

331. *The Ternary System Mercurous Oxide–Nitrogen Pentoxide–Water.*

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MUCH confusion exists in the literature concerning the salts of mercurous oxide and nitric acid, more than thirty different compounds having been described, most of them of a basic nature (Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. IV, p. 988). Of the methods recorded, that used by Cox (*Z. anorg. Chem.*, 1904, **40**, 146) is alone likely to have led to the isolation of anything in the nature of a definite chemical compound, and even his procedure can scarcely be relied upon to give incontrovertible evidence of the chemical identity of the basic salt obtained. A study of the above system at 25° was therefore undertaken by the Schreinemakers "residue method" (*Z. physikal. Chem.*, 1893, **11**, 76).

In the case of the normal salt, mixtures of the required amounts of nitric acid, water, and finely ground mercurous nitrate were shaken in sealed glass bottles until equilibrium was established. For the preparation of basic salts two methods were used: (1) the nitrate was shaken with the necessary amount of water, (2) mercurous oxide was shaken with nitric acid. The mercurous oxide was prepared, as required, by the action of aqueous sodium hydroxide on a solution of mercurous nitrate containing excess of nitric acid. The precipitation and washing were done at 0° and all operations were carried out in a dark room. Every endeavour was thus made to prevent auto-oxidation of the oxide prior to use. Rapid formation of a precipitate of uniform appearance took place, but the mixtures were always shaken for 4 or more days

before analysis, considerably longer than experiments showed to be actually necessary. After filtration the solution and the wet solid were separately analysed.

Analysis of the Solution.—A convenient fraction was treated with dilute nitric acid and electrolysed at 50° with a current density of 1 amp. per sq. cm., flag electrodes being used. For the estimation of the nitrate a modification of the Devarda method (*Z. anal. Chem.*, 1894, 33, 113) was rendered necessary through the formation of mercury–ammonia compounds. It was found advisable to remove the mercury by adding an excess of concentrated sodium hydroxide solution, the precipitated oxide after thorough washing being rejected. The method was checked by the analysis of a solution of sodium nitrate shaken with mercurous oxide, and proved accurate.

Analysis of the Solid.—The wet solid was stirred, first in the weighing-bottle and then in a beaker, with concentrated sodium hydroxide solution, the oxide removed, and the nitrate estimated in an aliquot part of the filtrate. The residue of mercurous oxide was dissolved in nitric acid, and an aliquot fraction taken for analysis: to compensate for the small but definite solubility of mercurous oxide, there was added to this solution of mercurous nitrate an equal fraction of the solution used for the nitrate estimation, and the mercury content was determined.

The results are in Table I. The percentage of water was obtained by difference.

TABLE I.

D.	Solution.		Wet solid.		Solid phase.	D.	Solution.		Wet solid.		Solid phase.	
	Hg ₂ O.	N ₂ O ₅ .	Hg ₂ O.	N ₂ O ₅ .			Hg ₂ O.	N ₂ O ₅ .	Hg ₂ O.	N ₂ O ₅ .		
1·039	3·03	1·00	61·1	7·80	A	1·370	31·40	12·12	68·20	18·37	α-D	
1·058	4·64	1·40	52·40	7·20		1·557	31·00	12·10	67·60	18·14		
1·058	4·71	1·43	61·80	8·35		1·447	26·88	12·27	67·60	18·36		
1·060	4·85	1·50	52·95	7·00		1·436	24·93	12·67	66·13	18·00		
1·082	6·55	2·30	64·10	8·25		1·396	22·30	12·87	65·40	18·37		
1·095	7·57	2·44	67·48	8·80		1·394	22·13	13·00	66·65	18·50		
1·113	8·66	3·01	71·20	9·65		1·382	21·21	13·30	66·30	18·39		
1·117	9·10	3·20	68·00	10·08		1·368	20·16	13·30	65·25	18·27		
1·117	9·14	3·24	65·13	9·95		1·359	19·25	14·00	64·83	18·50		α- and β-D
1·139	10·46	3·61	69·90	10·90		1·364	19·51	14·35	—	—		
1·200	15·10	5·44	66·25	11·10	1·366	19·63	14·53	65·80	18·53	α-D metastable		
1·227	15·90	5·68	66·10	11·21	1·374	19·93	14·63	66·83	18·68			
1·275	18·42	6·60	67·50	11·40	1·455	22·97	15·84	65·80	18·82			
1·328	21·10	7·70	61·80	11·45	1·464	23·30	16·20	66·86	18·80			
1·366	23·53	8·22	68·90	11·98	1·563	27·65	17·20	65·35	18·75			
1·450	27·28	9·61	70·53	12·47	1·638	30·80	18·00	62·10	18·80			
1·465	27·87	9·80	64·90	12·07	1·781	34·88	19·35	64·20	19·30			
1·502	29·30	10·40	68·20	13·55	1·485	26·38	13·29	—	—			
1·503	29·33	10·47	69·55	12·61	1·468	25·38	13·30	68·12	18·60			
1·510	29·70	10·50	71·52	14·82	1·442	24·22	13·55	66·00	18·35			
1·517	29·86	10·69	65·95	14·20	1·372	20·18	13·81	—	—	β-D metastable		
1·527	30·18	10·75	69·15	14·20	1·405	22·12	13·82	67·60	18·62			
1·565	31·76	11·20	68·70	14·64	1·365	19·84	13·87	—	—			
1·608	32·98	11·78	69·47	16·68	1·364	19·62	13·90	—	—			
1·608	33·01	11·80	68·10	15·63	1·359	19·25	14·00	64·85	18·50	β-D		
					1·358	18·17	16·30	65·58	18·82			
					1·426	20·66	17·70	66·50	18·70			

