

Summary

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

A concentrate containing 2.5×10^{-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.

AUBURN, ALABAMA

NOTES

Iodine Monochloride in Hydrochloric Acid Solution.—Recently¹ 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's² interpretation of Sullivan's³ potential observations. However, Forbes, Glass and Fuoss⁴ 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.⁵ 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 Sullivan³ 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

¹ Philbrick, *J. Chem. Soc.*, 2254 (1930).

² Abegg, "Handbuch der anorganischen Chemie," 1913, IV², p. 472.

³ Sullivan, *Z. physik. Chem.*, **28**, 523 (1899).

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

⁵ Schützenberger, *Compt. rend.*, **84**, 389 (1877).

migration of the iodine during electrolysis. If iodine occurs as I^+ it should migrate to the cathode; if it occurs as ICl_2^- it should migrate to the anode. A solution 4 *N* in hydrochloric acid and 1.6 *m* in iodine monochloride was introduced in the apparatus shown in the figure. The beakers surrounding the stopcocks contained pure hydrochloric acid. After passing 15 milliamperes through the closed stopcocks for several hours, the anode beaker, B_1 , had a strong yellow color, while the cathode beaker, B_2 , was colorless. Portions from both beakers were reduced with sodium bisulfite and tested for iodine with starch and chlorine water. Iodine in large amount was invariably found in the anode beaker. The test on the cathode beaker showed no trace of iodine. To show that this was not due to leakage of ICl into the anode beaker, we used fresh acid and reversed the current; again iodine was found in the anode beaker and none in the cathode beaker.

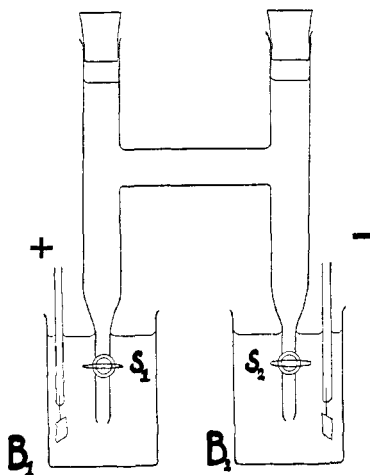


Fig. 1.

We believe that these experiments furnish strong additional evidence that the ion I^+ is present in negligible concentration, if at all, and that iodine monochloride forms extensively a negative complex ion with chloride ion.

CONTRIBUTION FROM THE
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CAMBRIDGE, MASSACHUSETTS
RECEIVED AUGUST 17, 1931
PUBLISHED FEBRUARY 5, 1932

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The Preparation of Germanium Tetrabromide and Germanium Tetraiodide

Germanium Tetrabromide.—The only method which has been described for preparing germanium tetrabromide involves the action of bromine vapor on heated metallic germanium.¹ This procedure is laborious since it requires the preliminary preparation of elementary germanium. By modifying the method which Tabern, Orndorff and Dennis² used for the preparation of germanium tetrachloride it was found possible to obtain germanium tetrabromide directly from germanium dioxide and hydrobromic acid.

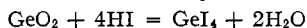
¹ Dennis and Hance, *THIS JOURNAL*, **44**, 299–307 (1922).

² Tabern, Orndorff and Dennis, *ibid.*, **47**, 2039 (1925).

