# CCXXXVII.—*The Ternary System Zinc Oxide–Nitric Acid–Water.*

By Henry George Denham and David Andrew Dick.

Although at least sixteen basic nitrates of zinc have been described (Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. IV, pp. 654 *et seq.*), the methods adopted by the various workers have generally been such as to render it highly improbable that the conditions were likely to lead to the separation of a solid in stable equilibrium with the solution. The systematic application of the phase rule to ternary systems—basic oxides, acid, water—has generally proved conclusively that many of the reported basic compounds of the metals are merely mixtures, the presence of mother-liquor or incipient decomposition of the solid through injudicious washing causing an analytical result which was likely to lead to a fallacious conclusion. It was therefore decided to make such a study of the above system at 25° and 50° in order to fix the identity of the basic nitrates which were capable of existence in stable equilibrium with the solutions chosen. The graphical method of representation used is the equilateral triangular diagram originally suggested by Gibbs. The composition of the solid phases was found by Schreinemakers's "residue" method (*Z. physikal. Chem.*, 1893, **11**, 76).

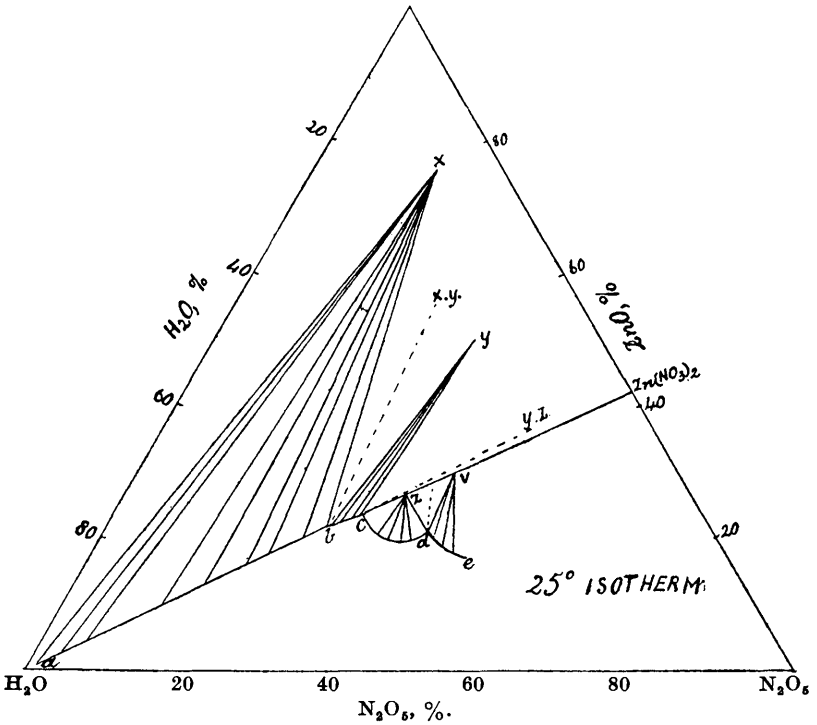
## Experimental.

The method of estimating the zinc was as described by Holland (J., 1930, 643) except that, in order to prevent reaction of nitric acid with the diphenylbenzidine indicator, it was found advisable to expel the acid by evaporation with sulphuric acid as subsequently described. Nitric acid was determined by the Kjeldahl method, reduction to ammonia being effected by powdered

Devarda's alloy in the presence of an excess of nitrogen-free sodium hydroxide. All solutions were standardised in triplicate and repeatedly checked throughout the work. Chemicals of A.R. quality were used, and all volumetric apparatus standardised before use.

Complexes were never made up from zinc nitrate, but always from zinc oxide, nitric acid, and water. A stock of solution of nitric

FIG. 1.



