SCIENCE

NEW YORK, JULY 7, 1893.

HYDRAZOIC ACID: A NEW FORM OF APPARATUS FOR ITS PREPARATION; ITS PHYSIOLOGICAL ACTION.

BY CYRIL G. HOPKINS, SOUTH DAKOTA AGRICULTURAL COLLEGE, BROOKINGS, SOUTH DAKOTA.

MOST of the text-books on the subject of chemistry in use at the present time still recognize but one compound of hydrogen and nitrogen, viz., ammonia. There are, however, now known to science, several compounds of these two elements. Of these the most important are ammonia, NH_3; hydrazoic acid, HN_3; and hydrazine, N_2H_4. There is a remarkable difference in the properties of the first two substances. Ammonia, the volatile alkali, has very strong basic properties, uniting directly with acids to form the ammonium salts. Only with the strongest basic elements does it act like an acid, forming sodium amide, $NaNH_2$, with sodium, and potassium amide, KNH_2, with potassium.

Hydrazoic acid, on the contrary, is a comparatively strong acid. Being a binary compound of hydrogen and nitrogen, it might well be called *hydronitric* acid, after the analogy of hydrochloric acid, hydrobromic acid, etc. Its structural formula is represented thus:—

$$H - N \begin{array}{l} \diagup N \\ \quad \| \\ \diagdown N \end{array}$$

Its hydrogen atom is readily replaced by metals and radicals, the salts of hydrazoic acid being thus formed. The ammonium salt contains only hydrogen and nitrogen, and is formed by direct union of ammonia and hydrazoic acid:—

$$NH_3 + HN_3 = NH_4N_3 = N_4H_4.$$

Hydrazoic acid also unites with hydrazine, another compound of hydrogen and nitrogen, possessing the formula

$$N_2H_4, \text{ or } \begin{array}{c} NH_2 \\ | \\ NH_2 \end{array}.$$

This substance, hydrazine, or diamine, as it is sometimes called, bears to ammonia the same relation that ethane, C_2H_6, or $\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$, bears to marsh gas, CH_4; or that diphenyl, $\begin{array}{c} C_6H_5 \\ | \\ C_6H_5 \end{array}$, bears to benzine, C_6H_6. Like ammonia, hydrazine possesses strong basic properties. With hydrazoic acid it forms two compounds by direct addition:—

$$\begin{array}{c} NH_2 \\ | \\ NH_2 \end{array} + HN_3 = \begin{array}{c} NH_3N_3 \\ | \\ NH_2 \end{array} = N_5H_5,$$

and

$$\begin{array}{c} NH_2 \\ | \\ NH_2 \end{array} + 2HN_3 = \begin{array}{c} NH_3N_3 \\ | \\ NH_3N_3 \end{array} = N_8H_6.$$

Thus we have at least six compounds of the elements hydrogen and nitrogen, their general formulas being:—

$$NH_3,\ N_2H_4,\ N_4H_4,\ N_5H_5,\ N_8H_6, \text{ and } HN_3.$$

Heretofore hydrazoic acid and its derivatives have been made only by reactions[1] of organic chemistry; but within the past few months a method has been devised by Wislecenus[2] by which the acid is made entirely from inorganic substances. This is done by first treating molten metallic sodium (or potassium) with dry ammonia gas, and then treating the sodium amide thus formed with dry nitrous oxide. The sodium salt of hydrazoic acid is thus formed; and, by treating this with dilute sulphuric acid, the hydrazoic acid itself is liberated, and may then be distilled off with water, thus giving a dilute aqueous solution.

Wislecenus performed the operation in a small porcelain boat within a glass tube. The porcelain is strongly attacked by the sodium compounds, and the yield of hydrazoic acid which Wislecenus obtained was nearly 50 per cent of the theoretical amount, and, besides, only a small quantity of the acid (about one-half a gramme) could be made at a time.

These objections to the apparatus used by Wislecenus induced the author to seek for a better form of apparatus with which to prepare the acid.

A cylindrical copper air-bath was selected, which was provided with two mica windows placed opposite each other, through which any operation that was carried on within the bath could be easily observed. The bath was about fifteen centimetres from top to bottom and of about an equal diameter. The cover was of heavy asbestos board. In the centre of this a large circular opening was made, through which a glass beaker of 750 cubic centimetres capacity was inserted into the bath until its rim rested upon the asbestos board, the bottom of the beaker not being allowed to touch the bottom of the bath. A small quantity of clean sand was placed in the bottom of the beaker, and upon this a small iron sand-bath, hemispherical in shape, and having a capacity of 100 cubic centimetres. The mouth of the beaker was closed with a large flat cork, provided with three holes. Through the central hole passes a glass tube which reaches a little way into the iron dish, and through which the gases are conducted into the apparatus. The second hole carries a short exit tube, and the third a thermometer.

