

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, ALABAMA POLYTECHNIC INSTITUTE]

**CONCENTRATION, ACIDS AND LITHIUM SALTS OF ELEMENT 85**

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Evidence of the detection of element 85 by means of the magneto-optic method<sup>1</sup> was announced from this Laboratory.<sup>2</sup> Since that time, concentrations have been made and the studies of the oxidation and reduction reactions greatly extended to include the compounds formed. We suggest the name Alabamine and symbol Am for element 85.

**Concentration.**—The amount of alabamine was very small in all substances examined. Monazite sand (Brazilian) was chosen for the concentration work because of its availability and the ease with which the other substances present can be eliminated. Preliminary experiments which were checked by the magneto-optic method determined the method of procedure.

One hundred pounds of monazite were finely ground in a ball mill, digested with aqua regia and evaporated to dryness on a steam-bath. This was then extracted with water three times; appropriate minima showed that alabamine went into solution as peralabamic acid,  $\text{HAMO}_4$ . The solution was evaporated on a steam-bath and the remaining aqua regia displaced by sulfuric acid. When the volume was reduced to 800 cc., it was saturated with sulfur dioxide, which reduced the peralabamic acid to hydroalabamic acid,  $\text{HAM}$ ; this was shown by the disappearance of minima of the former and the appearance of minima of the latter. The solution was made alkaline with lithium hydroxide, which precipitated out most of the heavy metals present. The filtrate was evaporated to 150 cc. and 600 cc. of alcohol was added to precipitate the lithium sulfate. The solution was filtered; the precipitate was washed with alcohol and the filtrate which contained the lithium alabamide was evaporated to 85 cc. Tests with the magneto-optic method showed that this solution contained approximately  $2.5 \times 10^{-6}$  g. of alabamine as lithium alabamide, which represents a concentration of about 160 times.

**Acids and Lithium Salts of Element 85.**—In order to know where to expect minima for the oxygen compounds of alabamine and to identify what compounds are formed, minima were located for the corresponding hydrogen and lithium compounds of the other halogens. The results are shown in Tables I and II and are represented graphically in Fig. 1 by plotting scale readings against equivalent weights of the anion. These curves include many other oxygen acids and lithium salts in addition to those of the halogens. To change scale readings of the tables and curves

<sup>1</sup> Allison and Murphy, *THIS JOURNAL*, **52**, 3796 (1930).

<sup>2</sup> Allison, Murphy, Bishop and Sommer, *Phys. Rev.*, **37**, 1178 (1931).

TABLE I  
SCALE READINGS OF HALOGEN ACIDS

	HX	HXO	HXO <sub>2</sub>	HXO <sub>3</sub>	HXO <sub>4</sub>	H <sub>2</sub> XO <sub>4</sub>
Cl	15.75	8.25	4.75	2.46	1.86	
	15.85	8.35	4.85	2.55	1.95	
Br	12.95	2.03	1.48	0.89	0.35	
	13.10	2.12	1.59	1.01	0.47	
I	11.90	0.18	-0.05	-0.30	-0.62	9.66
	12.05	0.28	+0.05	-0.19	-0.49	9.76
Am	10.98	-1.64	-1.94	-2.28	-2.60	
	11.10	-1.55	-1.83	-2.17	-2.50	

TABLE II  
SCALE READINGS OF HALOGEN SALTS

	LiX	LiXO	LiXO <sub>2</sub>	LiXO <sub>3</sub>	LiXO <sub>4</sub>	Li <sub>2</sub> XO <sub>4</sub>
Cl	16.22	8.80	5.17	2.85	2.14	
	16.45	8.95	5.28	2.95	2.28	
Br	13.40	2.27	1.82	1.10	0.68	
	13.60	2.38	1.93	1.20	0.78	
I	12.37	0.42	0.23	0.03	-0.36	10.05
	12.58	0.51	0.33	0.14	-0.26	10.16
Am	11.37	-1.33	-1.88	-2.02	-2.19	
	11.61	-1.22	-1.77	-1.90	-2.12	

to differential time lags<sup>1</sup> subtract 15 from the scale reading and multiply the difference by 10<sup>-9</sup> second.