Twenty-five grams of germanium dioxide was suspended in 250 cc. of 48% hydrobromic acid. The mixture was heated to a temperature somewhat short of the boiling point of the hydrobromic acid, and hydrogen bromide, prepared by the method given by Biltz³ from bromine, red phosphorus and water, was passed into the solution until the acid concentration was built up to that of the constant boiling mixture. The reaction by this time had gone almost to completion and it was finished by refluxing for a short time. It is easy to tell when a sufficient amount of hydrogen bromide has been passed into the flask, since up to that point germanium tetrabromide and water (or possibly a dilute acid solution) condense together in the reflux condenser, and the germanium tetrabromide is hydrolyzed to germanium dioxide, which deposits on the condenser tube. As soon as sufficient acidity is reached in the flask, the condensate becomes acid enough to dissolve the germanium dioxide which has been formed in the condenser. When the reaction was complete, as shown by the disappearance of practically all of the germanium dioxide in the reaction mixture and the appearance of two liquid layers in the flask, the mixture was cooled, and the tetrabromide, the lower layer, was separated by means of a separatory funnel. The crude product was separated from traces of unchanged germanium dioxide by distillation. As much as possible of the hydrobromic acid still contained in the distillate was removed by holding the liquid at 26° (the freezing point of germanium tetrabromide), and evacuating the container by means of a water pump which was connected through a drying tube. The final removal of hydrogen bromide was effected by allowing the liquid to stand over solid anhydrous sodium carbonate. The germanium tetrabromide was then redistilled and the middle fraction was found to have the proper boiling point as given by Dennis and Hance.¹ The yield of purified product was approximately 90%.

Germanium Tetraiodide.—As in the case of germanium tetrabromide, germanium tetraiodide had been prepared only by the action of the halogen on metallic germanium, a tedious procedure. Since it had been found that the tetrabromide could be prepared with ease by the action of hydrobromic acid on a suspension of the dioxide, it seemed probable that a similar direct procedure could be used for making the tetraiodide.

Twenty-five grams of germanium dioxide was placed in a flask with 250 cc. of 57% hydriodic acid (constant boiling) and the flask was fitted with a distilling column connected with a condenser. The mixture was heated by means of an oil-bath, the temperature of which was not permitted to rise above 160°. Water was formed by the reaction



but by the use of the distilling column it was possible to remove water and

³ Biltz, "Laboratory Methods of Inorganic Chemistry," translated by Hall and Blanchard, John Wiley and Sons, Inc., New York, 1928, p. 71.

keep the solution acid enough so that the reaction went in large measure to completion. As the reaction proceeded red crystals of germanium tetraiodide collected in the bottom of the flask. The tetraiodide was removed from the cold reaction mixture by filtering on a Büchner funnel and was dried in the air on a porous plate. Some unchanged germanium dioxide contaminating the tetraiodide was removed by treating the crude product with boiling carbon tetrachloride, filtering the hot solution, and crystallizing the tetraiodide from the filtrate. The yields of two separate experiments were 80 and 85% and it seems probable that stirring would increase these since the germanium tetraiodide tends to form a protective layer around the unchanged germanium dioxide.

The purified material had a melting point of 146° , the determination being made on the electric bar described by Dennis and Shelton.⁴ This agrees well with the value 144° obtained by Dennis and Hance¹ using the older capillary tube method. Analyses for germanium showed that the sample was pure.

⁴ Dennis and Shelton, *THIS JOURNAL*, **52**, 3128 (1930).

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RECEIVED SEPTEMBER 26, 1931
PUBLISHED FEBRUARY 5, 1932

Note on Some Periodical Properties of Atomic Nuclei.—In a recent paper Latimer¹ has described an interesting model of the nucleus of an atom consisting of a number of tetrahedra. Each of them, representing an α -particle, is built of four protons located at the corners and two electrons located in the center.

Taking such tetrahedra as elements it is easy to build larger tetrahedra consisting each of 4, 10, 20, 35 and 54 elements. The numbers of protons in such nuclei will be as follows: 16, 40, 80, 140 and 216.

If we assume, now, that atomic nuclei having analogous geometrical forms must have also analogous physical properties, we must expect some periodic regularities in the system of atomic nuclei arranged according to their weight. It is possible to prove this in the following ways.

(1) Representing the number of additional nuclear electrons in a nucleus built from α -particles as a function of the atomic weight N and taking mean values for each N , we obtain a periodic curve, the periods corresponding well to the above-mentioned law (Fig. 1).²

(2) Representing the numbers of isotopes Q as a function of N , we obtain

¹ Wendell M. Latimer, *THIS JOURNAL*, **53**, 981 (1931).