Neither the metallic sodium nor the compounds formed have any action upon the iron dish, and the reactions which take place in the dish can be readily observed through the mica windows of the air-bath and the glass beaker.

The ammonia gas was obtained by gently heating on a water-bath a flask containing strong ammonia water, and the nitrous oxide by the decomposition of ammonium nitrate by heat. The gases were dried as directed by Wislecenus, by passing them over soda-lime and solid potassium hydroxide.

To perform the operation 25 grammes of metallic sodium were placed in the iron dish, the temperature of the bath raised to 300° – 360° C., and dry ammonia gas conducted in and delivered just above the surface of the molten sodium. The specific gravity of sodium being less than that of the amide formed, the metal floats on the surface until the action is finished. The reaction is represented by the equation:—

$$NH_3 + Na = Na\,NH_2 + H.$$

When the globules of sodium had all disappeared, the nitrous oxide was substituted for the ammonia, and the temperature of the bath lowered to 230° – 250° C. Two reactions now take place. The two atoms of hydrogen in the sodium amide are replaced by the bivalent group, N_2, contained in the nitrous oxide, the hydrogen and oxygen uniting to form water. This then reacts with a second molecule of sodium amide, forming sodium hydroxide and ammonia:—

$$NaNH_2 + N_2O = (NaNN_2 = NaN_3) + H_2O, \text{ and}$$
$$NaNH_2 + H_2O = NaOH + NH_3.$$

The sodium compounds have a strong tendency to creep over the edge of the iron dish as fast as they are formed; but they only fall upon the sand in the bottom of the beaker, from which they are readily dissolved out by water.

When the odor of ammonia ceases to be given off, the reaction is complete. The apparatus was allowed to cool, the mixture of sodium hydroxide and the sodium salt of hydrazoic acid was dis-

[1] Berichte der deutsch. Chem. Gesellschaft (Curtius), xxiii., 3023; xxiv., 3345. Ibid (Noeting and Grandmongin), xxiv., 2546.

[2] Ibid, xxv., 2084.

solved in 500 cubic centimetres of water, and then dilute sulphuric acid added till the hydrazoic acid was liberated. The solution was then distilled till the distillate ceased to give a precipitate with silver nitrate.

The distillate was then diluted to a definite volume and its strength determined by titration with standard ammonia solution. The yield of the acid was 87 per cent of the theoretical, 500 cubic centimetres of nearly 4 per cent solution being obtained.

A part of the acid solution was neutralized with potassium carbonate, and evaporated to crystallization. Beautiful, tabular, transparent crystals of the potassium salt, KN_3, were formed.

The salts of hydrazoic acid, excepting the salts of the alkali metals and the metals of the alkaline earths, are explosive. In some respects the acid resembles hydrochloric acid. With soluble silver salts a white precipitate, AgN_3, is formed. Lead acts similarly. These salts explode very violently when heated.

The most remarkable property of hydrazoic acid and its soluble salts is their physiological action. In this respect they resemble the nitrite of amyl, $C_5H_{11}NO_2$, having a marked influence upon the action of the heart. The author found by experiment that one-tenth of a grain of the potassium salt, KN_3, dissolved upon the tongue (the resulting solution not being swallowed, but ejected from the mouth) was sufficient to increase the pulse from 96 beats per minute to 153. This required only five minutes' time after the dose was taken. This rate of heart-beat is not sustained, however. A sudden and rapid reduction takes place, and ten minutes after the dose was taken the heart was giving 60 feeble beats per minute, making a total variation of 97 beats per minute. Considering the fact that this effect was produced by the small quantity of the substance which was absorbed by the mucous membrane of the tongue, this property is certainly remarkable. The vapors of the hydrazoic acid produce similar effects when inhaled.

The laboratory work reported in this article was performed in the chemical laboratory of Cornell University; and the author wishes to acknowledge that the success of the work was largely due to the aid and direction given by Dr. W. R. Orndorff. Thanks are also due him for his kindness in reading and correcting the manuscript.

ON PROTOPTERUS ANNECTENS.

BY DR. R. W. SHUFELDT, WASHINGTON, D.C.

THERE has been very recently published in the Transactions of the Royal Irish Academy (Vol. XXX., Part III., pp 109–230, Plates vii. to xvii.) the long-delayed work of Professor W. N. Parker of the University College, at Cardiff, Wales, "On the Anatomy and Physiology of *Protopterus annectens.*" Through the courtesy of its author, a reprint of that most valuable quarto is now before me, and it is my wish to write a brief notice here in regard to it. The elaborate manner in which the Transactions of the Academy are published is too well know to require remark, but in the present instance it is impossible to pass this work without a word upon the truly superb plates that illustrate it. These, some ten in number, were chromo-lithographed by Professor Parker's younger brother, M. P. Parker, and printed by West, Newman. They present us with much of the anatomy and histology of *Protopterus*, and are throughout perfect masterpieces of the kind, and of the very highest order of merit.

