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Review of American Chemical Research, Vol. IV, 1898 by Arthur A. Noyes & Henry P. Talbot

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ARTHUR A. NOYES & HENRY P. TALBOT

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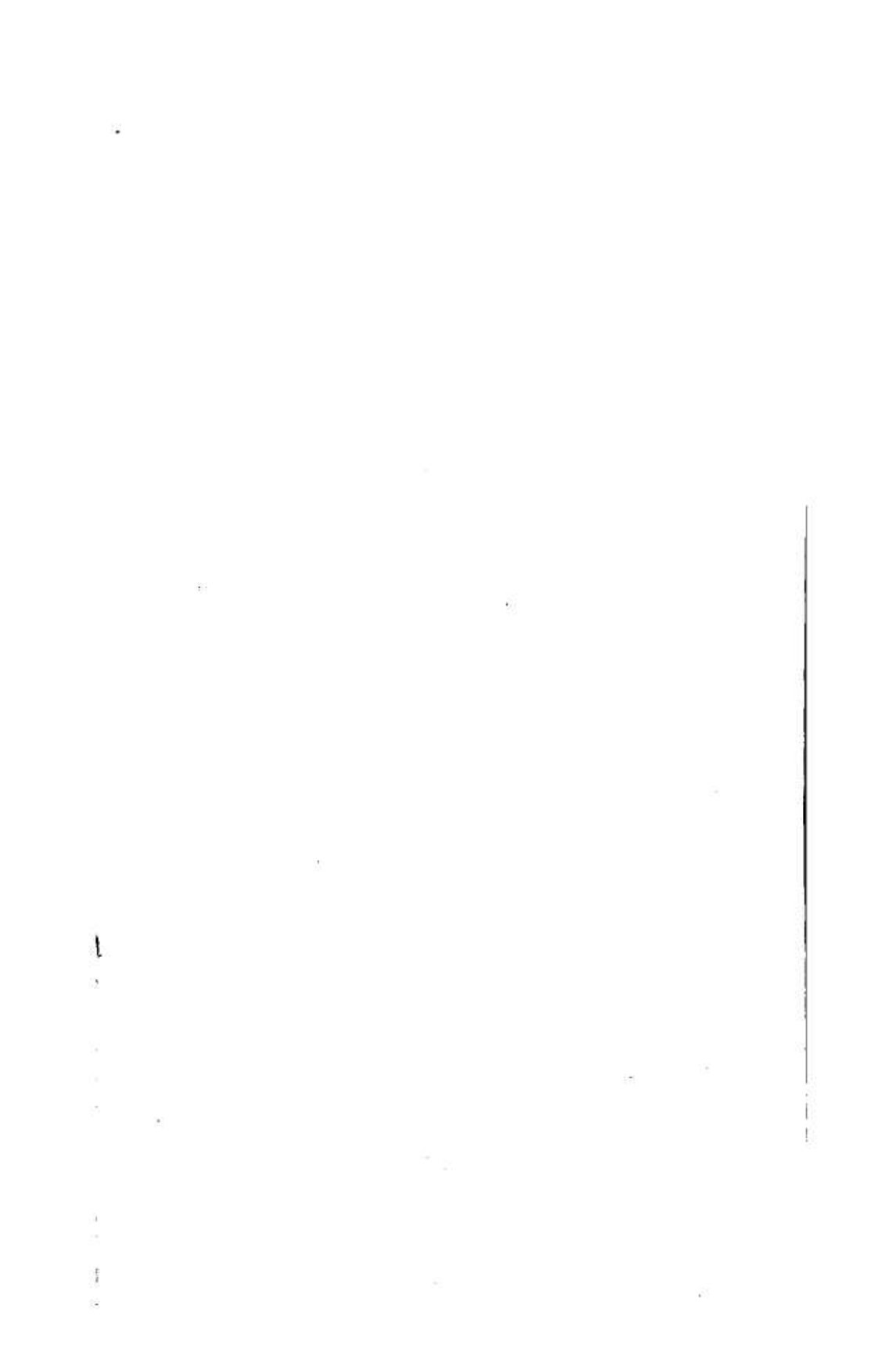
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REVIEW OF AMERICAN CHEMICAL RESEARCH.