² R. A. Sonder, *Z. allgem. anorg. Chem.*, **192**, Heft 3 (1930).

also the same periodicity (Fig. 2), here are given mean values for an interval of ten values of N .³

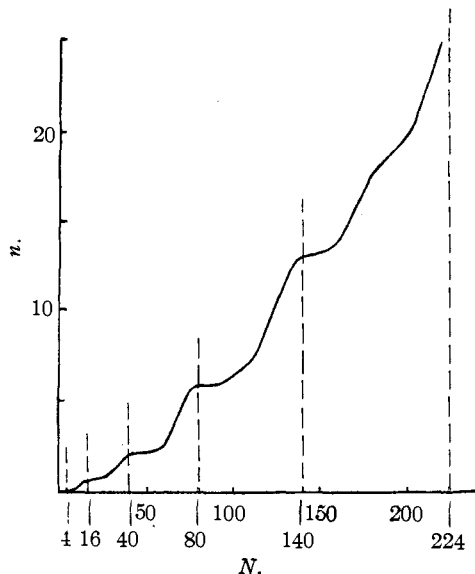


Fig. 1.—The relation between the additional electrons n and the atomic weight N .

(3) Taking the logarithms of relative numbers of elements with even and with odd numbers of electrons as a function of N , and representing the

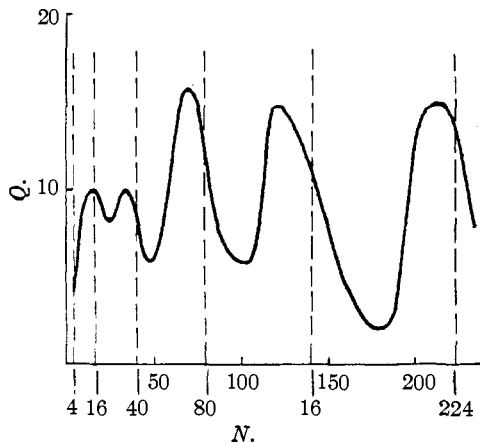


Fig. 2.—The relation between the number of isotopes Q and the atomic weight N .

³ G. I. Pokrowski, *Naturwiss.*, 19, 573 (1931).

differences of these values E for two neighboring elements also as a function of N , or of the atomic number Z , we obtain a curve with the same periodicity (Fig. 3).⁴

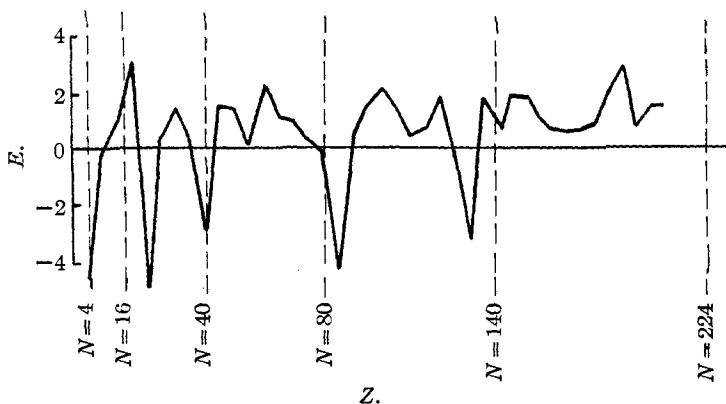


Fig. 3.—The relation between the value of E and the atomic number Z .

Nearly the same periodicity can be deduced theoretically from de Broglie's equation. This possibility will be discussed in another place.

⁴ According to experimental data given by J. and W. Noddak, *Naturwiss.*, **18**, 757 (1930).

