XVI.—*Cadmium and Zinc Nitrites.*

By PRAFULLA CHANDRA RÂY.

IN view of the contradictory statements of the previous workers in this field, it seemed desirable to undertake a fresh investigation of cadmium and zinc nitrites.

At the outset it may be pointed out that, so far as the nitrite-forming capacity of mercury and cadmium is concerned, the question is not one of the basic character of the metal. Mercury,* which occupies the lowest position in group II B (in the electro-potential series), yields a fairly stable normal nitrite, because both its chloride and nitrite are very feebly dissociated in aqueous solution (Rây and Dhar, T., 1912, **101**, 966). Thomsen found that mercuric oxide with its equivalent of aqueous hydrochloric acid evolves 18,920 calories, whereas with its equivalent of nitric acid it evolves only 6400 calories, and to this difference he ascribes the reason that an aqueous solution of mercuric nitrate is completely converted into chloride by the addition of an aqueous solution of hydrochloric acid. Mercuric chloride in aqueous solution is again completely converted into the cyanide by the addition of hydrocyanic acid. Cadmium hydroxide also behaves differently towards the ordinary mineral acids. Thus, whilst zinc and magnesium hydroxides with hydrochloric, hydrobromic, and hydriodic acids, respectively, give almost the same value for the heat of neutralisation, namely, about 19,500 calories, with cadmium hydroxide the heat of neutralisation goes on increasing. Thomsen regarded the behaviour of cadmium oxide towards the above acids as exceptional, and on that account he refused to class cadmium hydroxide in the magnesium group ("Thermochemische Untersuchungen," III, 279 *et seq.*; also English translation by Miss Burke, p. 129). The anomalous behaviour of cadmium is now easily accounted for. Its haloids are more feebly ionised than those of zinc and magnesium under similar conditions of dilution. In fact, it may be laid down as a safe guiding principle that a metal the haloid of which shows comparatively poor conductivity in aqueous solutions may be expected to yield a corresponding normal nitrite, because, as a rule, its nitrite is also feebly ionised. The case of cadmium has been chosen as a crucial one.

Conductivity measurements of cadmium chloride have been carried out by several investigators, but as their results show con-

* The author has pointed out that mercury occupies a twofold position in the Periodic System (see T., 1905, **87**, 180; also *Chem. News*, 1914, **109**, 85)

siderable discrepancy, a fresh measurement has been made. It will be seen on reference to table I (p. 161) that at a dilution of 10 litres, the equivalent conductivity of potassium chloride is 134 at 29°, that of cadmium chloride is 53, whilst that of cadmium nitrite is only 33. Both these circumstances conduce to the stability of the nitrite, and it has thus been isolated as a normal salt.

Zinc nitrite, which can exist only in dilute solution, under similar conditions has a conductivity of 73 (Rây and Dhar, T., 1913, **103**, 13). It is well known that zinc chloride is so readily hydrolysed that, on the addition of water, a turbid liquid is obtained, due to the formation of the compound Zn(OH)Cl . Zinc nitrite solution is acid, and, on concentration, the nitrous acid set free decomposes according to the equation

and thus zinc nitrate is continuously formed. The residue, even if the evaporation is conducted in a vacuum, is thus found to be a basic nitrate.

EXPERIMENTAL.

Cadmium Nitrite.

Pure, recrystallised cadmium chloride and silver nitrite were triturated in a mortar, water being added from time to time until the filtrate gave no indication of excess of either of the parent substances; it was then evaporated in a vacuum over sulphuric acid. Bright, pale yellow crystals were obtained which dissolved readily to a clear solution. Preparation III was the product of double decomposition between calculated quantities of barium nitrite and cadmium sulphate:

I. 0.3465 gave 0.2474 CdS. Cd=55.53.

0.035 „ 4.35 c.c. N_2 (nitritic) at 29° and 760 mm.
N=13.79.

