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Sodium Arsenites: The System Na_2O–As_2O_3–H_2O at 35°*

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In the past few years sodium arsenite has been used in large quantities in the control of harmful insects. For the years 1938–39–40 Federal and State agencies used annually 1,442,000 gallons of sodium arsenite solution (equivalent to 6,885,000 pounds of dry sodium arsenite) for the control of grasshoppers and white-fringed beetles, and 352,000 pounds of sodium arsenite powder against Mormon crickets—a total of well over 7.25 million pounds for these insects alone.

During the examination of some samples of commercial sodium arsenites used as insecticides, the writer made observations that appeared to be inconsistent with the data obtained by Schreinemakers and De Baat[1] in their phase investigation of the system comprising sodium hydroxide–arsenious oxide–water. He found, for example, that the commercial products analyzed 82 to 85% As_2O_3 and dissolved readily in water. According to Schreinemakers and De Baat's phase diagram such a product would be a mixture of the meta-sodium arsenite ($Na_2O·As_2O_3$) and white arsenic (As_2O_3), from which the white arsenic should dissolve with difficulty. Because of the economic importance of this product, and the incomplete knowledge of its chemistry, a new phase investigation of the system Na_2O–As_2O_3–H_2O was undertaken.

Procedure

The experimental procedure was essentially the same as that used by Nelson and Haring[2] in their phase study of calcium arsenates. In each of a number of 3- or 4-oz. bottles was placed 25 cc. of sodium hydroxide solution of successively decreased concentrations followed by white arsenic in such quantities as to produce at 35° sufficient precipitate for analysis. The mixtures were heated on the steam-bath to effect greater solution, and then cooled and placed in a revolving rack kept at 35 ± 0.1° in a constant-temperature bath until equilibrium was established. Samples were withdrawn at different intervals of time and analyzed to ascertain when no further change in composition was taking place. After this had been done, the bottles were left on the revolving rack for long periods to leave no doubt that equilibrium conditions had been attained. The contents of the bottles were suction-filtered through fritted-glass filters at 35°, and both the liquid and solid phases were immediately analyzed. Sodium oxide was determined by titration with 0.1 *N* hydrochloric acid.

TABLE I

EXPERIMENTAL RESULTS FOR THE SYSTEM Na_2O–As_2O_3–H_2O AT 35°

	Liquid phase, %		Wet residue, %		
Expt.	As_2O_3	Na_2O	As_2O_3	Na_2O	Solid phase
1	6.3	42.0	3.6	47.3	$NaOH·H_2O$
2	6.3	41.5	23.9	40.4	$2Na_2O·As_2O_3$
3	5.7	41.0	29.7	39.9	
4	9.2	38.4	26.4	38.6	
5	9.8	38.4	30.5	38.4	
6	11.6	36.4	37.7	37.6	
7	12.8	35.8	39.5	37.2	
8	15.4	34.9	37.6	36.8	
9	16.3	34.4	40.1	36.5	
10	20.0	33.4	43.4	36.2	
11	19.5	32.6	30.8	30.1	$2Na_2O·As_2O_3·7H_2O$
12	17.9	31.0	35.3	28.7	
13	18.0	28.9	36.0	28.1	
14	18.8	28.2	34.4	27.9	
15	20.2	26.1	31.8	26.8	
16	22.8	24.9	36.9	26.6	
17	25.5	24.0	37.2	26.5	
18	26.3	24.1	35.8	26.0	
19	29.4	23.2	37.1	25.5	
20	34.5	23.1	65.0	23.6	$Na_2O·As_2O_3$
21	34.4	22.5	72.8	23.8	
22	36.2	20.2	69.6	23.2	
23	37.3	18.5	64.3	22.4	
24	39.6	16.9	67.7	22.5	
25	45.8	15.2	69.0	21.9	
26	48.9	14.7	74.2	23.1	
27	54.2	13.9	71.6	21.9	
28	58.0	13.7	72.9	22.0	
29	58.7	13.5	81.2	10.6	$Na_2O·3As_2O_3$
30	55.2	12.8	73.2	11.0	
31	53.1	12.2	71.6	10.9	
32	52.1	11.2	78.5	9.9	
33	50.3	11.0	75.2	9.9	
34	48.2	10.2	75.4	9.7	
35	47.1	9.1	79.0	9.1	
36	45.3	7.6	76.2	4.9	$Na_2O·3As_2O_3$ + As_2O_3
37	45.5	7.7	82.0	3.3	
38	44.6	7.5	81.2	2.6	As_2O_3
39	40.1	6.8	73.0	3.2	
40	36.9	6.2	90.0	1.0	
41	32.5	5.4	..	..	
42	31.8	5.4	..	..	
43	23.3	3.9	..	..	
44	19.8	3.3	87.7	0.6	
45	18.2	3.0	..	..	
46	14.9	2.5	..	..	

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(1) F. A. H. Schreinemakers and W. C. De Baat, *Chem. Weekbl.*, **14**, 262, 288 (1917).