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RECEIVED OCTOBER 29, 1931
PUBLISHED FEBRUARY 5, 1932

Molecular Rotation in Solid Sodium Nitrate

It was shown by Kracek and his co-workers,¹ that the gradual transition in sodium nitrate at 275° is accompanied by an important change of the intensities of the diffraction lines in the powder diagrams given by this substance. They conclude "that there is no serious objection to the hypothesis of molecular rotation as an explanation of the gradual transition in sodium nitrate," this conclusion being reached by a qualitative intensity discussion, the quantitative calculation of the rotating model presenting "a most interesting difficulty."

Now the scattering power of a ring model has been calculated by Coster² and by Kolkmeier³ with a view to the possibility of electron binding rings in diamond and by one of us⁴ in testing electronic models of lithium. For the case of sodium nitrate we have now performed the intensity

¹ Kracek, Posnjak and Hendricks, *THIS JOURNAL*, **53**, 3339 (1931).

² Coster, *Verslag. Akad. Wetenschappen Amsterdam*, **28**, 391 (1919).

³ Kolkmeier, *ibid.*, **28**, 767 (1920).

⁴ Bijvoet, *Rec. trav. chim.*, **42**, 874 (1923).

calculation along these lines and reached a fair interpretation of the observed intensities, which offers a strong affirmation of the model proposed.

The calculation of the scattering power of a ring of electrons (atoms) can be made in the following way. All points in the same lattice reflection plane have the same phase. A point at a distance d from this plane has a phase difference of $4\pi d \sin \theta / \lambda$ where θ represents the glancing angle.

Let the angle between the reflecting lattice plane and the plane containing the orbit of the N rotating electrons (atoms) be α and $d\varphi$ an element of the orbit containing $N(d\varphi/2\pi)$ electrons. The distance of this element to the lattice plane is then $\rho \sin \alpha \sin \varphi$ (ρ = radius of the orbit).

The diffracted amplitude is

$$\frac{N}{2\pi} e^{4\pi i d \sin \theta / \lambda} d\varphi$$

Integrating this over the circle we find the amplitude of the ring diffraction (phase compared with rays scattered by a point in the plane, *e. g.*, the center of the orbit)

$$\frac{N}{2\pi} \int_0^{2\pi} e^{4\pi i \rho \sin \alpha \sin \theta \sin \varphi / \lambda} d\varphi = NJ_0 \left(4\pi \frac{\rho}{\lambda} \sin \alpha \sin \theta \right)$$

where $J_0(x)$ represents the Bessel function of the 0th order of the argument (x).

This calculation is based on the very probable supposition that there is no strict phase relation between the rotation in neighboring cells.

In the case of the rotating NO_2 group we substitute $N = 3F(\text{O})$ where $F(\text{O})$ is the atomic scattering factor for oxygenium. The phase is compared with that of the center of the orbit, the nitrogen atom.

We have calculated the intensities in the usual way on the basis of the equation $I = P \frac{1 + \cos^2 2\theta}{\cos \theta \sin^2 \theta} S^2$ with

$$S = \begin{cases} 2F(\text{Na}) + 2F(\text{N}) + 6F(\text{O}) I_0(x) & h + k + l = 4p \\ -2F(\text{Na}) + 2F(\text{N}) + 6F(\text{O}) I_0(x) & h + k + l = 2p \\ 0 & h + k + l \neq 2p \end{cases}$$

Here $I_0(x)$ represents the scattering power of a ring, x being equal to $4\pi (\rho/\lambda) \sin \theta \sin \alpha$; ρ , radius of the ring, and α the angle between reflecting and orbit plane.

The atomic scattering factors were taken according to James and Brindley.⁵ For nitrogen the factor curve for neutral atoms was taken, as N^{+5} was found not to be in accordance with the observed intensities. For oxygenium also the factor for neutral atoms is used, which only slightly differs from that of O^{-2} and only for small diffraction angles.

