On some of the Combinations of Mercury. By Mr. Reid.

[Read at the South African Institution.]

Mercury combines in two proportions with oxygen: the peroxide, that is the oxide containing the maximum of oxygen, being of a red colour; the protoxide or oxide containing the minimum of oxygen being blue. Each of these oxides may be combined with nitric acid, forming metallic salts.

Pernitrate of mercury, or nitric acid in combination with peroxide of mercury, is formed by the action of concentrated nitric acid, but always with an intermixture of pronitrate or acid in combination with protoxide of mercury. In order to obtain the pernitrate, pure peroxide of mercury is dissolved in nitric acid, the solution by evaporation yielding small acicular chrystals. It is extremely soluble in water, is very acrid and tinges the skin of a brown colour. The addition of water decomposes it, one part remaining in solution contains peroxide of mercury with an excess of acid, a precipitate being formed which consists of the same oxide with a diminished proportion of acid. The solution when again evaporated yields acicular chrystals as before, the excess of acid remaining in solution. When mercury is added to this solution it attracts a proportion of the oxygen from the peroxide, and both are converted into protoxide, which, uniting with the nitric acid, a pronitrate of mercury is formed instead of the pernitrate.

When mercury is exposed to the action of nitric acid diluted with two parts of water, it is slowly dissolved and pronitrate of mercury formed. The combination ceases before the whole of the acid is acted upon, but when heat is applied it recommences, and by gradually increasing the temperature when the action stops, the whole of the acid may be made to combine with the mercury forming pronitrate. In this case, however, the combination is not limited to one proportion of acid and protoxide. If the combination is stopped before the whole of the acid is taken up, it appears in the form of hexagons or hexagonal plates. If it is continued till no acid remains, the form of the chrystals is that of acicular prisms. When boiling

water is poured upon either of these salts a precipitate falls down which is of a yellow colour, and the solution deposits chrystals which are in the form of rhombs. If, instead of boiling water, cold water is poured upon the same chrystals, the precipitate which falls down is white.

It appears, therefore, that protoxide of mercury forms with nitric acid three chrystalizable compounds which may be named from their form, hexagonal, acicular, and rhombic pronitrates of mercury. Besides these, the protoxide may be united in other proportions with the acid. Thus by triturating 92 parts of mercury and 100 of peroxide with 50 of acid, adding so much water as is necessary to give the materials the consistence of a paste, a compound is formed of a white colour. The acid may be made to take up even a larger quantity of metallic oxide, but in this case more labour is necessary. The theory of the action is that the peroxide imparts one proportion of oxygen to the metal, both being converted into protoxide, which unites with the acid. The compound formed by using the above proportions is probably the same as the rhombic pronitrate, and as the precipitate which falls down when cold water is added to the hexagonal or acicular pronitrate, and probably between this compound and the yellow precipitate formerly mentioned, combination takes place in every proportion.

The hexagonal pronitrate is most readily obtained by dissolving mercury in diluted acid in the manner formerly described, the process being stopped before the whole of the acid is taken up, or, if continued, till no acid remains, by adding a small quantity of acid to the solution previously to cooling it. The solution of it in water when hot bears dilution to a considerable extent without decomposition, but when the chrystals are acted upon either by hot or cold water they are decomposed. The chrystalized salt remains permanent, in the air.

The acicular pronitrate may be obtained in the same manner as the hexagonal, continuing the process till all the acid is taken up. The solution bears dilution in the same manner as the solution of the hexagonal pronitrate, but not to the same extent. The dry chrystals when exposed to the air become yellow, a change probably resulting from the formation of hexagonal pronitrate on the one hand and of the yellow insoluble salt on the other. The presence of a very slight excess of acid prevents this change, the chrystals remaining permanent.

These two salts are convertible, the one with the other, according to circumstances. When a saturated solution of pronitrate contains only a slight excess of acid, it sometimes deposits acicular chrystals, after which the acid which remains in the solution, acting upon the chrystals, combines with them.

and changes their form into that of minute hexagons. On the other hand it sometimes happens, that, under similar circumstances, hexagonal pronitrate is formed, after which the superabundant acid in them is abstracted by the solution, and the chrystals are changed into acicular prisms.

The rhombic pronitrate is insoluble in cold water, but when acted upon by boiling water is decomposed, the water dissolving a portion of protoxide in combination with an excess of acid, and a portion of yellow insoluble pronitrate being precipitated. The rhombic pronitrate is soluble in a solution of hexagonal or acicular pronitrate, a property which enables us to obtain it rapidly. For this purpose the compound obtained by triturating peroxide of mercury, metallic mercury, and nitric acid together, in the proportions already mentioned, is exposed to a heated solution of pronitrate when a fourteenth part of the compound is dissolved, and is deposited in the form of rhombic chrystals upon cooling. By repeating this process any quantity of the chrystals may be obtained.

All the pronitrates are decomposed by ammonia, which throws down a black precipitate from each of them. This precipitate when washed with boiling water becomes blue, and this blue powder when exposed to heat is again decomposed, metallic mercury being evolved, and being evaporated, a reddish powder remains. This red powder when further urged with heat, diminishes in quantity, and a small quantity of white powder is left. From these results I am led to conclude, that this blue precipitate is not a pure protoxide of mercury, but protoxide containing a portion of the alkali.

Potash added to hexagonal or acicular pronitrate, attacts first a portion of acid, and causes the formation of a white precipitate; an additional quantity changes this to yellow; and a still larger quantity changes it to blue. These successive changes are no doubt owing to the gradual abstraction of acid from the oxide of mercury, and consequent formation, first, of the white pronitrate, similar in composition to rhombic pronitrate, and lastly of a compound containing no acid. This compound when washed with water is similar in appearance to the compound obtained from the action of ammonia, and is probably protoxide of mercury in combination with a portion of potash. Whether they shall be found to be pure protoxide, or protoxide in combination with an alkali, this and the preceding substance may, I would suggest, be advantageously employed in any case where a mild preparation of mercury is wanted.

