most part appears to be about seventy-five per cent. No titanium dioxide seems to be dissolved by the acid at 100° C. during one hour, but as the temperature rises the solubility increases, and when brought to fumes considerably more than half is dissolved. The variations in the amount dissolved may be due to variations of the form in which the titanium dioxide is present, but on this point we have no definite information. In summing up the chief points in this paper, we desire to call attention to the following:

1. The importance of discriminating in the analysis of bauxite between the trihydrate of alumina, easily soluble in sulphuric acid, and the other compounds of alumina, difficultly soluble.

2. A change in the basis of valuation, by which the trihydrate of alumina is to be given a higher value than the alumina present in some other form.

3. The adoption of a new nomenclature, calling the alumina soluble in 50° B. sulphuric acid at 100° C. during one hour "free alumina," and that soluble in sulphuric acid to fumes "available alumina," the difference between them to be known as "combined alumina."

4. The adoption of a standard method of analysis binding alike on the producer, the broker, and the consumer of bauxite for alum-making.

THE PHILLIPS TESTING LABORATORY,
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## UPON THE SALTS OF HYDRONITRIC ACID.

By L. M. DENNIS AND C. H. BENEDICT, with Crystallographic Notes by A. C. GILL.

Received January 20, 1898.

IN the year 1890 Th. Curtius announced[1] his successful preparation of hydronitric acid ($HN_3$), and briefly described the trinitrides of barium ($BaN_6$), silver ($AgN_3$), and mercury ($Hg_2N_6$). He mentioned also the existence of trinitrides of copper, iron, sodium, and ammonium. Since that time no further work upon the inorganic compounds of this most interesting acid was published until last year when thallous trinitride ($TlN_3$) and thallous thallic trinitride ($TlN_3.TlN_9$) were added to the list.[2] Having a large amount of the acid on hand, we have entered upon the systematic study of the compounds of hydroni-

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[1] *Ber. d. chem. Ges.*, **23**, 3023.

[2] Dennis and Doan: this Journal, **18**, 970.

tric acid, and in this paper are given the results obtained with the elements in the principal group of Group I and the alkaline earths of Group II.

### GROUP I.

*Lithium Trinitride*, $LiN_3.H_2O$.—This was made by neutralizing lithium hydroxide with hydronitric acid and allowing the solution to evaporate in the air. It separated in the form of colorless, glistening needles. It is very soluble in water and is hygroscopic. It is also soluble in alcohol. On being gently heated, the crystals lose their luster and water of crystallization is driven off. On further heating the salt breaks down, the decomposition being somewhat more violent than with the other compounds in this group. Upon standing, the lithium trinitride loses some hydronitric acid.

The hydronitric acid was determined by dissolving the salt in water, precipitating with silver nitrate, and converting the silver trinitride into silver chloride.[1] To the filtrate and washings from the first precipitation hydrochloric acid was added to precipitate the excess of silver, the silver chloride was filtered off, and the filtrate and washings were evaporated to dryness with sulphuric acid. The lithium was then weighed as the anhydrous sulphate. Analysis gave as follows :

| | Calculated for $LiN_3.H_2O$. | Found. |
|---|---|---|
| Lithium | 62.72 | 63.03 |
| Nitrogen | 10.46 | 10.17 |
| Water | 26.82 | (Diff.) 26.90 |

*Sodium Trinitride*, $NaN_3$.—This salt is mentioned by Curtius but he gives no analysis. It was prepared by the same method as that used for lithium, and upon evaporation of the solution it separates in clear colorless crystals. A freshly prepared aqueous solution of the crystals is neutral in reaction, but, upon standing, it becomes alkaline. The salt does not decompose easily when heated, but on the contrary may be melted and kept in a state of fusion for some hours without breaking down.