Now it is the problem to ascertain whether it is possible to fix a value for ρ which gives good agreement between calculated and observed intensities. As the Bessel function has alternating positive and negative values, it is easy to limit this value. From the fact that $32\bar{1}$ is much stronger than the corresponding neighboring reflections, it follows that the value of ρ lies between 1.1 Å. and 1.65 Å. or between 2.4 Å. and 2.9 Å. The latter value

⁵ James and Brindley, *Z. Krist.*, **78**, 470 (1931).

is at once excluded by 211, which is a very strong reflection. The intensities calculated with a radius $\rho = 1.15 \pm 0.05 \text{ \AA}$. are in very good agreement with the observed intensities (last columns, Table I). (In some films traces of reflections are reported exclusively due to oxygenium. This may be caused by uncertainty or unsteadiness of the temperature of the sample, the calculated density also indicating that the temperature of the diffracting layer is lower than that given by Kracek and his co-workers.)

TABLE I

<i>hkl</i>	$\sin \theta$	α	x	$J_0(x)^a$	$1/2\Sigma F(0)$	$1/2\Sigma F(N)$	$1/2\Sigma F(Na)$	$1/2S$	$1/2p$	Cont. fact.	I_1 calcd.	I_1 obs.
110	0.127	62°	1.61	+0.45	19.95	5.4	-8.85	5.55	3	252	2.3	3.2
211	.161	44°	1.62	+0.44	18.0	4.8	+8.7	21.6	3	150	21.0	>10
222	.170	0°	0.00	+1.00	17.55	4.7	-8.6	13.65	1	134	2.5	2.5
1 $\bar{1}$ 0	.197	90°	2.86	-0.21	15.9	4.2	+8.2	9.1	3	100	2.5	3.4
210	.214	66°	2.84	-0.20	0.0	0.0	0.0	0.0	6	80	0.0	<0.5
200	.234	75°	3.26	-0.33	14.4	3.8	-7.7	8.65	3	67	1.5	2.4
220	.254	62°	3.24	-0.33	13.65	3.55	+7.4	6.4	3	60	0.7	7.7
332	.254	25°	1.56	+0.48	13.65	3.55	+7.4	17.5	3	60	5.5	
321	.260	48°	2.78	-0.18	13.5	3.5	-7.3	6.25	6	55	1.3	2.2
2 $\bar{1}$ 0	.302	63°	3.88	-0.40	0.0	0.0	0.0	0.0	3	42	0.0	<0.5
2 $\bar{1}$ 1	.306	47°	3.24	-0.33	11.25	2.95	-6.6	7.35	3	40	0.7	1.2
433	.316	20°	1.56	+0.48	11.1	2.9	-6.45	2.25	3	38	0.0	...
310	.322	78°	4.56	-0.31	10.95	2.85	+6.4	5.85	6	36	0.7	1.1
422	.322	44°	3.25	-0.33	10.95	2.85	+6.4	5.65	3	36	0.4	
432	.323	35°	2.67	-0.13	0.0	0.0	0.0	0.0	6	36	0.0	...
320	.332	64°	4.33	-0.36	0.0	0.0	0.0	0.0	6	33	0.0	<0.5
2 $\bar{1}$ 1	.341	26°	2.16	+0.13	10.35	2.7	+6.1	10.15	3	31	0.9	1.2
444	.341	0°	0.00	+1.00	10.35	2.7	+6.1	19.15	1	31	1.1	
421	.361	56°	4.33	-0.36	0.0	0.0	0.0	0.0	6	28	0.0	...
442	.364	37°	3.16	-0.31	9.7	2.55	-5.75	6.2	3	27	0.3	...
431	.377	53°	4.38	-0.35	9.3	2.45	+5.6	4.8	6	25	0.4	0.5
330	.382	62°	4.88	-0.22	9.15	2.45	-5.5	5.05	3	25	0.2	...
2 $\bar{2}$ 0	.394	90°	5.71	+0.06	8.8	2.35	+5.3	8.15	3	23	0.4	0.5
543	.394	28°	2.69	-0.14	8.8	2.35	+5.3	6.4	6	23	0.6	
3 $\bar{1}$ 0	.408	81°	5.83	+0.10	8.55	2.25	-5.15	2.05	6	22	0.0	...
532	.413	45°	4.24	-0.37	8.3	2.25	-5.1	6.0	6	20	0.4	...
554	.422	15°	1.58	+0.47	8.1	2.2	-4.95	1.05	3	19	0.0	...
32 $\bar{1}$.425	74°	5.88	+0.12	8.1	2.2	+4.95	8.15	6	19	0.8	1.1
420	.428	66°	5.67	+0.05	8.1	2.2	-5.0	2.4	6	16	0.0	...
542	.443	40°	4.12	-0.39	0.0	0.0	0.0	0.0	6	16	0.0	...
2 $\bar{2}$ 2	.466	82°	6.70	+0.29	7.4	2.1	-4.3	0.0	3	16	0.0	...
400	.469	75°	6.40	+0.24	7.2	2.1	+4.3	8.0	3	16	0.3	1.1
521	.469	60°	5.80	+0.09	7.2	2.1	+4.3	6.95	6	16	0.5	