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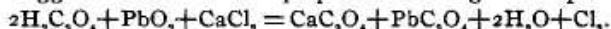
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INORGANIC CHEMISTRY.

HENRY FAY, REVIEWER.

A New Explosive Compound Formed by the Action of Liquid Ammonia upon Iodine. BY HAMILTON P. CADY. *Kan. Univ. Quart.*, 6, 71-75.—When 25-30 cc. of liquid ammonia are added to 4-5 grams of iodine in a vacuum-jacketed tube protected from moisture, the iodine is dissolved, forming a dark, opaque liquid which changes to olive-green and deposits a dark-green, crystalline precipitate. This substance, dried over sulphuric acid, dissolves in ether, alcohol, and chloroform; but it is insoluble in dilute acids, and is decomposed by them, generally with explosive violence. It is instantly decomposed by strong acids. Potassium iodide solution dissolves the crystals, and they are decomposed and dissolved by hydrogen sulphide, sulphurous acid and potassium hydroxide. The composition of the substance, as shown by analysis, agrees well with the formula HN_3I ; and the formation of the compound is supposed to take place according to the equation: $11\text{NH}_3 + 9\text{I} = \text{HN}_3\text{I} + 8\text{NH}_3$.

Note on Extemporaneous Chlorine Water. BY F. B. POWER. *Pharm. Rev.*, 15, 108.—The author criticises the statement made by Griggs that chlorine can be prepared according to the equation:



It was shown that what was taken for chlorine was probably ozone; and that while the oxalic acid was mostly oxidized to carbon dioxide, practically all of the calcium chloride was unacted upon.

The Action of Carbon Dioxide upon Sodium Aluminate and the Formation of Basic Aluminium Carbonate. BY WILLIAM

C. DAY. *Am. Chem. J.*, 19, 707-728.—The author has analyzed a series of preparations made by precipitating sodium aluminate by carbon dioxide. The sodium aluminate was prepared from Connetable phosphate rock, by treating it with sodium carbonate and quicklime, which leaves all iron compounds and calcium phosphate undissolved. Before working with the samples prepared, a commercial product, "Alumina soluble in acids," was analyzed, and found to contain 26.38 per cent. CO_2 , and 21.30 per cent. Na_2O . Some of the original substance was then washed with water until no alkali could be detected by litmus or phenol-phthalein. The dried residue from the washing effervesced with acid, and gave on analysis 17.35 per cent. CO_2 , and 12.22 per cent. Na_2O , amounts corresponding closely to that required for sodium bicarbonate. Several preparations were then made and washed with hot water until apparently free from alkali; they were then dried on the water-bath and analyzed; but it was found that all portions contained sodium oxide and carbon dioxide. This dried sample showed alkali on washing, and continued to show it after apparently washed free from it a second time. Preparations washed with cold water by decantation until apparently free from alkali always showed it on analysis, but gave off more after drying and washing again. In two samples it was possible to wash the sodium out until only 0.23 and 0.34 per cent. remained; and in the same preparations there were left respectively 9.06 and 3.99 per cent. of carbon dioxide, which is more than that needed for the formation of sodium bicarbonate, indicating that a basic aluminum carbonate of varying composition might exist.

On the Chloronitrides of Phosphorus. (II). By H. N. STOKES. *Am. Chem. J.*, 19, 782-796.—In a previous paper (this *Rev.*, 3, 4), the author described the phosphonitrilic chlorides having the composition $\text{P}_3\text{N}_3\text{Cl}_3$ and $\text{P}_4\text{N}_4\text{Cl}_4$, and their corresponding acids. This paper is a continuation of the work describing the polymers of the same series. The following table shows the additional members which have been isolated, together with their properties:

	Melting-point.	Boiling-point.	
		13 mm.	760 mm.
Triphosphonitrilic chloride, $(\text{PNCl}_2)_3$	114°	127°	256.5°
Tetraphosphonitrilic chloride, $(\text{PNCl}_2)_4$	123.5°	188°	328.5°
Pentaphosphonitrilic chloride, $(\text{PNCl}_2)_5$	40.5-41°	223-224.3°	Polymerizes
Hexaphosphonitrilic chloride, $(\text{PNCl}_2)_6$	91°	261-263°	Polymerizes
Heptaphosphonitrilic chloride, $(\text{PNCl}_2)_7$	liquid at -18°	289-294°	Polymerizes
Polyphosphonitrilic chloride, $(\text{PNCl}_2)_x$	Below red heat.	Depolymerizes on distillation.	

There was also obtained a liquid residue of the same empirical composition of a *mean* molecular weight corresponding nearly to $(\text{PNCl}_2)_{11}$; but it has not yet been prepared in a pure condition. The method that gives the best results in the preparation of these compounds is to heat a mixture of four parts of dry phosphorus pentachloride with one part of ammonium chloride. As the mixture liberates hydrochloric acid, it is necessary to open the tube occasionally to relieve the pressure; and this is best accomplished by heating to 150°C ., allowing to cool to 100° ., and opening the tubes while in the furnace. This process is repeated several times, each time heating 1° – 2° higher. After most of the hydrochloric acid has been removed in this way, the tube can be safely heated to 200°C . The contents of the tube are then distilled off, and the distillate is found to consist of a crystalline mass impregnated with a yellow oil, amounting to 95 per cent. of the theoretical quantity of phosphonitrilic chlorides, of a small amount of phosphorus pentachloride, of some chloronitride of the composition $\text{P}_2\text{N}_2\text{Cl}_4$, and of traces of an unknown compound. The melted distillate is poured into cold water to remove phosphorus pentachloride; and it is then heated for about two hours. The product is then fractionated up to 200°C . at 13–15 mm., using an Anschütz flask. The distillate at this temperature consists of about 70 per cent. $\text{P}_2\text{N}_2\text{Cl}_4$ and $\text{P}_3\text{N}_3\text{Cl}_6$; the residue of $\text{P}_4\text{N}_4\text{Cl}_{10}$ and the higher members. If the distillate is not desired, it is best to take advantage of the peculiar properties of the substance and polymerize it to the compound $(\text{PNCl}_2)_x$ which can in turn be depolymerized, giving the different lower members of the series. The residue of $\text{P}_4\text{N}_4\text{Cl}_{10}$ and higher members is fractionated above 200°C . Polymerization often takes place during the heating, as is indicated by the frothing; but this may be overcome by heating with water and removing the small amount of oil formed, and again continuing the fractionation. It has not been found advisable to heat above 370° , as polymerization takes place rapidly at that temperature. Pentaphosphonitrilic chloride at its melting-point is soluble in all proportions of benzene, ether, carbon bisulphide, and gasoline; but it cannot be crystallized from any of them. It shows a decided tendency to superfusion. The next two members of the series are soluble in benzene, ether, carbon bisulphide and gasoline; hexaphosphonitrilic chloride possessing a strong crystallizing power. When any of the lower members are heated polyphosphonitrilic chloride is formed slowly at 250°C ., and rapidly at 350°C . As the change is reversible, complete transformation cannot be effected; but it reaches 90 per cent. The pure chloride is colorless, transparent, and elastic; it is insoluble in all neutral solvents; but it readily absorbs ben-

zene, swelling to a rubber-like compound of many times its own volume. Hot water slowly dissolves it with decomposition; it swells, gelatinizes, and finally dissolves in ammonia. Depolymerization begins at 350° C., and this change is rapid below a red heat.