The analysis, which was made as described under lithium, gave as follows :

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[1] Dennis : This Journal, **18**, 950.

| | Calculated for $NaN_3$. | Found. |
|---|---|---|
| Sodium | 35.38 | 35.42 |
| Nitrogen | 64.62 | 64.71 |

*Potassium Trinitride*, $KN_3$.—This compound, like all of the other trinitrides in this group, was made by neutralizing the hydroxide with hydronitric acid. On attempting to concentrate this solution on the water-bath, it became strongly alkaline. This loss of hydronitric acid was determined in one case by neutralizing a solution of potassium hydroxide with a known amount of the acid, evaporating to dryness on the water-bath and determining the acid in the residue. It was found that about four per cent. of the acid had passed off during the evaporation. To obtain crystals of the potassium salt the solution was allowed to evaporate spontaneously in the air and was kept very slightly acid by adding a drop or two of hydronitric acid every day. The salt crystallizes well and the crystals are stable in the air. They melt when heated and decompose only at a high temperature. Potassium trinitride is but slightly soluble in alcohol and is precipitated from aqueous solution by the addition of an excess of alcohol. Analysis gave

| | Calculated for $KN_3$. | Found. |
|---|---|---|
| Potassium | 48.21 | 47.92 |
| Nitrogen | 51.79 | 51.72 |

*Rubidium Trinitride*, $RbN_3$.—This salt crystallizes in the form of fine needles. It is extremely soluble in water but is less soluble in alcohol than the potassium salt and, like it, can be thrown out of solution by the addition of alcohol. It fuses when gently heated and at a high temperature it decomposes with a puff and a flash. Analysis gave

| | Calculated for $RbN_3$. | Found. |
|---|---|---|
| Rubidium | 32.99 | 32.58 |
| Nitrogen | 67.01 | 67.01 |

*Cesium Trinitride*, $CsN_3$.—On evaporating the solution of this salt it was found to lose hydronitric acid in spite of the strongly basic nature of the cesium. The trinitride was so very soluble in water that crystallization was brought about only by placing it over sulphuric acid. The crystals appeared as clear, colorless needles, gathered together in fern-like clusters. The salt is almost completely insoluble in alcohol. The crystals decompose only when highly heated. Analysis gave

| | Calculated for $CsN_3$. | Found. |
|---|---|---|
| Cesium | 75.99 | 76.03 |
| Nitrogen | 24.01 | 24.36 |

All of these trinitrides of the alkalies are quite stable in the air, the lithium salt being the only one that tends to lose a part of its acid on exposure. None of the salts are what we should term explosive and the ease of decomposition by heat decreases as the atomic mass of the base rises. In solubility they resemble the chlorides of the alkalies, all of them being soluble in water and the solubility increasing with the atomic mass of the base. The solubility in alcohol is the reverse of that in water, lithium trinitride being quite soluble in alcohol and cesium trinitride being insoluble.

## THE ALKALINE EARTHS.

*Calcium Trinitride*, $CaN_6$.—This was prepared by dissolving calcium oxide in a dilute solution of the acid and crystallizing over sulphuric acid, the solution decomposing if evaporated on the water-bath. The crystals separate as small, white hemispherical aggregations which under the microscope are seen to be made up of very small crystals of unrecognizable form. The salt explodes with considerable violence when heated. In analyzing the trinitrides of the alkaline earths, the hydronitric acid was determined in one portion by the method above described, and another portion was treated with sulphuric acid and the base weighed as the sulphate. The results for the calcium salt were

| | Calculated for $CaN_6$. | Found. |
|---|---|---|
| Calcium | 67.74 | 67.63 |
| Nitrogen | 32.26 | 31.97 |

*Strontium Trinitride*, $SrN_6$.—This was prepared by dissolving strontium oxide in a two per cent. solution of hydronitric acid, and crystallizing over sulphuric acid. The crystals separate in the same peculiar hemispherical form as does the calcium trinitride. The strontium trinitride is more soluble in water than is the calcium salt, and is less soluble than the barium trinitride. Analysis gave

| | Calculated for $SrN_6$. | Found. |
|---|---|---|
| Strontium | 51.05 | 51.21 |
| Nitrogen | 48.95 | 48.71 |

