Recent evidence concerning the isotopic character of the following elements has been given by Aston.[23]

ISOTOPIC CHARACTER OF ELEMENTS

Element	Atomic number	Atomic weight	Minimum number of isotopes	Mass number in order of intensity
Sc	21	45.1	1	45
Ti	22	48.1	1	48
V	23	51.0	1	51
Cr	24	52.0	1	52
Mn	25	54.93	1	55
Co	27	58.94	1	59
Cu	29	63.57	2	63, 65
Ga	31	69.72	2	69, 71
Ge	32	72.42	3	74, 72, 70
Sr	38	87.63	1	88
Y	39	88.9	1	89
Ag	47	107.88	2	107, 109
Sb	51	121.77	2	121, 123

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THE ACTION OF ARSENIC TRIOXIDE IN WATER SOLUTION ON CERTAIN METALLIC HYDROXIDES

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Many arsenites have been described in the literature,[1] some of which have a complex composition. Frequently these substances were prepared under conditions that might easily give rise to mixtures. Indeed, the analyses of the products often do not agree with the formulas assigned to them. Biltz[2] studied the action of ferric hydroxide, aluminum hydroxide and silicic acid separately on water solutions of arsenic trioxide and found that no compounds were formed but adsorption phenomena occurred. The results in the case of ferric hydroxide could be represented by an equation. The amounts of arsenic trioxide adsorbed by aluminum hydroxide and silicic acid were very small and practically independent of the concentration of the arsenic trioxide in solution. These facts led to the investigation of the action of arsenic trioxide in water solution on certain metallic hydroxides in order to determine the composition of the products formed.

[23] Aston, *Nature*, **110**, 732 (1922); **112**, 449 (1923).

[1] Stavenhagen, *J. prakt. Chem.*, **51**, 1 (1895). Reichard, *Ber.*, **27**, 1019 (1894), and **31**, 2165 (1898).

[2] Biltz, *Ber.*, **37**, 3138 (1904).

Since the method of procedure for studying systems similar to the above has been worked out and used by other investigators,[3] it will not be described in detail. In general, various weights of pure arsenic trioxide[4] and metallic hydroxide were placed in 250cc. bottles containing approximately 200 cc. of water. The bottles were stoppered and mechanically shaken in a thermostat kept at the desired temperature until analyses showed that equilibrium had been reached. The solutions were then quickly filtered and the residue dried in a desiccator at room temperature. In each case the filtrate and residue were analyzed for metallic oxide and arsenic trioxide, and in some cases for carbon dioxide and water. The time required for equilibrium to be reached varied with the temperature, ranging from three days at 99° to more than a week at lower temperatures.

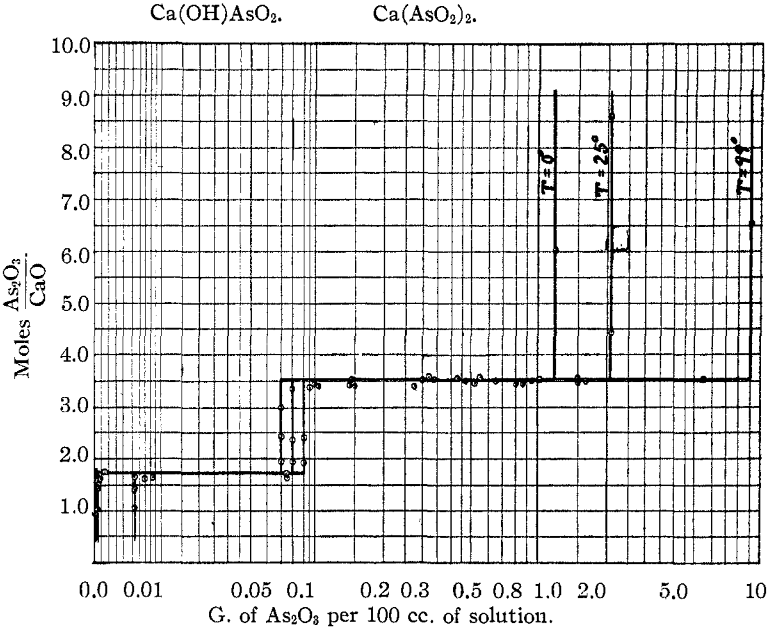

Fig. 1.—Curves for the system, $CaO-As_2O_3-H_2O$.