On the Solubility of Ammonia in Water at Temperatures below 0°. BY J. W. MALLET. *Am. Chem. J.*, 19, 804-809.—The author has extended the determination of the solubility of ammonia made by Roscoe and Ditmar from 0° to -40° C. Strong aqueous ammonia was placed in a burette-like tube surrounded by a freezing mixture, and gaseous ammonia, previously cooled by being passed through tubes placed in freezing mixtures, was passed into the already strong solution. The temperature was recorded by means of a standardized alcohol thermometer. Measured portions were drawn off, beginning at -40° C. at intervals of 10° into water cooled to 0° and titrated with sulphuric acid. The solution of enough ammonia to form ammonium hydroxide was not attended with any apparent change of behavior; and continuous liquefaction went on smoothly to the lowest temperature reached, without separation of any solid product. The table expresses the amount of ammonia dissolved in one gram of water at a pressure of 743-744.4 mm. :

°C.	Grams.	°C.	Grams.
-3.9	0.947	-25	2.554
-10	1.115	-30	2.781
-20	1.768	-40	2.946

The amount dissolved at -3.9° C. corresponds almost exactly to that calculated for ammonium hydroxide.

The Action of Nitric Acid on Aluminum and the Formation of Aluminum Nitrate. BY THOMAS B. STILLMAN. *J. Am. Chem. Soc.*, 19, 711-717.—The author shows that aluminum in the form of coarse turnings is readily acted upon by nitric acid, hot or cold, of specific gravity 1.15 or 1.45, the weaker acid acting the more rapidly. The reaction is retarded if the aluminum is in the form of plates, the retardation being very slight with cold acid, but considerable if the acid is warm. The solutions deposited crystals of the composition $Al(NO_3)_3 \cdot 9H_2O$.

Notes on Selenium and Tellurium. BY EDWARD KELLAR. *J. Am. Chem. Soc.*, 19, 771-778.—It is shown that ferric hydroxide carries down both selenium and tellurium, the amount needed for the precipitation of the former element being much greater than for the latter. To obtain both elements quantitatively in precipitating from hydrochloric acid solutions, it is necessary to

have the acidity of the solution between definite limits, 30-50 per cent. Figures are given for the partial precipitation of both elements, showing that the amount of precipitate varies with the time, temperature, and the acidity of the solutions. There is complete precipitation of tellurium when the solution contains 0.5 per cent. acid, but then none of the selenium is precipitated. When the acidity has reached 80 per cent., all of the selenium, but no tellurium, is precipitated. The reducing action of ferrous sulphate is almost identical with that of sulphurous acid. In precipitating copper solutions containing selenium with hydrogen sulphide, some of the latter is always carried down, probably in combination with copper as selenide.

Further Study on the Influence of Heat Treatment and Carbon upon the Solubility of Phosphorus in Steel. BY E. D. CAMPBELL AND S. C. BABCOCK. *J. Am. Chem. Soc.*, 19, 786-790.—This is a continuation of a previous paper (this *Rev.*, 3, 2) greater care having been taken here to measure temperatures by means of a Le Chatelier pyrometer. The general results reached are: that phosphorus may exist in at least two forms in steel; that carbon and the different heat treatment, annealing and quenching, considerably affect the solubility of the phosphorus in acid mercuric chloride solution, the amount going into solution apparently increasing with increase of the temperature at which the metal is quenched, and also with the percentage of carbon.

Contribution to the Chemistry of Didymium. BY L. M. DENNIS AND E. M. CHAMOT. *J. Am. Chem. Soc.*, 19, 799-809.—The mixture of earths used in this work was extracted from monazite sand from Brazil. The sand was decomposed by sulphuric acid, and the rare earths separated from the other elements in the usual way. Cerium was separated from the didymium group by the chlorine process in apparatus specially devised for the purpose. The oxalates were then decomposed by heat and converted into nitrates, their solution being treated with an excess of potassium sulphate for the purpose of removing the yttrium group. The double sulphates were then dissolved in dilute ammonium acetate, converted into the hydroxides and then into nitrates. Fractionation of the double ammonium nitrates by the methods of Welsbach and Bettendorf did not yield satisfactory results; and it was found that the best results were obtained by slow spontaneous evaporation. In this way there was more rapid separation of neodidymium from praseodidymium. A large portion of lanthanum salts was separated in the first fractions, disappearing for a time, and