E. Ford, Professor of Mineralogy, and Curator of Mineralogical Collections, for his report on the crystallography of the new plant purine; Dr. James M. Sprague, Sterling Research Assistaint, for analytical assistance and aid in the synthesis of tetramethyluric acid, and Dr. Frank H. Stadola, National Tuberculosis Association Fellow, for microchemical analyses.

(3) Adenine-nucleotide from tea leaves, H. O. Calvery, *J. Biol. Chem.*, **68**, 593 (1926).