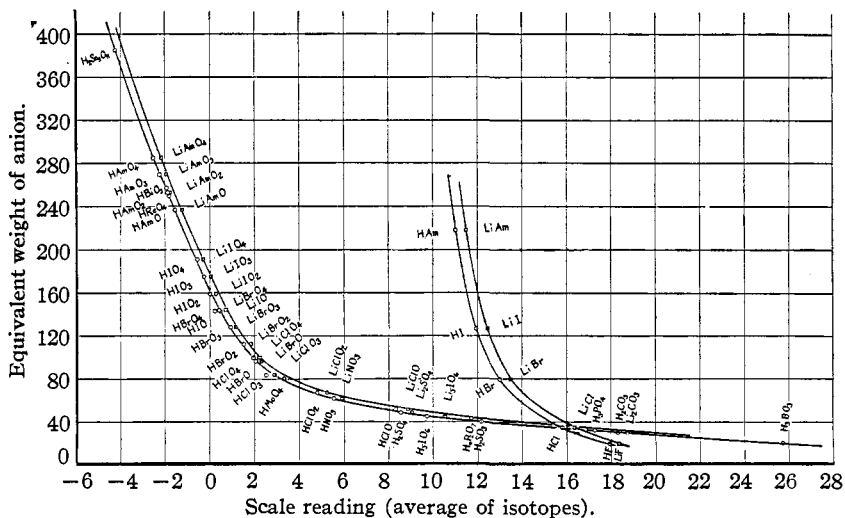


Fig. 1.—Scale readings of light minima as a function of equivalent weight of anion.

**Oxygen Compounds of Chlorine.**—Chlorine gas was passed into cold water and the minima for hypochlorous acid obtained. After stand-

ing for five days, these minima had disappeared and those of chlorous acid were present. Chloric acid minima were obtained from a solution made by passing chlorine through hot water and also checked with a potassium chlorate solution to which sulfuric acid had been added. Perchloric acid minima were read from a Merck commercial preparation.

Lithium hypochlorite, chlorite and chlorate were obtained by passing chlorine through a hot lithium hydroxide solution. Lithium perchlorate was prepared by adding an excess of lithium hydroxide to perchloric acid.

**Oxygen Compounds of Bromine.**—Bromine was added to water to give hypobromous acid and to lithium hydroxide to give lithium hypobromite. Bromous acid was prepared<sup>3</sup> by adding excess bromine water to silver nitrate solution, extracting the bromine with carbon disulfide and filtering. Lithium hydroxide was added to give lithium bromite. Bromic acid minima were obtained by adding sulfuric acid to potassium bromate.

Kämmerer<sup>4</sup> reported obtaining perbromic acid and chlorine gas by treating bromine with dilute perchloric acid. Other workers have generally failed to confirm his work.<sup>5</sup> The appearance of minima in the expected place substantiates his claim. The compound, however, is short lived. Perchloric acid was added to lithium hypobromite. The hypobromite and bromite minima disappeared. Bromate minima were present and two pairs appropriate to lithium perbromate and perbromic acid. These were gone after standing for twenty-four hours but were brought back by adding more perchloric acid. (These minima were not present in perchloric acid.) When the solution was made alkaline to litmus, the minima attributed to perbromic acid disappeared.

**Oxygen Compounds of Iodine.**—Iodine was added to water and two pairs of minima were obtained 0.18 and 0.28,  $-0.30$  and  $-0.19$ . Potassium biiodate was dissolved in water and only the latter pair obtained, which were therefore attributed to iodic acid and the former to hypoiodic acid. On the addition of perchloric acid to the iodine in water solution, hypoiodous acid disappeared, iodic acid persisted and minima appropriate to  $\text{HIO}_4$  and  $\text{H}_5\text{IO}_6$  were obtained. (Other periodic acids were not looked for.) Work was interrupted for twenty days. The tube which contained undissolved iodine crystals had acquired a deep color and had to be diluted to let sufficient light through to make readings.  $\text{H}_5\text{IO}_6$  minima were absent;  $\text{HIO}_4$ ,  $\text{HIO}_3$ ,  $\text{HIO}$  and two new minima at 0.05 and  $-0.05$  which must be those of  $\text{HIO}_2$  were present. Twenty-four hours later, only  $\text{HIO}_2$  and  $\text{HIO}$  were present and both persisted for another twenty-four hours. Lithium hydroxide was added and lithium iodite minima were obtained.

<sup>3</sup> Richards, *J. Soc. Chem. Ind.*, **25**, 4 (1906).

<sup>4</sup> Kämmerer, *J. prakt. Chem.*, **90**, 190 (1863).

<sup>5</sup> Muir, *J. Chem. Soc.*, ii, 469 (1876); Wolfram, *Ann.*, **195**, 95 (1879); MacIvor, *Chem. News*, **33**, 35 (1876); **55**, 203 (1887); Robertson, *ibid.*, **106**, 50 (1912).

Iodine added to lithium hydroxide gave minima appropriate to lithium hypiodite and lithium iodate. The latter was checked by adding lithium hydroxide to potassium biiodate. Perchloric acid was added to the iodine in lithium hydroxide solution, keeping it alkaline to litmus. Minima for  $\text{LiIO}$ ,  $\text{LiIO}_3$ ,  $\text{LiIO}_4$  and  $\text{Li}_5\text{IO}_6$  were obtained. After standing for twenty days this solution gave minima for  $\text{Li}_5\text{IO}_6$  and  $\text{LiIO}_4$  only.

