KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

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CONTENTS.

J. W. Dito: "The action of phosphorus on hydrazine". (Communicated by Prof. C. A. Lobry de Bruyn), p. 1.

J. W. Commelin and Ernst Cohen: "The electromotive force of the Daniell-cells". (Communicated by Prof. W. H. Julius), p. 4.

Jan de Vries: "On complexes of rays in relation to a rational skew curve", p. 12.

W. A. Versluys: "The singularities of the focal curve of a curve in space". (Communicated by Prof. P. H. Schoute), p. 17.

P. Zeeman and J. Geest: "On the double refraction in a magnetic field near the components of a quadruplet", p. 19.

J. J. van Laar: "The course of the melting-point-line of alloys (3 d communication). (Communicated by Prof. H. W. Bakhuis Roozeboom), p. 21.

M. C. Dekhuyzen and P. Vermaat: "On the epithelium of the surface of the stomach". (Communicated by Prof. C. A. Pekelharing), p. 30.

E. Hekma: "On the liberation of trypsin from trypsin-zymogen". (Communicated by Prof. H. J. Hamburger), p. 34.

A. Pannekoek: "Some remarks on the reversibility of molecular motions". (Communicated by Prof. H. A. Lorentz), p. 42.

C. A. J. A. Oudemans and C. J. Koning: "On a Sclerotinia hitherto unknown and injurious to the cultivation of Tobacco (Sclerotinia Nicotianae Oud. et Koning), p. 48 (with one plate).

J. E. Verschaffelt: "Contributions to the knowledge of van der Waals' ψ-surface. VII. (part 3). The equations of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components". (Communicated by Prof. H. Kamerlingh Onnes), p. 59.

The following papers were read:

Chemistry. — "*The action of phosphorus on hydrazine.*" By Mr. J. W. Dito. (Communicated by Prof. C. A. Lobry de Bruyn).

(Communicated in the meeting of April 24, 1903.)

The last number of the Berichte [1]) contains a research on phosphorus by R. Schenck. Several of his observations quite corroborate those which have been announced some time ago [2]) and which were made

[1]) Ber. **36**. 979.

[2]) Recueil **18**. 297. (1899).

in 1900—1901, but the publication of which was postponed owing to other studies which are not yet complete.

In 1895 [1]) and also afterwards [2]) LOBRY DE BRUYN, in his studies on hydrazine, observed that yellow phosphorus in contact with aqueous hydrazine turns the solution first yellow, then dark brown and finally black. After some time brownish black amorphous flakes are deposited. As already stated, I submitted this reaction some years ago to a closer examination and studied it, both with aqueous and with anhydrous hydrazine.

I. If we introduce into vacuum tubes 16 gr.(=6 at.) yellow phosphorus and 5 c.c. of a concentrated 90 % (= 1 mol.) aqueous solution of hydrazine and allow these to be in contact for 1 or 2 months at the ordinary temperature the whole solidifies to a black amorphous mass in which a white well-crystallised substance is distributed. On opening the tubes a large quantity of hydrogen phosphide appears to be present. As preliminary experiments had shown that the white substance was soluble in absolute alcohol but not the black substances, the tubes were filled with absolute alcohol out of contact with the air, the black substance was freed from the white crystals by repeated washing with absolute alcohol and then dried over sulphuric acid in vacuum.

The crystalline product obtained on evaporating the alcohol, was particularly hygroscopic. The analysis agreed best with the assumption that it consisted of hydrazine phosphite. Found 30.4 % P and 12.3 % N (this was determined in a nitrometer by means of vanadic acid) [3]). If however notwithstanding the necessary precautions, the substance has attracted a good deal of moisture in the course of the different manipulations, there is a possibility of its being hydrazine hypophosphite [4]).

The black mass is insoluble in alcohol, ether and carbon disulphide and free from excess of yellow phosphorus. It has an odour of hydrogen phosphide; in contact with the air it becomes moist and the black colour changes to yellow. It contains chemically combined hydrazine which, in company with a little hydrogen phosphide, is obtained on distilling with dilute sodium hydroxide and which could be identified by means of its dibenzaldehyde-derivative which melts at 93°.

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[1]) Recueil **14**. 87.

[2]) Recueil **15**. 183.

