The Oxychlorides of Mercury. Equilibrium in the System: Mercuric Chloride, Yellow Mercuric Oxide and Water at 35°C.

By

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The oxychlorides of mercury have been studied by many investigators and a series of the compounds have been described.[1] The following is a summary of those oxychlorides found in the literature:

Compounds.	Observers.
$2HgCl_2.HgO$	Roucher, Thuemmel, Arctowski, Schoch.
$HgCl_2.HgO$	Roucher, Thuemmel, Tarugi.
$HgCl_2 2.HgO$	Millon, Roucher (in 3 modifications), Thuemmel, Arctowski, Tarugi, Volhard, Schoch (in 3 modifications).
$HgCl_2.2HgO.\frac{1}{2}H_2O$	Ray.
$BgCl_2\,3HgO$	Millon, Roucher (in 3 modifications),

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1 E. Millon, Ann. chim. phys., (3) **18**, 372 (1846);
C. Roucher, ibid, (3) **27**, 353 (1849); J. pr. Chem., **49**, 363 (1850);
K. Thuemmel, Arch. Pharm., **227**, 589 (1886);
M. G. André, C. R., **104**, 431 (1887);
H. Arctowski, Z. anorg. Chem., **9**, 176 (1895);
J. Volhard, Ann. Chem., **255**, 252 (1889);
P. C. Ray, Proc. Chem. Soc., **15**, 103 (1899); Ann. Chem., **316**, 255 (1901);
N. Tarugi, Chem. Centralbl., **72 II**, 1147 (1901) from Gaz. chim. ital., **31 II.**, 313;
E. P. Schoch, Amer. Chem. J., **29**, 319 (1903).

	Andre, Tarugi, Schoch (in 3 modifications).
$2HgCl_2.3HgO$	André, Arctowski.
$HgCl_2.4HgO$	Millon, Roucher (in 4 modifications), Thuemmel, Arctowski, Schoch (in 3 modifications).
$HgCl_2.5HgO$	Roucher.
$HgCl_2.6HgO$	Roucher (in 2 modifications).
$HgCl_2.6HgO\ H_2O$	Roucher.

Tarugi explained all the oxychlorides except the three compounds, $HgCl_2.3HgO$, $HgCl_2.2HgO$, and $HgCl_2.HgO$, to be mixtures of indefinite chemical composition.

As seen from the above cited literature, a systematic investigation of the oxychlorides of mercury was desirable and on the suggestion of Prof. Y. Osaka, the writer took up the problem to study it from the standpoint of the phase rule, taking mercuric chloride, yellow mercuric oxide and water as the components.

The materials were prepared as follows: Mercuric chloride of Jap. Pharm. was purified by thrice recrystallisation, and mercuric oxide was prepared by the methods given in L. Vanino's Handbuch.[1]

The experiments were carried out in the following way: Mixtures of salts in different proportions were put each in an Erlenmeyer flask of a capacity of about 30 c.c. with a well ground stopper, which was made to rotate in a thermostat at 35°C. for about three days and nights. When equilibrium was attained, the flask was allowed to stand still in the same thermostat until the suspended matter had completely subsided, then a proper portion of the mother liquor was taken out by a pipette, through a short glass tube filled with purified cotton and attached to the pipette by a rubber tubing, to a weighing bottle and subjected to analysis.

To prepare the residue for analysis, it was pressed down between folded filter paper to remove the adhering mother liquor as much as possible, then a part of it, previously weighed, was redissolved in water with the addition of the necessary quantity of nitric acid. The solution thus obtained was diluted to a definite volume and divided into proper portions, for analysis.

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[1] Handbuch der preparativen Chemie, I, 461.

The methods of analysis used were as follows: Hydrogen sulphide solution which was absolutely free from chlorine was added to the sample to remove the mercury. It was gently boiled until the excess of hydrogen sulphide was expelled, then the precipitate was filtered and washed five times with hot water. The filtrate was used for the determination of chlorine according to Volhard's method, improved by V. Rothmund and A. Burgstaller.

Mercury was precipitated as mercuric sulphide with ammonium sulphide, prepared as directed in Vanino's Handbuch.[1] It was collected in a Gooch crucible, dried at 110°C. and weighed.

Results.

The results are given in the following table:—

TABLE I.