The concentrations of arsenic trioxide in the filtrate were plotted as abscissas and the ratio of the moles of arsenic trioxide to metal oxide in the precipitates as ordinates. When the resulting curve consisted of horizontal and vertical portions, definite compounds were being formed. The composition of the compound corresponding to the horizontal portion of the curve is given by the value of the ordinate.

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[3] Miller and Kenrick, *J. Phys. Chem.*, **7**, 259 (1903); Allen, *Am. Chem. J.*, **25**, 307 (1901).

[4] Anderson and Story, THIS JOURNAL, **45**, 1103 (1923).

The System, Calcium Oxide-Arsenic Trioxide-Water

The data in this case, Table I and Fig. 1, prove conclusively that when mixtures of calcium hydroxide and arsenic trioxide are shaken in water at the temperatures 0°, 25° and 99°, two arsenites may result, depending on the concentration of the arsenic trioxide in the solution. When the

TABLE I

DATA FOR THE SYSTEM, CALCIUM OXIDE-ARSENIC TRIOXIDE-WATER

Total volume approximately 200 cc.

Ratio moles $\frac{As_2O_3}{CaO}$ in (1) $Ca(AsO_2)_2$ = 3.53; (2) $Ca(OH)AsO_2$ = 1.76

CaO used G.	As_2O_3 used G.	Grams of As_2O_3 per 100 cc. of H_2O in solution	Moles $\frac{As_2O_3}{CaO}$ in solid	CaO used G.	As_2O_3 used G.	Grams of As_2O_3 per 100 cc. of H_2O in solution	Moles $\frac{As_2O_3}{CaO}$ in solid
	Temp. 0°				Temp. 25°		
1.00	1.00	0.0001	1.68	1.35	1.00	0.0002	0.96
1.00	1.00	.0001	1.70	1.00	1.30	.0002	1.38
				1.00	1.40	.0002	1.46
1.00	1.18	.0002	1.73				
1.00	1.30	.0003	1.70	1.00	1.48	.0003	1.68
1.00	1.40	.0004	1.70	1.10	1.77	.0009	1.65
1.00	1.50	.0006	1.72	1.00	1.77	.0660	1.74
1.00	1.90	.0016	1.76				
				1.00	2.00	.07	1.98
1.00	2.00	.06	1.98	1.50	3.54	.07	2.34
1.00	2.50	.06	2.40	1.10	3.54	.07	3.32
1.00	3.00	.06	3.00	1.20	4.00	.07	3.31
1.10	3.54	.10	3.42	1.00	3.54	.09	3.46
1.00	3.54	.14	3.32	1.00	3.60	.10	3.46
1.00	3.60	.15	3.33	0.85	3.40	.04	3.52
1.00	3.80	.28	3.32	.80	3.54	.52	3.48
1.00	3.90	.37	3.60	.50	3.54	.86	3.48
1.00	4.10	.43	3.52	.50	3.73	1.01	3.52
0.52	2.10	.55	3.60	.50	4.00	1.50	3.50
0.50	2.20	.66	3.50	.50	4.50	1.70	3.48
0.50	2.70	.93	3.50				
				.50	5.50	2.21	4.40
0.50	5.00	1.23	6.00	.70	12.00	2.22	8.72
	Temp. 99°				Temp. 99° Cont.		
1.00	1.00	0.006	1.09	1.00	3.54	.30	3.51
1.00	1.18	.006	1.45	1.00	3.60	.34	3.53
1.00	1.20	.006	1.46	0.80	2.77	.47	3.50
1.10	1.50	.006	1.50	0.80	3.54	.80	3.40
				1.00	5.00	1.50	3.53
1.10	2.00	.006	1.70	1.00	10.00	5.60	3.53
1.00	1.50	.007	1.70				
1.00	1.80	.008	1.75	0.50	20.00	9.00	6.60
1.00	2.00	.08	1.91				
1.20	3.60	.08	2.38				