(2) O. A. Nelson and M. M. Haring, THIS JOURNAL, **59**, 2216 (1937).

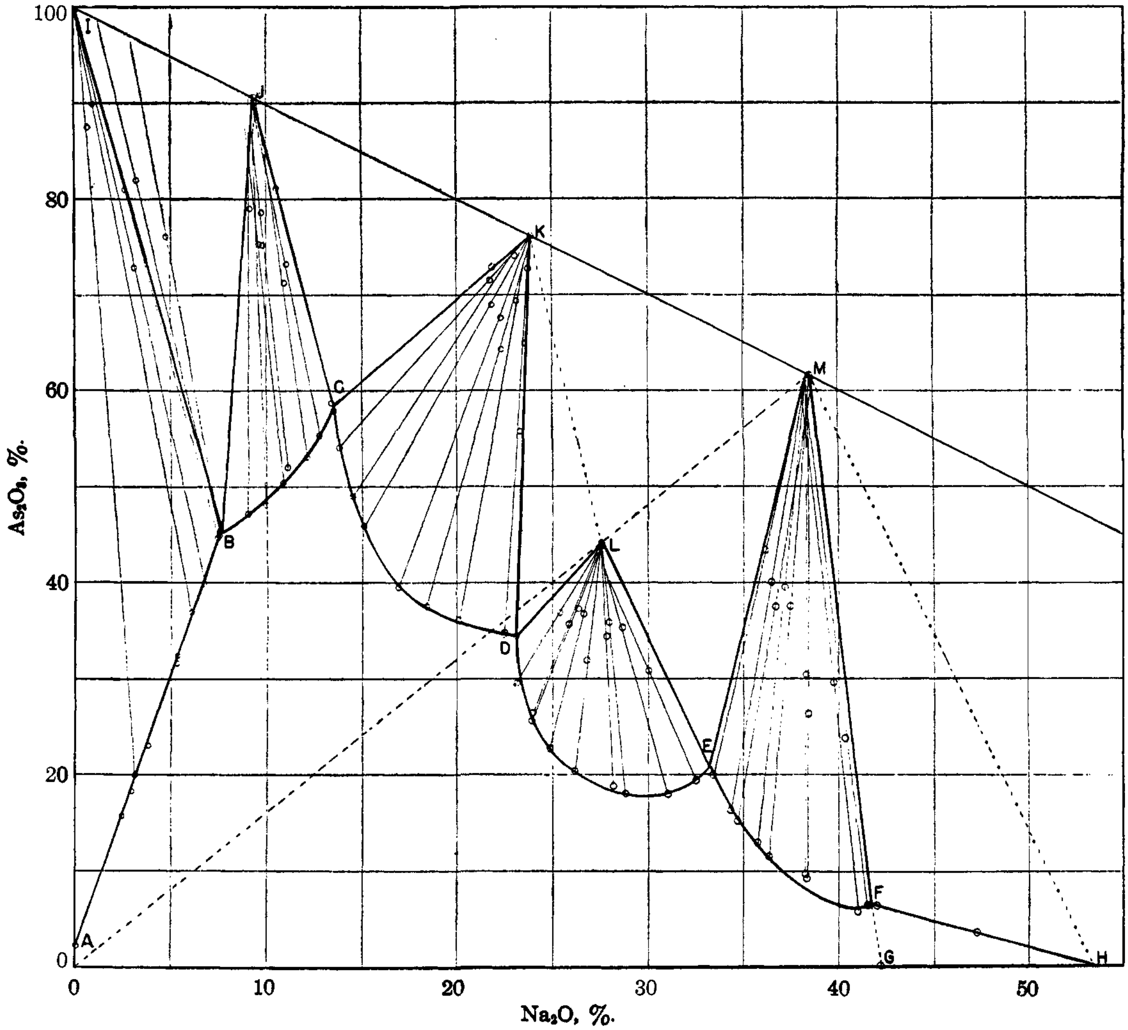

Fig. 1.—Experimental data for the system $Na_2O-As_2O_3-H_2O$ at 35°.

using methyl orange indicator, and the arsenious acid by iodimetry, using 0.05 *N* iodine solution.

Experimental Data.—The experimental data obtained are listed in Table I, and shown graphically in Fig. 1.

Discussion of Results

The region A-B-C-D-E-F-G-A represents a region of solution, and the points I to H represent different chemical compounds, as follows

I = As_2O_3
J = $Na_2O \cdot 3As_2O_3$
K = $Na_2O \cdot As_2O_3$
L = $2Na_2O \cdot As_2O_3 \cdot 7H_2O$
M = $2Na_2O \cdot As_2O_3$
H = $NaOH \cdot H_2O$

A-B is the solubility curve of As_2O_3 in sodium hydroxide solution, and the region A-B-I-A contains solid As_2O_3 and solutions of As_2O_3 and Na_2O. Point B represents the maximum solubility of As_2O_3 in a caustic solution and was established at 45.4% As_2O_3 and 7.65% Na_2O. Points C to F represent solutions of the following percentage composition:

Solution	As_2O_3, %	Na_2O, %
C	58.9	13.6
D	34.3	23.1
E	20.6	33.2
F	6.5	41.7

G = solubility of Na_2O in H_2O at 35° = 42.8 per cent.[3]

The other regions represent the following phases:

Region	Phases represented
B-I-J-B	I, J, and B
B-J-C-B	J and solution
C-J-K-C	J, K, and C
C-K-D-C	K and solution
D-K-L-D	K, L, and D

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[3] This figure is derived from data taken from "International Critical Tables," Vol. 4, p. 236.