As is well known, this genus formerly was written *Lepidosiren*, the South American species being *L. paradoxa*, and the African one *L. annectens*,[1] and among the first to pay any attention to it, of a reliable nature, was Sir Richard Owen, who, in 1839–1841, published his "Description of *Lepidosiren annectens*" in the Transactions of the Linnæan Society of London (Vol. XVIII.), since which time naturalists have never ceased to furnish various accounts of the biology of this extremely important form, but usually based, as Professor Parker remarks, upon badly preserved material. Our present author was far more fortunate as he had perfectly fresh specimens to work upon. Of these he has said in his "Introduction," that "All my material, with the exception of two specimens, purchased last autumn, were placed at my disposal by Professor Wiedersheim. These were received alive direct from the neighborhood of the Gambia, and to Dr. J. Beard is due the credit of having arranged for their transport. While in the torpid condition about one hundred specimens had been dug out, each surrounded by a clod of earth,[2] and the clods were then packed together in open crates. In this manner they travelled without harm, nearly all of them being alive and in a healthy condition on their arrival in Freiburg. On being removed from the clods, they were, by the kind permission of Professor Hildebrandt, placed in a large wire cage, sunk beneath the water in a basin used for the culture of water plants in one of the hot-houses of the Botanical Gardens, in which a constant temperature of 22.5° C. was maintained."[3] . . . "Protopterus lives probably to a great age, and this supposition is supported by the somewhat incredible statement of the natives mentioned by Stuhlmann, that some specimens reach a length of six feet. From the observations of Hyrtl and Bischoff, it appears that Lepidosiren also attains a large size, reaching, at any rate, three feet in length" (p 112).

It was found that *Protopterus* grows very rapidly, has great vitality, and, although able to sustain fasts, is exceedingly voracious, devouring all the abundant snails, earth-worms, and small fish given them, and then killing and eating each other, making it difficult in the extreme to preserve the specimens.

Protopterus is most active at night, and appears to keep mostly to the shallow water, where they move deliberately about on the bottom, alternately using the peculiar limbs of either side, though their movements do not seem to be guided by any strict regularity. "Gray has compared these movements with those of a Triton, and several other observers have noticed them. The powerful tail forms a most efficient organ for swimming rapidly through the water."

"It is well known that Protopterus comes to the surface to breathe at short intervals, and thus it is evident that the lungs perform an important, if not the chief, part in respiration during the active life of the animal. The air passes out again through the opercular aperture, and the movements of the operculum itself indicate the fact that bronchial as well as pulmonary respiration takes place."

Externally, the sexes present no characters whatever distinguishing them apart, and even in immature specimens it is difficult to tell ovary from testis.

In the present brief notice it will be impossible for us to even abstract the positive advances Professor Parker has made for us in our knowledge of both the anatomy and physiology of this instructive Dipnoan. He sums up handsomely on page 213, under his "General Abstract, Summary of Chief Resu'ts, and Conclusions."

His researches convince him that, although many points of resemblance exist between Protopterus and certain Elasmobranchs and Ganoids on the one hand, and on the other to some of the lower Amphibians, it exhibits numerous distinctive characters of its own, both primitive and specialized, and so, together with Lepidosiren and Ceratodus, must be placed at a great distance from either class. Further, he believes that the Dipnoi, as a group, should not be retained among the fishes, still less among the Amphibia.

[1] Dr. Günther classifies them as follows: —

	Suborder III.	Families.	Genera.
ORDER II.— Ganoidei	Dipnoi.	1. Sirenidæ	Lepidosiren, incl. Protopterus Ceratodus.
		2. Ctenododipteridæ	Two extinct genera, Dipterus and Heliodus.
		3 Phancropleuridæ	Extinct Phancropleuron.

And he remarks that "Two species are known, L. paradoxa, from the system of the river Amazon, and L. (Protopterus) annectens, which abounds in many localities of the west coast of Africa, is spread over the whole of tropical Africa, and in many districts of the central parts forms a regular article of diet."

[2] To those less familiar with the habits of this extraordinary fish, I would say that the species averages about four feet in length, and is an inhabitant of the Gambia River in Africa. They bury themselves in the mud during the dry season, making a kind of nest in which they pass a period of torpidity. Here they may remain for the best part of the year, but on the return of the wet season resume again their aquatic mode of life.

[3] In 1889, it will be remembered, Stuhlmann also gave an interesting account of Protopterus, published in German. (Berlin.)