concentration of arsenic trioxide in solution is 0.06 g. per 100 cc. at 25° (it would be 0.07 at 50° and 0.078 at 99°) or greater, calcium meta-arsenite, $Ca(AsO_2)_2$, is formed. On the other hand, when the concentration of arsenic trioxide in solution is less than 0.06 g. per 100 cc., basic calcium meta-arsenite, $Ca(OH)AsO_2$, results. This is clearly shown in Fig. 1. The first vertical part of the curve represents the solubility of the basic calcium meta-arsenite when excess calcium hydroxide is in the solid phase. As more arsenic trioxide is added to the solution the free calcium hydroxide disappears and we pass along the horizontal portion of the curve until the concentration of the arsenic trioxide becomes 0.06 g. per 100 cc. At this point calcium meta-arsenite begins forming. The second vertical portion of the curve represents a mixture of calcium meta-arsenite and basic calcium meta-arsenite, the meta-arsenite increasing in amount as the vertical part of the curve is ascended. The second horizontal portion of the curve represents the formation of the meta-arsenite with increasing amounts of uncombined arsenic trioxide in solution. The third vertical sections of the curves represent saturated solutions of arsenic trioxide in water at that temperature and the points where free arsenic trioxide begins to appear in the solid phase.

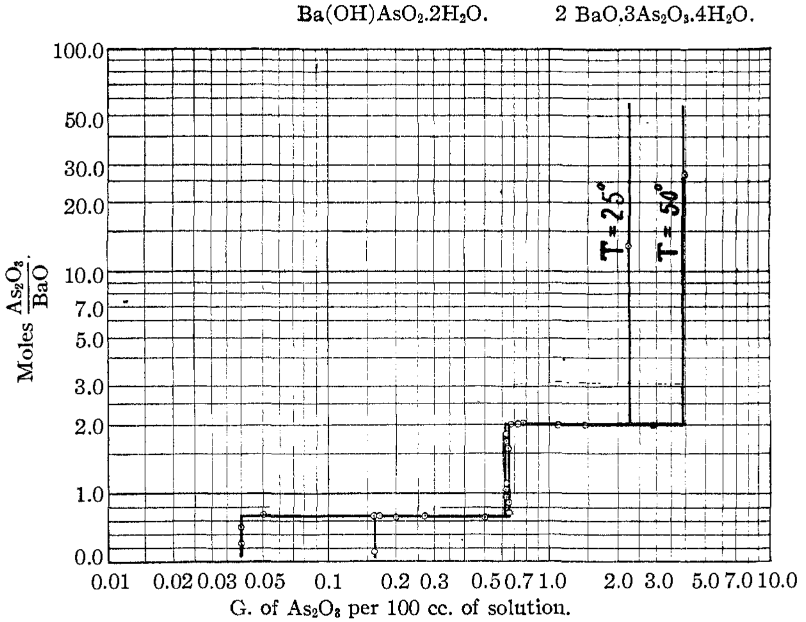

Fig. 2.—Curves for the system, BaO-As_2O_3-H_2O.