*Barium Trinitride*, $BaN_6.H_2O$.—Curtius has described[1] the anhydrous barium trinitride. Although we used the same method of preparation, the crystals contained water, as could be seen by gently heating the salt in a glass tube, and as is indicated by the analysis :

| | Calculated for $BaN_6.H_2O$. | Found. |
|---|---|---|
| Barium | 57.32 | 57.10 |
| Nitrogen | 35.14 | 35.01 |
| Water | 7.54 | (Diff.) 7.89 |

The salt crystallizes in glistening needles which lose luster on standing. They explode with quite a loud report when heated, the particles shooting about like miniature rockets.

The trinitrides of this group are soluble in water, the solubility increasing with the rise in the atomic mass of the base. All of them explode when heated, the violence of the explosion diminishing as the strength of the base increases. They become basic when exposed to the air. The solutions of the trinitrides in water also slowly lose some hydronitric acid upon standing, and quickly become basic when heated upon the water-bath.

## CRYSTALLOGRAPHIC NOTES BY A. C. GILL.

The following crystallographic notes on the salts of the acid $HN_3$ with the bases Li, Na, K, Rb, Cs, Ca, Sr, and Ba were made from a study of material furnished by Mr. C. H. Benedict of the Chemical Department of Cornell University.

Since the lithium and barium compounds crystallize with a molecule of water each, they are not strictly comparable with the others, though the fact in itself proves, of course, a certain difference in their character. The series of anhydrous alkali salts presents the not uncommon phenomenon that the sodium compound behaves differently in its crystallization from the corresponding compounds of K, Rb, and Cs. The latter three are

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[1] *Loc. cit.*, p. 3032.

strictly isomorphous, as might have been predicted *a priori*. In the case of the alkaline earths, however, the unusual condition obtains that calcium acts more like strontium than does barium. The detailed observations made on the material in hand are as follows :

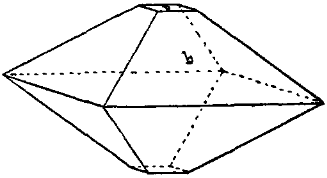
$LiN_3.H_2O$, *hexagonal* (?).—The fine colorless needles, one to three mm. in length, deliquesce on exposure to the air so that no measurements were obtained on the goniometer. The cross-section of these needles, as seen by setting them on end in wax under a microscope with low power objective, seems to be hexagonal or triangular, though the rapid deliquescence entirely rounds off the angles almost before an observation can be made. The crystals have parallel extinction with greatest optical elasticity in the direction of elongation. They are, thus, probably hexagonal and optically negative. The double refraction is very strong,—about 0.250 as determined by interference colors under crossed nicols.

$NaN_3$, *hexagonal.*—Crystals of this substance exhibit a very varied habitus, but only the extremely thin basal plates, among the crystals studied, furnished any crystallographic data. These show irregular outlines, and have a diameter of one to two and one-half mm., with a thickness of 0.02 to 0.1 mm. Lines of cleavage making an angle of 60° (rarely 30°) are plainly visible in many places. In converged polarized light the optical interference figure is uniaxial and positive. The hexagonal form is thus established beyond question. The strength of the double refraction of this substance is remarkable, for a 0.1 mm. plate shows the colored rings of its interference figure much closer together than in a calcite plate two and one-half times as thick.

$KN_3$, *tetragonal.*—Brilliant colorless transparent crystals from two to five mm. in diameter gave excellent measurements on the goniometer. The shape of these is seen in the figure where $p =$ the base, (001), and $b =$ the pyramid (111). The axial ratio $a : c = 1 : 0.57976$. This is computed from twenty-one measurements of the angle 111 to $\bar{1}\bar{1}1$ which varied from 78° 40′ to 78° 44′, averaging 78° 41′ 45″. The calculated polar angle 111 to $\bar{1}11$ is 53° 16′ 34″; found, 53° 16′ 15″. The base is too rough to give good reflections, but is always present. The prism (110), on the other hand, is very rarely to be seen, but in one case gave a sharp image in the telescope of the goniometer. The crystals are optically uniaxial, negative, and very strongly doubly-refracting.