**Oxygen Compounds of Alabamine.**—An iodine crystal was added to lithium alabamide solution which was neutral to litmus. The minima of lithium alabamide disappeared and those attributed to lithium hypoalabamite appeared. Later these disappeared and only those appropriate to lithium alabamite were present, while still later only those of lithium peralabamate were obtained.

When iodine was added to hydroalabamic acid, minima appropriate to all four oxygen acids were obtained. After standing, only peralabamic acid remained.

Bromine added to lithium alabamide gave minima of lithium hypoalabamite and alabamate immediately and only peralabamate after standing.

Perchloric acid was added to lithium alabamide in the presence of excess lithium hydroxide. Lithium hypoalabamite, alabamite and alabamate appeared at once and peralabamate in about ten minutes. The lower oxidation products disappeared on standing, leaving only peralabamate.

### Discussion of Results

As would be expected alabamine is easily oxidized in either acid or alkaline solution. The rate of oxidation, however, is greater in acid solution. Peralabamate is the most stable form, even as weak an oxidizing agent as iodine oxidizing alabamides all the way to peralabamates. Perhalates show a steady increase in stability from perbromates through peralabamates, with the stability of perchlorates standing out as the exception. Much more work is needed to establish the mechanism and intermediate products of these reactions. The magneto-optic method lends itself beautifully to such a study.

Examination of Table I and Fig. 1 shows a difference of 0.30, 0.34 and 0.32 between successive alabamine oxygen acids. Perrhenic acid (minima at  $-1.89$  and  $-1.78$ ) is 0.05 greater than alabamous acid. Since perrhenate ion has an equivalent weight of 250.3, we estimate alabamite at 253 and a probable atomic weight of 221 for alabamine. To check this value minima for bismuthic acid (equivalent weight of anion 257) were looked for and found at  $-2.01$  and  $-1.90$ . That is, alabamous acid is five-twelfths of the way between perrhenic and bismuthic acids, which agrees with the above estimate.

We wish to express our thanks to Mr. J. H. Christensen and Mr. George V. Waldo for plotting the curves.

### Summary

The name alabamine and symbol Am have been suggested for element 85.

A concentrate containing  $2.5 \times 10^{-6}$  g. of alabamine in the form of lithium alabamide has been prepared.

Minima have been determined for the oxygen halogen compounds.

Alabamides are easily oxidized forming hypoalabamites, alabamites, alabamates and peralabamates and their corresponding acids. Peralabamates are the most stable of these compounds.

The atomic weight of alabamine is estimated at 221.

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### NOTES

**Iodine Monochloride in Hydrochloric Acid Solution.**—Recently<sup>1</sup> the contention has been made that iodine monochloride in aqueous solutions exists as  $I^+$  and  $Cl^-$  because iodine is more soluble in hydrochloric acid containing iodine monochloride than in the pure acid. This difference might be attributed to the increased similarity between solvent and solute, although Philbrick's view is in agreement with Abel and Halla's<sup>2</sup> interpretation of Sullivan's<sup>3</sup> potential observations. However, Forbes, Glass and Fuoss<sup>4</sup> have already pointed out the difficulties of reconciling such ionization with a mathematical analysis of titration curves in these solutions, and concluded that the ion  $ICl_2^-$  must predominate, in agreement with Schützenberger.<sup>5</sup> Philbrick fails to recognize that slow hydrolysis of iodine monochloride in aqueous salt solutions, rather than ionization, better explains the slowly increasing conductance and freezing point depression observed by Sullivan<sup>3</sup> in freshly prepared solutions.

We have subjected these opposing views to crucial experiments. The specific conductance of an approximately one normal solution of hydrochloric acid was measured at 25° in an oil-thermostated cell, using the accurate bridge of Grinnell Jones, and found to be 0.32405 mho per cm. On adding iodine monochloride to make the solution 0.14 molal in respect to  $ICl$ , the specific conductance decreased to 0.32229 mho. This experiment proves conclusively that iodine monochloride cannot exist appreciably in the ionized state in this solution.

A transference experiment was devised to observe the direction of

<sup>1</sup> Philbrick, *J. Chem. Soc.*, 2254 (1930).

<sup>2</sup> Abegg, "Handbuch der anorganischen Chemie," 1913, IV<sup>2</sup>, p. 472.

<sup>3</sup> Sullivan, *Z. physik. Chem.*, **28**, 523 (1899).

<sup>4</sup> Forbes, Glass and Fuoss, *THIS JOURNAL*, **47**, 2892 (1925); Forbes and Fuoss, *ibid.*, **49**, 142 (1927).

<sup>5</sup> Schützenberger, *Compt. rend.*, **84**, 389 (1877).