The System, Barium Oxide-Arsenic Trioxide-Water

Some difficulty was met in obtaining accurate data in this case but the results finally obtained, Table II and Fig. 2, prove that when mixtures of barium hydroxide and arsenic trioxide are shaken in water at the temperatures 25° and 50°, two arsenites may result, depending on the concentrations of arsenic trioxide in solution. Since the same compounds were formed at both temperatures, no experiments were made at other temperatures. An examination of Fig. 2 shows the presence of three vertical sections and two horizontal sections. The first vertical section represents the concentration of arsenic trioxide in solution when an excess of barium hydroxide is in the solid phase. As the concentration of arsenic trioxide is increased, the barium hydroxide disappears and leaves only hydrated basic barium meta-arsenite, $Ba(OH)AsO_2.2H_2O$, in the solid phase. When the concentration of arsenic trioxide reaches 0.6 g. per 100 cc. of solution, hydrated barium meta-arsenite, $2BaO.3As_2O_3.4H_2O$, begins to form. On increasing the concentration of arsenic trioxide, the basic arsenite disappears and we pass along the horizontal portion of the curve until the region of saturated solutions of arsenic trioxide in the presence of the meta-arsenite is reached.

TABLE II

DATA FOR THE SYSTEM, BARIUM OXIDE-ARSENIC TRIOXIDE-WATER

Total volume, approximately 200 cc.

Ratio moles $\frac{As_2O_3}{BaO}$ in (1) $Ba(OH)AsO_2.2H_2O$ = 0.64; (2) $2BaO.3As_2O_3.4H_2O$ = 1.94

BaO used G.	As_2O_3 used G.	As_2O_3 per 100 cc. of solution G.	Moles $\frac{As_2O_3}{BaO}$ in solid	BaO used G.	As_2O_3 used G.	As_2O_3 per 100 cc. of solution G.	Moles $\frac{As_2O_3}{BaO}$ in solid
	Temp. 25°				Temp. 50°		
19.20	4.00	0.04	0.29	19.20	1.00	0.16	0.168
13.44	4.00	.04	.53				
				19.20	4.00	.16	.66
9.60	4.00	.05	.70	13.44	4.00	.17	.64
5.76	4.00	.50	.64	9.60	4.00	.20	.62
				6.70	4.00	.27	.67
2.40	1.50	.63	.96				
4.80	4.00	.63	1.06	5.76	4.00	.67	.74
3.84	4.00	.63	1.12	4.80	4.00	.66	.82
1.44	2.00	.63	1.72	3.84	4.00	.65	1.10
3.84	6.00	.63	1.82	3.84	6.00	.66	1.66
0.96	2.00	.73	2.00				
3.84	8.00	.75	2.08				
0.67	3.00	1.15	2.00				
0.96	4.00	1.45	2.01				
6.68	10.00	2.30	13.17				

The System, Lead Oxide-Arsenic Trioxide-Water

Lead hydroxide was prepared by precipitating a weighed amount of lead nitrate with ammonium hydroxide. The precipitate was washed repeatedly by decantation and treated with arsenic trioxide as described above. The data obtained, Table III and Fig. 3, prove conclusively that when an excess of arsenic trioxide is used, lead meta-arsenite, $Pb(AsO_2)_2$, is formed. There are indications that basic lead arsenite is also formed when an excess of lead hydroxide is used, although because of experimental difficulties this latter was not obtained in a form suitable for analysis.

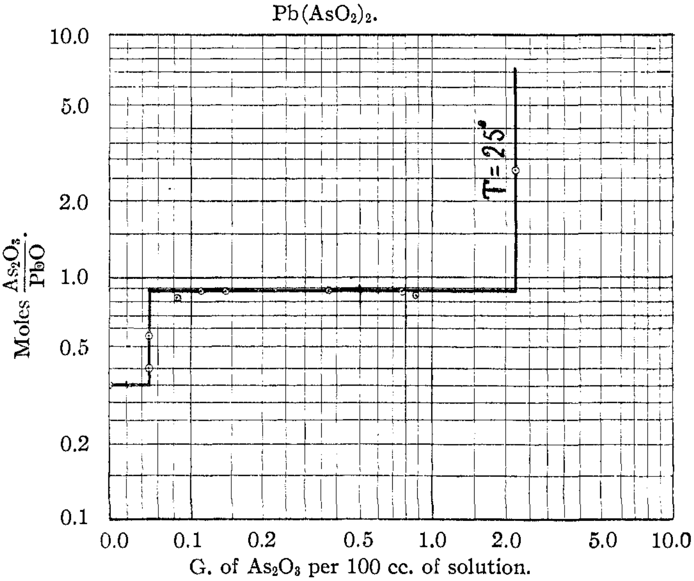

Fig. 3.—Curve for the system, $PbO-As_2O_3-H_2O$ at 25°.