In Table I and Fig. 1, A represents 2Hg₂O, N₂O₅, H₂O, B is 5Hg₂O, 3N₂O₅, 3H₂O, C is 4Hg₂O, 3N₂O₅, H₂O, and D is Hg₂(NO₃)₂, 2H₂O, which exists in an α- and a β- form (see p. 1418). A number of the basic solid phases prepared from mercurous oxide were somewhat grey in appearance—a point also noted by Cox—probably owing to the presence of mercury resulting from slight decomposition of this unstable oxide.

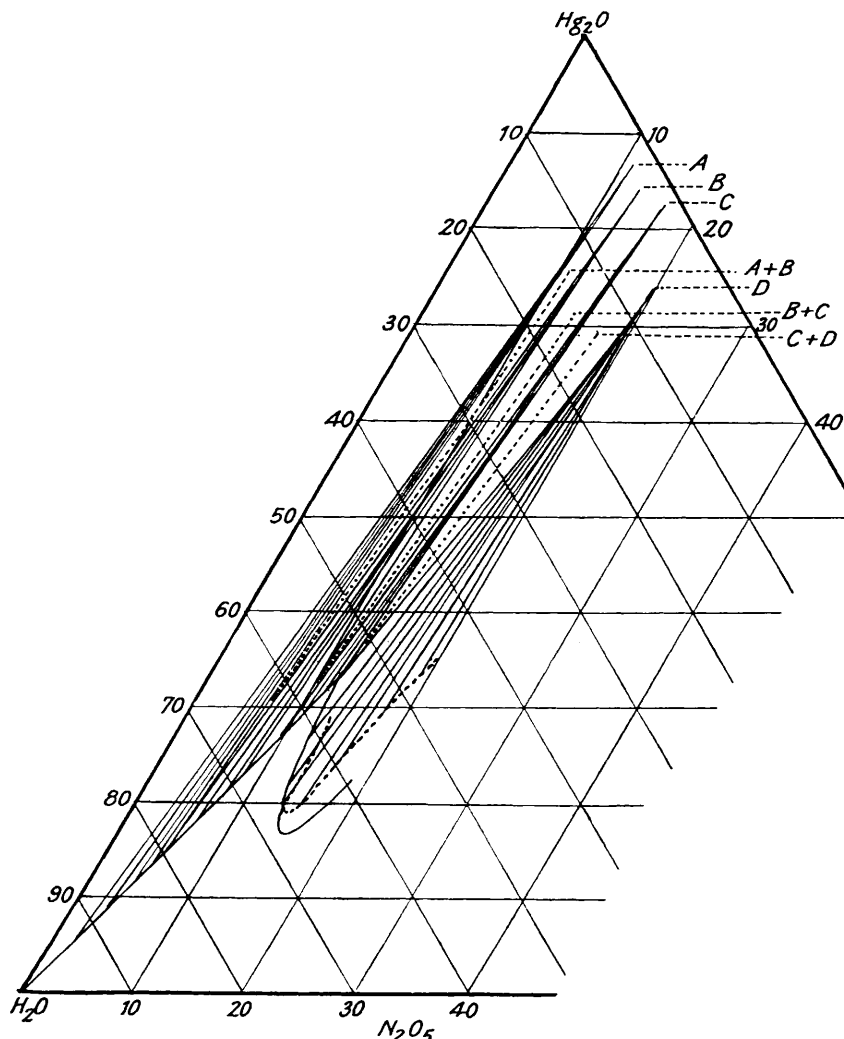
In view of the restricted area in which each basic salt exists, it was deemed advisable to confirm the degree of hydration of the basic nitrate as interpreted from the graph by preparing the dry solid in a reasonable state of purity. This was done by placing a thin layer of the wet solid on a porous plate, and a crucible containing some of the equilibrium solution, in a desiccator at 25°; after 48 hours the plate was removed and the solid analysed. In Table II the two samples of each basic salt analysed were taken from different complexes. The water content of the hydrated normal nitrate could be estimated accurately from the tie-lines, but a single porous-plate sample was prepared and analysed for comparison.