$RbN_3$, *tetragonal.*—In general appearance these crystals differ from those of $KN_9$ only in having the basal plane more largely developed, so that their habitus is tabular rather than pyramidal. The angle from base (001) to pyramid (111) is about 40° 13′ (average of eleven measurements varying from 39° 51′ to 40° 35′) whence $a : c = 1 : 0.5979$. The double refraction is negative, like that of $KN_3$, but decidedly weaker.

$CsN_3$, *tetragonal.*—No good crystals for goniometric measurement were at hand, but under the microscope they showed themselves similar in shape to the preceding. They are uniaxial, negative, and weaker in double refraction than $RbN_3$. Under crossed nicols the interference colors of crystal fragments indicate a double refraction of 0.050. The basal plates are often traversed by twin lamellae. One specimen having a sharp rectangular outline showed these lamellae at angles of 90° with each other, but turned 10° with reference to the outline of the crystal. Hence this substance, and probably the two foregoing, is very likely pyramidal hemihedral.



$CaN_6$, *orthorhombic* (?).—This substance was seen only in the shape of milk-white balls or spherules composed of radiating needles. On crushing, these showed under the microscope parallel extinction, with the greater elasticity in all cases in the direction of elongation of the needle. Since the double refraction appears to vary from 0.070 to 0.100, the substance is probably orthorhombic, rather than tetragonal or hexagonal.

$SrN_6$, *orthorhombic*, (?).—It resembles very closely the foregoing, and could be investigated only to the same limited extent. The double refraction is slightly stronger, and the spherulitic aggregates are less perfectly round than is the case with $CaN_6$.

$BaN_6 + H_2O$, *triclinic.*—The brilliant little crystals of the barium salt have a six-sided prismatic habitus, with terminating faces usually at only one end. The other end is frequently attached to another individual in twinning position, the long axes of the two making an angle of about 65°. The small size and irregular surface of the crystals prevented measurements of sufficient accuracy to determine the axial ratios. The angle which would be naturally chosen as that of the prism measures 66° 12′. Since the extinction angle is 22° when the obtuse interior angles of this prism are placed in a vertical plane one above the other, and 10½° when the crystal is turned 90° about its long axis, the crystal system must be triclinic. The double refraction is extremely high, above 0.200, and the mean index of refraction is about 1.7.

CORNELL UNIVERSITY,
JANUARY, 1898.

# INTRODUCTORY NOTE ON THE REDUCTION OF METALLIC OXIDES, AT HIGH TEMPERATURES.

By FANNY R. M. HITCHCOCK.

Received January 22, 1898.

A consideration of the results obtained by Dr. Friedheim and the author, when working on the atomic mass of tungsten in 1895, and 1896, led me to the conclusion that the loss in weight of the metallic oxides on reduction in hydrogen was not due solely to oxygen. Experiments made at high temperatures showed nitrogen was given off steadily though very slowly from tungstic oxide and from molybdic oxide, when reduced in a current of hydrogen. On decreasing the temperature the amount of nitrogen decreased ; on raising the temperature again, nitrogen was given off in greater quantities. While the spectrum of the gas gave only the appearance of nitrogen, and no trace of argon or helium could be found on sparking with oxygen, yet the densities were abnormal, and indicated the presence of gases both lighter and heavier than nitrogen. The nitrogen obtained on reduction in porcelain tubes at the temperature obtainable with a Glaser furnace gave densities varying from two to eight ($H = 1$). The gas obtained when a Lorenz furnace was used gave densities of from twenty-two to twenty-six.