TABLE III

DATA FOR THE SYSTEM, LEAD OXIDE-ARSENIC TRIOXIDE-WATER

Total volume, approximately 200 cc.

Ratio, moles $\frac{As_2O_3}{PbO}$ in $Pb(AsO_2)_2$ = 0.89

$Pb(OH)_2$ used G.	As_2O_3 used G.	As_2O_3 per 100 cc. solution G.	Moles $\frac{As_2O_3}{PbO}$
	Temp. 25°		
1.40	0.430	0.002	0.35
1.40	.602	.049	.40
1.40	.774	.048	.56
1.40	1.29	.088	.83
1.40	2.58	.770	.89
1.40	1.72	.329	.89
1.40	1.03	.140	.89
1.40	3.44	1.120	.89
1.40	6.00	2.200	2.64

The System, Magnesium Oxide-Arsenic Trioxide-Water

In this case freshly precipitated magnesium hydroxide was prepared by mixing water solutions containing equivalent amounts of potassium hydroxide and magnesium sulfate. The precipitated magnesium hydroxide was washed repeatedly by decantation before mixing with arsenic trioxide. Preliminary determinations showed that 1 g. of magnesium hydroxide removed approximately 0.12 g. of arsenic trioxide from aqueous solution of the latter, irrespective of the concentration. Since this amount was too small for the formation of any arsenite, the general method of procedure was varied in this case.

An accurately determined amount of the gelatinous magnesium hydroxide, 1.035 g., was mixed with 200 cc. of water in which various amounts of arsenic trioxide, accurately weighed, had been previously dissolved. The mixture was shaken until analysis showed that equilibrium had been reached. The arsenic trioxide remaining in solution was determined and that adsorbed by the magnesium hydroxide calculated. The data, Table IV, show that 1.035 g. of magnesium hydroxide adsorbs approximately 0.12 g. of arsenic trioxide from aqueous solutions of the latter, irrespective of the concentration.

TABLE IV

DATA FOR THE SYSTEM, MAGNESIUM OXIDE-ARSENIC TRIOXIDE-WATER

Total volume, approximately 200 cc.

$Mg(OH)_2$ used G.	Dissolved As_2O_3 used G.	As_2O_3 remaining in solution G.	As_2O_3 absorbed by 1.035 g. $Mg(OH)_2$ G.
1.035	0.066.	0.014	0.052
1.035	.133	.045	.088
1.035	.199	.095	.104
1.035	.266	.153	.113
1.035	.332	.210	.122
1.035	.664	.540	.124
1.035	1.328	1.200	.128
1.035	1.992	1.864	.128
1.035	3.968	3.840	.128

Summary

The systems, calcium oxide-arsenic trioxide-water, barium oxide-arsenic trioxide-water, plumbous oxide-arsenic trioxide-water and magnesium oxide-arsenic trioxide-water have been studied. In the first three systems definite arsenites were obtained with the following formulas: $Ca(OH)AsO_2$; $Ca(AsO_2)_2$; $Ba(OH)AsO_2.2H_2O$; $2BaO.3As_2O_3{:}4H_2O$ and $Pb(AsO_2)_2$. In the last system no arsenite was formed but an adsorption of the arsenic trioxide by the magnesium hydroxide resulted.

This work is being continued with other metallic hydroxides.

LINCOLN, NEBRASKA