These results confirm those indicated by the graphical method of triangular co-ordinates.

TABLE II.

No.	Phase.	% calc.			% found.		
		Hg ₂ O.	N ₂ O ₅ .	H ₂ O	Hg ₂ O.	N ₂ O ₅ .	H ₂ O.
1	2Hg ₂ O, N ₂ O ₅ , H ₂ O	86.88	11.25	1.87	86.31	11.86	1.83
		86.88	11.25	1.87	86.40	11.78	1.82
3	5Hg ₂ O, 3N ₂ O ₅ , 3H ₂ O	84.66	13.15	2.19	84.42	13.29	2.28
		84.66	13.15	2.19	84.42	13.37	2.21
5	4Hg ₂ O, 3N ₂ O ₅ , H ₂ O	83.00	16.10	0.90	83.20	15.98	0.82
		83.00	16.10	0.90	82.81	16.24	0.95
7	Hg ₂ (NO ₃) ₂ , 2H ₂ O	74.34	19.24	6.42	74.15	19.35	6.50

FIG. 1.

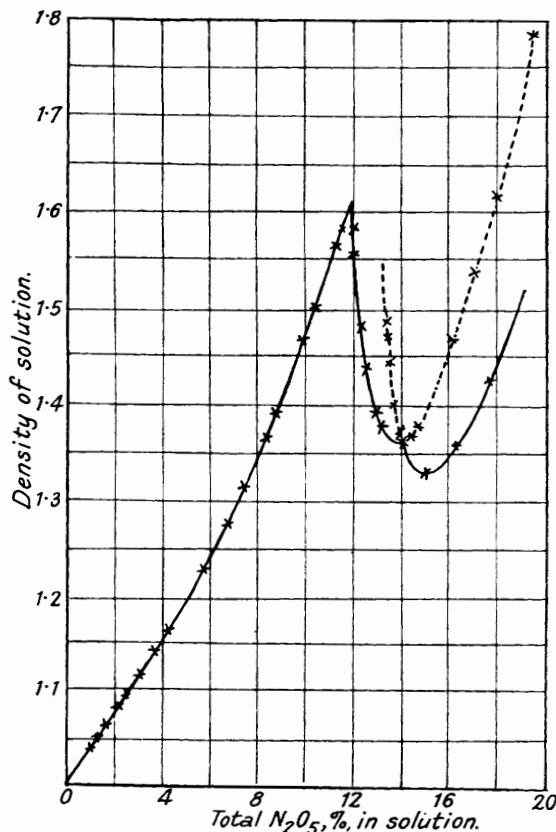


The monohydrated mercurous monoxynitrate, $\text{Hg}_2\text{O}, \text{Hg}_2(\text{NO}_3)_2, \text{H}_2\text{O}$, already described by Cane (*Trans. Irish Acad.*, 1838, **19**, 1), is probably the same salt as that described by Lefort (*J. Pharm. Chim.*, 1845, **8**, 5), who attributes to it two molecules of water. The *trihydrated mercurous dioxytrinitrate*, $2\text{Hg}_2\text{O}, 3\text{Hg}_2(\text{NO}_3)_2, 3\text{H}_2\text{O}$, is new, and the monohydrated monoxytrinitrate, $\text{Hg}_2\text{O}, 3\text{Hg}_2(\text{NO}_3)_2, \text{H}_2\text{O}$, has been described by de Marignac (*Ann. Chim. Phys.*, 1849, **27**, 332).

Fig. 1 indicates the existence of two forms of the hydrated normal nitrate, $\text{Hg}_2(\text{NO}_3)_2, 2\text{H}_2\text{O}$

(compare Cox, *loc. cit.*, for $\text{HgNO}_3 \cdot \text{H}_2\text{O}$), but no confirmation of the numerous hydrates postulated by Reuss ("Beiträge zur Kenntnis der salpetersäuren Quecksilber-oxydulsalze," Freiburg, Dissertation, 1886) was obtained. Both the α - and the β -modification belong to the orthorhombic system and are tabular in the plane of the lateral axes. In the β -form the only faces developed in addition to the basal planes are prism faces and macropinacoids. The α -form is

FIG. 2.



characterised by the presence of brachydomes, brachypinacoids, and pyramid faces in addition. The β -crystals also show a tendency to crystallise in half-forms, possibly hemimorphic. The solubility curves of each form can be followed into the metastable region. Confirmation of the conclusions concerning these two modifications arrived at from Fig. 1 is afforded by Fig. 2, wherein the density (D) of the solution is plotted against the percentage of "total N_2O_5 " in the solution.

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