[3]) HOFFMANN and KÜSPERT Ber. **31**. 64.

[4]) SABANEJEFF, Z. anorg. Ch. **20**. 21. (1899).

The black substance is strongly attacked by dilute nitric acid and also by bromine water. On heating at 100° in a current of dry hydrogen it loses weight continuously and the black colour changes to red.

On treatment with dilute acids it behaves exactly like the product isolated by SCHENCK from red phosphorus and ammonia [1]). It is then converted into a light red amorphous powder whilst the solution appears to contain a salt of hydrazine. The red powder has the external appearance of red phosphorus but is distinguished from this by a more orange tinge and its behaviour towards alkalis. Ammonia and dilute soda or potash yield black products, which however on prolonged washing with water lose their feebly combined alkali and assume their original red color. The substance, therefore, behaves as a weak acid which forms black alkali salts which readily undergo hydrolysis.

Strong alkalis act energetically on the red substance with formation of hydrogen phosphide and a salt of hypophosphorous acid.

In the analysis of the black and the red substance the phosphorus was determined by means of dilute nitric acid (in sealed tubes) and with bromine water. The nitrogen determination was done volumetrically with bromine water in a current of carbon dioxide and the hydrogen by an elementary analysis.

The average result was 45.9 % P, 19.8 N and 5.5 % H; total 71.2; the balance may be taken as representing oxygen.

The red compound was free from nitrogen so that the black product appears to be the hydrazine derivative of the red substance.

The product dried in a desiccator in vacuo contained 91.7 % P and 1.1 % H [2]).

2. If we place in a vacuum tube an excess of yellow phosphorus with free hydrazine N_2H_4, we also notice (although sooner than in the case of the aqueous solution) the formation of a black amorphous substance which in appearance quite resembles the product obtained from hydrated hydrazine. No white substance is of course formed, hardly any pressure is noticed and also little or no formation of hydrogen phosphide takes place. This gas, like the hydrazine phosphite, therefore owed its origin to the well-known reaction between phosphorus and a base.

[1]) That black compounds are also formed from liquefied ammonia and white phosphorus is shown by the experiments of GORE, Proc. Roy. Soc. **21**. 140. (1872), FRANKLIN and KRAUS, Amer. Ch. J. **20**. 820. (1898), and HUGOT, Ann. Chim. Phys. **21**. 28. (1900).

[2]) This figure is almost sure to be too high owing to the nature of the process (elementary analysis).

The black substance was washed with carbon disulphide and alkohol and dried in a desiccator in vacuo. Apparently it has absorbed oxygen during this operation for the analysis showed a deficit of about 13 %. We found: 78.5 % P, 1.9 % H and 6.5 % N.

When treated with dilute acids a red substance was again formed which in appearance and properties corresponded exactly with the one already described and contained the same amount of phosphorus [found, average 92 %]. The hydrazine has passed into the acid.

3. From the foregoing it follows that substances quite analogous to those formed by SCHENCK's (impure) red phosphorus and ammonia are generated directly from hydrazine and yellow phosphorus. Evidently, the black compounds which are formed from aqueous and anhydrous hydrazine are of a different nature; their investigation remains however very unsatisfactory, owing to their amorphous conditions and want of tests for purity, in addition to their unstability towards washing-liquids. But it is pretty certain that the orange red product which both yield, when treated with acids, is a weak acid composed of phosphorus, hydrogen (and oxygen?)

Hydrazine is therefore capable of directly giving up hydrogen, not only to sulphur but also to phosphorus.

Organic chem. Lab. University. *Amsterdam*, April 1903.

Chemistry. — "*The electromotive force of the* DANIELL-*cells.*" By Mr. J. W. COMMELIN and Prof. ERNST COHEN. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of April 24, 1903).

1. In the present state of our electro-chemical knowledge an exhaustive study of the electromotive force of the DANIELL-cell would have but little importance if it related to the use of this cell as a standard-cell, as we are now in possession of standard-cells which, if properly constructed, satisfy all requirements.

We have, nevertheless undertaken an exhaustive investigation of such a cell because J. CHAUDIER has published in the "Comptes Rendus" [1]) certain views which are entirely opposed to our modern theories on the origin of the electromotive force in cells of this kind.

[1]) 134, 277 (1902).