Region	Phases represented
K–L–M	K, L, M
D–L–E–D	L and solution
E–L–M–E	L, M, and E
E–M–F–E	M and solution
F–M–H–F	M, H, and F
F–H–G–F	H and solution

Similarly, B–C is the solubility curve of compound J, C–D of compound K, D–E of compound L, E–F of compound M, and F–G of compound H.

The only other investigation into the system Na_2O–As_2O_3–H_2O of which the author is aware was carried out by Schreinemakers and De Baat.[1] Their work was done at 25°, and a comparison of their results with those obtained in this investigation is of interest. Of the six chemical compounds indicated in Fig. 1, $Na_2O\cdot 3As_2O_3$ (J) and $2Na_2O\cdot As_2O_3\cdot 7H_2O$ (L) have not been isolated in previous investigations. It was somewhat surprising that Schreinemakers and De Baat failed to recognize the compound $Na_2O\cdot 3As_2O_3$ in their work, since it is very readily distinguishable from both As_2O_3 and $Na_2O\cdot As_2O_3$. It crystallized readily from a limpid solution and dissolved much more rapidly than did As_2O_3. On the other hand, $Na_2O\cdot As_2O_3$ crystallized from a very viscous or sirupy solution, and dissolved rapidly on addition of water. In no case was a solubility of 73% As_2O_3 in any concentration of sodium hydroxide realized during this investigation, although this was the figure claimed by Schreinemakers and De Baat for the solubility of As_2O_3 in 12% solution.

The compound $2Na_2O\cdot As_2O_3\cdot 7H_2O$ was not obtained by Schreinemakers and De Baat, although they claimed a 9 hydrate. An examination of the numerical data published by these investigators reveals that the evidence for the existence of the compound $2Na_2O\cdot As_2O_3\cdot 9H_2O$ is not very conclusive. Two of the three lines shown by them converge at a point corresponding to the approximate composition of $Na_4As_2O_5\cdot 11H_2O$, while the third points to an 8 hydrate. On the basis of their published data, therefore, the existence of any of the hydrates of $2Na_2O\cdot As_2O_3$ was not proved. These investigators also claimed the existence of a compound corresponding to the formula $5Na_2O\cdot 2As_2O_3\cdot 26H_2O$. In the present investigation there was no indication of such a compound, although numerous attempts were made to obtain it, or another hydrate of it.

From a theoretical point of view it seems impossible that the compound $5Na_2O\cdot 2As_2O_3\cdot 26H_2O$ could form under the conditions shown by these investigations. This formula thus represents a more basic arsenite than the $2Na_2O\cdot As_2O_3$ compound. An anomalous condition therefore presents itself—that of obtaining a more acidic arsenite by adding strong base to a basic compound. That this would be the case is evident from the phase diagram of Schreinemakers and De Baat. According to this diagram the compound $5\ Na_2O\cdot 2As_2O_3\cdot 26H_2O$ crystallized from a solution containing 25% As_2O_3 and 27% Na_2O, but by increasing the concentration of Na_2O to 35% the less basic $2Na_2O\cdot As_2O_3$ was precipitated.

Behavior of Sodium Arsenites on Treatment with Water.—The phase rule requires that for a compound to dissolve congruently a line drawn from the point representing the composition of the compound to the origin (100% water) must cut the solubility curve of that compound. In Fig. 1 it is observed that when water is added to $2Na_2O\cdot As_2O_3$ hydration takes place to give the compound $2Na_2O\cdot As_2O_3\cdot 7H_2O$ (which may be written $2Na_2HAsO_3\cdot 3H_2O$). Upon further addition of water the hydrate loses Na_2O and H_2O to yield $Na_2O\cdot As_2O_3$. This compound dissolves congruently, since a line drawn from the point representing the composition $Na_2O\cdot As_2O_3$ and the origin cuts curve C–D. $Na_2O\cdot 3As_2O_3$ on treatment with water precipitates As_2O_3.

Summary

The three-component system Na_2O–As_2O_3–H_2O has been investigated. The new sodium arsenites were discovered, $Na_2O\cdot 3As_2O_3$ and $2Na_2O\cdot 3As_2O_3\cdot 7H_2O$.

The compound $5Na_2O\cdot 2As_2O_3\cdot 26H_2O$ claimed by Schreinemakers and De Baat was not obtained in these experiments. Reasons are present for the improbability of the existence of such a compound.

The behavior of the different sodium arsenites on treatment with water is discussed.

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