II. 0.2740 gave 0.1926 CdS. Cd=54.66.

0.1387 „ 16.4 c.c. N_2 (by combustion) at 26° and 760 mm. N=13.26.

III. 0.0820 gave 0.0582 CdS. Cd=55.20.

$\text{Cd(NO}_2)_2$ requires Cd=54.90; N=13.73 per cent.

Apart from the results of the analysis, the fact that the salt did not lose its lustre, even in an exhausted desiccator, proves that it is anhydrous. Lang (*J. pr. Chem.*, 1862, **86**, 299), however, assigns to it the formula $\text{Cd(NO}_2)_2 \cdot \text{H}_2\text{O}$. Several preparations were undertaken, but in only two instances was the evaporated mass found to be partly insoluble in water (compare Vogel,

Zeitsch. anorg. Chem., 1903, **35**, 402). Cadmium nitrite is ionised to a far greater extent than mercuric nitrite (Rây and Dhar, T., 1912, **101**, 966), and the tendency towards the formation of a basic salt is thus easily explained.

Conductivity Measurements.

The chloride was purified by recrystallisation (0.4391 gave 0.6284 AgCl; $\text{CdCl}_2 = 91.43$. $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ requires $\text{CdCl}_2 = 91.50$ per cent.).

TABLE I.

Equivalent Conductivity of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ at 29.5° .

v	10	20	40	80	160	320	640
λ	53.53	63.60	73.76	84.4	94.31	102.1	104.15

Equivalent Conductivity of $\text{Cd}(\text{NO}_2)_2$ at 29° .

v	10	20	40	80	160	320	640	1024
λ	33.7	43.9	55.1	67.1	78.3	88.3	96.1	104.6

Decomposition by Heat.

The method of heating has been described in detail in the case of the alkali nitrites (*loc. cit.*, p. 180). The salt began to decompose slowly at 150° . The temperature was gradually raised to 165° , and finally to 230° , when the 'click' remained persistent.

The gas which was collected in the reservoir of the mercury pump was found to be pure nitric oxide, it being completely absorbed by an alkaline solution of sodium sulphite. The alkaline liquid in the glass spiral was washed out, and was found to consist of a mixture of nitrite and nitrate in the following proportion :

$$\frac{\text{Nitritic nitrogen}}{\text{Nitratie nitrogen}} = 3.$$

The brown residue was found to be cadmium nitrate mixed with cadmium oxide. As nitric oxide was the chief gaseous product, the main portion of the salt evidently decomposed according to the equation

Side by side, a parallel decomposition goes on thus :

Divers has shown that when nitrogen peroxide mixed with an excess of nitric oxide is passed into a solution of alkali, pure nitrite is thereby produced (T., 1899, **75**, 86). In the present instance, although there was a large excess of nitric oxide, the conditions of reaction were not comparable. The gaseous mixture was not

bubbled through a liquid, but was quickly drawn across the glass beads moistened with alkali hydroxide. Moreover, Dixon and Peterkin have shown that "the peroxide enters into a limited combination with nitric oxide" (*ibid.*, p. 629). A small quantity of nitrogen peroxide is absorbed as such, giving rise to the formation of a nitrate as well.

Zinc Nitrite.

The salt was prepared by double decomposition between molecular proportions of zinc sulphate and barium nitrite. The filtrate, on evaporation in a vacuum, left a white, swollen mass, which was practically insoluble in water. There was a thin membrane coating the surface which, on being broken up, evolved nitrous fumes. During the concentration of the liquid, nitric oxide was continuously evolved, a portion of which remained imprisoned inside the thin, superficial coating. The residue was boiled with a solution of pure sodium hydroxide, and the alkaline liquid was found to be free from nitrite and to contain only nitrate. It will thus be seen that zinc nitrite solution, on evaporation to dryness, leaves a residue only of a basic nitrate.

CHEMICAL LABORATORIES,
PRESIDENCY COLLEGE AND COLLEGE OF SCIENCE,
UNIVERSITY OF CALCUTTA.

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