^a Jahnke, "Emde Funktionentafeln."

The calculated radius is somewhat smaller than that expected from the parameter value $1/4$ of the non-rotating oxygenium atoms, which corresponds to a distance of 1.26 \AA . between nitrogen and oxygenium.

From optical data, however, a distance is calculated of 1.15 \AA .⁶ and even of 1.09 \AA .⁷

⁶ Zachariassen cited from V. M. Goldschmidt, *Geochem. V.*, **2**, 66 (1926).

⁷ W. L. Bragg, *Proc. Roy. Soc. (London)*, **A106**, 356 (1924).

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RECEIVED DECEMBER 11, 1931
PUBLISHED FEBRUARY 5, 1932

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

POLYMERIZATION REACTIONS UNDER HIGH PRESSURE. II. THE MECHANISM OF THE REACTION

By J. B. CONANT AND W. R. PETERSON

RECEIVED AUGUST 13, 1931

PUBLISHED FEBRUARY 5, 1932

Unsaturated hydrocarbons and certain aliphatic aldehydes are polymerized at room temperature by the application of very high pressure (3000–12,000 atm.).¹ In the case of isoprene the product is rubber-like; in the case of *n*-butyraldehyde the final polymer is a hard solid which reverts to the original aldehyde on standing at room temperature and atmospheric pressure. The previous work¹ showed that peroxides and ozonides were effective catalysts for both types of polymerization. However, it was concluded that peroxide catalysis was not essential since a sample of isoprene distilled in nitrogen and compressed without exposure to air polymerized at a rate only slightly less than that of material freshly distilled in air. The results of the experiments recorded in this paper have led us to revise this conclusion. We are now strongly inclined to the opinion that peroxide catalysis is essential to the polymerization and the effect of increased pressure is only to accelerate the catalytic reaction.

The evidence that peroxide catalysis is essential to the pressure polymerization of isoprene is as follows. Peroxides and ozonides have a strong positive catalytic action. Freshly distilled isoprene polymerizes at a rate only one-fifth to one-tenth of that of isoprene which has stood in the air for some days. This increased tendency to polymerize on standing is almost certainly due to the formation of peroxides from the dissolved oxygen. If peroxides (or dissolved oxygen which will form a peroxide) are essential to the polymerization, we must assume that when the isoprene was distilled in nitrogen some trace of oxygen or volatile peroxides was in the distillate. We have now strong evidence for this assumption since we have found that by adding hexaphenylethane (which reacts rapidly with oxygen) to isoprene in nitrogen and distilling, the rate of polymeriza-

¹ THIS JOURNAL, **52**, 1659 (1930).