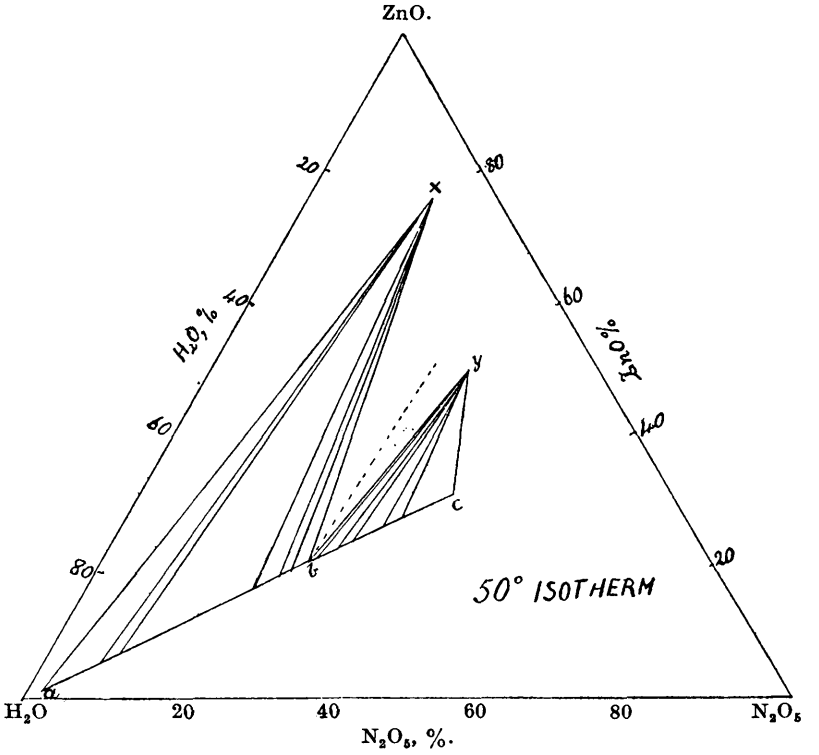

acid neutralised with zinc oxide of known concentration was first prepared and a definite volume of this solution together with a calculated quantity of zinc oxide and water was used to make up a series of well-spread complexes containing convenient quantities of wet solid. Each complex was calculated to give 10—15 g. of wet solid and 20—30 c.c. of solution. Care had to be exercised to prevent the formation of lumps during the mixing. In some cases cautious sprinkling of the oxide into the solution sufficed, but in the dilute solutions it was generally found advisable to add a

thoroughly incorporated thin paste of oxide and water to the nitrate solution. Occasionally it was found necessary to warm the mixture and after vigorous shaking to decant the milky liquid with its fine precipitate of oxy-nitrates into another bottle which was then cooled and sealed. The bottles containing the complexes were then shaken in a thermostat at 25° or 50° for 3 days. That the contents had reached a state of real and not apparent equilibrium was proved by the agreement obtained between complexes prepared at atmospheric temperature and in boiling solution and then shaken for another day at the final temperature, also by the agreement given in tests run for 3 and for 5 days. The solutions were then filtered in a small filtering apparatus immersed in the thermostat, a convenient quantity of the filtered solution delivered into a weighing bottle, and used for the density determination and for analysis. The residual solid still containing roughly twice as much solution as solid was similarly treated. Generally about 10 g. of the wet solid were weighed out, dissolved in a little sulphuric acid, and diluted to 250 c.c. Of this, 25 or 50 c.c. were taken according to concentration, and used in the estimation of nitrate; a similar quantity was placed in an evaporating dish with 5—10 c.c. of concentrated sulphuric acid, and the nitric acid expelled by heating in an air-bath, so constructed that the heat was radiated on to the solution from above. The nitrate-free solution was then diluted to 200 c.c. and a convenient portion taken for the zinc titration. From the weights of zinc and nitrogen thus found by analysis in a known weight of residue or of solution, their percentage composition was readily calculated.

| | | Solution. | | | Residue. | | | |
|---|---|---|---|---|---|---|---|---|
| No. | *D*. | $N_2O_5$. | ZnO. | $H_2O$. | $N_2O_5$. | ZnO. | $H_2O$. | |
| | | | | *Data at 25°.* | | | | |
| 1 | 1·015 | 1·0 | 0·8 | 98·2 | 5·3 | 21·0 | 73·7 | |
| 2 | 1·047 | 3·2 | 2·5 | 94·3 | 6·2 | 25·2 | 68·6 | |
| 3 | 1·094 | 5·7 | 4·6 | 89·7 | 9·0 | 25·0 | 66·0 | |
| 4 | 1·218 | 12·7 | 9·7 | 77·6 | 13·6 | 28·4 | 58·0 | X |
| 5 | 1·302 | 16·9 | 12·7 | 70·4 | 16·7 | 31·4 | 51·9 | |
| 6 | 1·380 | 20·3 | 15·5 | 64·2 | 17·6 | 42·3 | 40·1 | |
| 7 | 1·438 | 22·5 | 17·2 | 60·3 | 21·2 | 30·5 | 48·3 | |
| 8 | 1·545 | 26·5 | 20·4 | 53·1 | 23·9 | 34·8 | 41·3 | |
| 9 | 1·585 | 27·9 | 21·5 | 50·6 | 24·9 | 41·2 | 33·9 | X, Y |
| 10 | 1·615 | 28·9 | 22·0 | 49·1 | 30·5 | 31·1 | 38·4 | |
| 11 | 1·657 | 30·6 | 22·0 | 46·5 | 31·0 | 27·2 | 41·8 | Y |
| 12 | 1·680 | 31·2 | 23·3 | 45·5 | 31·7 | 29·2 | 39·1 | |
| 13 | 1·695 | 31·8 | 23·5 | 44·7 | 36·5 | 28·0 | 35·5 | Y, Z |
| 14 | 1·674 | 33·5 | 22·0 | 44·5 | 35·0 | 24·0 | 41·0 | Z |
| 14 | 1·679 | 39·6 | 20·2 | 40·2 | 38·7 | 22·4 | 38·9 | Z |
| 15 | 1·736 | 42·7 | 21·4 | 36·1 | 40·6 | 23·4 | 36·0 | Z |
| 16 | 1·737 | 42·6 | 21·4 | 36·0 | 40·4 | 25·0 | 34·6 | Z, V |
| 17 | 1·737 | 42·6 | 21·3 | 36·1 | 42·2 | 25·0 | 32·8 | V |
| 18 | 1·695 | 45·6 | 18·6 | 35·8 | 44·0 | 23·2 | 32·8 | V |