Pernitrate of mercury when exposed to a temperature of about 600°, is converted into a red compound which has received the name of red precipitate, and of nitroxide of mercury.

The pronitrates are converted by a gentle heat into a red compound, in a state of minute mechanical subdivision. Rhombic and yellow pronitrates, by exposure to a gentle heat, also give the same compound, the proportion obtained from yellow pronitrate being smallest, and increasing according to the quantity of acid contained in each pronitrate, that from the hexagonal pronitrate being nearly equal to the quantity of mercury which it contains. The reason of this obviously is, that the oxygen required for the peroxidation of the mercury is derived from the acid, which in the yellow and rhombic pronitrates being comparatively small, there is but a small quantity of metal peroxidized, the remainder being evaporated and lost.

Red precipitate, or nitroxide of mercury, has been usually considered as a peroxide of mercury containing a small quantity of nitric acid and a larger quantity of oxygen than is contained in any other oxide of mercury. I am led to conclude, however, that this view is erroneous, and that, when properly prepared, it contains no nitric acid, and no more oxygen than is contained in the red oxide procured from the pronitrates, or in that procured by exposing mercury to the action of oxygen with the assistance of heat; that in fact, these processes all give the same compound, for each, when triturated with metallic mercury and nitric acid in the manner formerly described, oxydates the same quantity of mercury and affords the same compound. I therefore am inclined to believe, that, in making the experiments from which the common opinion is drawn, a preparation had been used in which the process of its preparation had not been continued sufficiently long, and that a portion of the pernitrate of mercury had remained undecomposed, thus influencing the products of the analysis. It appears to me, therefore, that the pronitrates may be used with advantage in preparing the red oxide of mercury instead of pernitrate; or instead of exposing mercury to heat in the open air; because of the comparatively little trouble with which it may be procured, and because, compared with the oxide procured from the pernitrate, of the greater facility with which it may be obtained pure, and in a state of minute subdivision.

Having shown that pronitrate of mercury may without difficulty be obtained free from intermixture with pernitrate, it appears to me that pure protochloride of mercury (calomel) may be made advantageously by precipitation. The process usually recommended for this purpose does not succeed, not merely because a pure pronitrate is frequently not obtained, but because the compounds resulting from the action of chloride of sodium (common salt) and pronitrate of mercury, are not nitrate of soda and protochloride of mercury, alone, but to-

gether with these, deutochloride of mercury (corrosive sublimate) and a portion of pronitrate of mercury with an excess of oxide. To prove the accuracy of this result, I triturated together chloride of sodium and protochloride of mercury, adding a little water and applying a gentle heat, and found the materials gradually became blue, a change attributable to the decomposition of the protochloride, and proving the unfitness of the chloride of sodium for the purpose intended. I think it is probable that the change is owing to the formation of a triple compound of deutochloride of mercury and sodium, in which the proportion of chlorine to mercury is as two to one, one proportion of which being abstracted from a portion of protochloride leaves in it an excess of oxide, and hence results the blue colour.

Finding these results, I employed muriatic acid instead of the chloride of sodium, which threw down a precipitate of pure calomel, and this preparation appears to me to act upon the system more mildly than calomel obtained by sublimation. To procure it, the following formula may be employed:

Take of purified mercury seven ounces, nitric acid two ounces and a half, water five ounces, pour the acid diluted with the water upon the mercury in a glass vessel, and when the effervescence has ceased, digest with a gentle heat, till the effervescence again ceases. Raise the heat as the effervescence ceases till it boils, and continue to boil for one hour, adding boiling water from time to time as the fluid evaporates. Pour off the solution from the residual mercury, and add ten pounds of boiling water. Lastly, add muriatic acid till it ceases to throw down a precipitate. Wash this precipitate with warm distilled water, so long as the fluid poured off changes the colour of litmus, and then dry it.

More mercury is here directed to be used than the acid can dissolve, but, by using an excess, the whole of the acid is more readily neutralized. By using no heat at first, and raising it gradually, the formation of pernitrate is prevented, but should any portion of it be formed, it is in the course of the action decomposed by the mercury and converted into pronitrate. However, should any portion of it when formed, not be decomposed as it forms with chlorine a soluble compound, it is removed by the washing, thus leaving the calomel perfectly pure.

To prepare the red oxide from the pronitrate, the following process may be used:

Dissolve the mercury in the acid and water as before directed, using the same proportions. Having poured off the solution from the mercury, add nitric acid half an ounce. Evaporate till a white mass remains, which being rubbed to a

powder, put it into a shallow vessel; then expose it to a heat gradually raised till it cease to emit red vapours.

Nitric acid is here directed to be added to the solution in order that the protoxide of mercury may be saturated with acid, from which a sufficient quantity of oxygen may be derived to convert the mercury into peroxide, and thus the largest quantity from the materials used be obtained.

It deserves notice, that when calomel, red oxide of mercury, and mercury, are rubbed together, moistened with water, they combine and form a blue compound, a result which does not appear strange if we adopt the old theory of the constitution of muriatic salts, and consider this as a compound of muriatic acid and protoxide of mercury, the protoxide being in excess analogous to the combination of protoxide of mercury and nitric acid; but if we adopt the new theory, that calomel is a compound of chlorine and mercury, and does not contain oxygen, the result appears rather singular, for, in this instance, we obtain a compound altogether different from the other chlorides, in this respect, that oxygen does enter into its composition. According to this view it is a compound of chlorine, mercury, and protoxide of mercury.