| No. | *D*. | Solution. $N_2O_5$. | ZnO. | $H_2O$. | Residue. $N_2O_5$. | ZnO. | $H_2O$. | |
|---|---|---|---|---|---|---|---|---|
| | | | | *Data at* 50°. | | | | |
| 1 | 1·022 | 1·6 | 1·4 | 97·0 | 6·2 | 24·0 | 69·8 | |
| 2 | 1·116 | 7·5 | 5·9 | 86·6 | 10·6 | 32·1 | 57·3 | |
| 3 | 1·401 | 21·6 | 16·9 | 61·5 | 20·0 | 34·1 | 45·9 | X |
| 4 | 1·476 | 24·7 | 19·0 | 56·3 | 22·3 | 35·0 | 42·7 | |
| 5 | 1·503 | 25·6 | 19·9 | 54·5 | 23·7 | 30·1 | 46·2 | |
| 6 | 1·544 | 26·7 | 20·8 | 52·5 | 27·8 | 31·0 | 41·2 | X, Y |
| 7 | 1·571 | 27·4 | 21·3 | 51·3 | 29·2 | 30·0 | 40·8 | |
| 8 | 1·613 | 29·5 | 22·6 | 47·9 | 30·8 | 31·0 | 38·2 | |
| 9 | 1·660 | 31·1 | 23·8 | 45·1 | 31·6 | 31·7 | 36·7 | Y |
| 10 | 1·750 | 34·4 | 26·4 | 39·2 | 34·5 | 30·0 | 35·5 | |
| 11 | 1·793 | 36·0 | 27·2 | 36·8 | 35·5 | 31·4 | 33·1 | |
| 12 | 1·941 | 40·8 | 30·9 | 28·3 | 39·0 | 35·5 | 25·5 | |

FIG. 2.




From the points of intersection of the tie-lines in the diagrams the composition and hence the formula of the solids may be inferred. In both diagrams X = $Zn(NO_3)_2,5ZnO,3H_2O$ and Y = $Zn(NO_3)_2,ZnO,3H_2O$. These are the only basic nitrates of which any indication has been given by the experiments carried out under the conditions specified. The diagrams for both temperatures bear

a strong resemblance to each other, the only difference being that the area Ybc for the higher temperature is considerably enlarged, indicating that $Zn(NO_3)_2,ZnO,3H_2O$ may exist at 50° in stable equilibrium with solutions considerably stronger in zinc nitrate than is the case at 25°. The above basic nitrates have already been described, the pentoxy-nitrate by Ordway (*Amer. J. Sci.*, 1859, **32**, 14) and Bettels (Mitt. Laborat. von Hilger, 1874, 11), and the monoxynitrate by Wells (*Amer. Chem. J.*, 1887, **9**, 304).

At 25° definite evidence was obtained concerning the existence of a hexahydrate [Z = $Zn(NO_3)_2,6H_2O$], colourless four-sided prisms, and of a tetrahydrate [V = $Zn(NO_3)_2,4H_2O$], thin rhomboidal crystals. The tetrahydrate was described by Wasilieff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 744), and the hexahydrate by Graham (*Phil. Trans.*, 1837, **127**, 47) and Millon (*Compt. rend.*, 1842, **14**, 905), and their results were confirmed by Mylius and Funk's solubility measurements of zinc nitrate (*Z. anorg. Chem.*, 1897, **30**, 1718).

*Summary.*

1. The composition of the solid phases in equilibrium with solutions in the three-component systems $ZnO–HNO_3–H_2O$ has been studied at 25° and 50° by the " residue " method of Schreinemakers.

2. Definite evidence of two basic nitrates only was obtained in the range of solution studied, *viz.*, $Zn(NO_3)_2,5ZnO,3H_2O$ and $Zn(NO_3)_2,ZnO,3H_2O$.

3. The existence of a normal hexahydrate and tetrahydrate has been confirmed.

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