	Solution.		Residue.[2]	
No.	$HgCl_2$ in gram percentage.	HgO in gram percentage.	$HgCl_2$ in gram percentage.	HgO in gram percentage.
1	8·58	—	—	—
2	8·72	0·14	96·82	1·65
3	8·68	0·07	76·88	16·50
4	8·69	0·10	60·55	30·67
5	8·81	0·03	53·07	37·68
6	8·70	0·11	40·34	50.03
7	8·69	0·10	37·01	55·19
8	4·39	0·09	36·13	58·41
9	3·42	0·06	37·01	55·19
10	0·66	0·02	36·13	58·42
11	0·66	0·02	30·14	57·70
12	0·61	0·02	22·28	59·20
13	0·23	0·03	21·68	61·07
14	0·20	0·06	20·84	59·46
15	0·13	0·04	16·55	55·09
16	0·07	0·04	16·40	50·05
17	0·05	0·03	10·36	69·80
18	0·05	0·04	6·48	77·24

[1] Loc. cit., 337.

[2] The residue was slightly wet with the mother liquor.

19	0·04	0·04	1·10	83·26
20	0·01	0·03	0·35	90·04
21	—	0·001	—	—

The following table was calculated from the last, using the following formula to represent the compositions of the solutions and residues:

$$100m\ H_2O\ x HgCl_2\ (100\text{-}x)HgO$$

and in the table, a function of m, $N = \frac{100m}{100+m}$, was calculated to represent the amount of water.

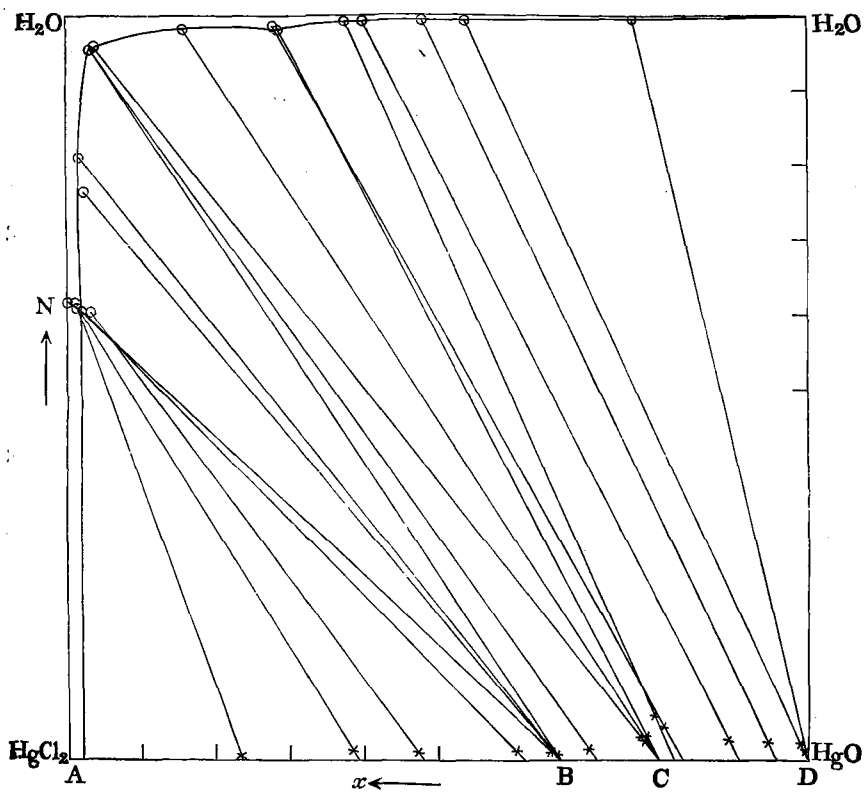
TABLE 2.

	Solution.		Residue.		
No.	N	x	N	x	Formula of the residue found graphically.
1	61·63	100·00	—	—	$HgCl_2$
2	60·69	97·99	0·23	97·92	$HgCl_2 + HgCl_2.2HgO$
3	61·50	99·00	0·69	76·83	,, ,,
4	60·98	98·64	1·32	61.16	,, ,,
5	60·06	96·58	1·37	52·89	,, ,,
6	60·88	98·50	1·39	39·15	,, ,,
7	60·94	98·64	1·09	34·86	$HgCl.2HgO$
8	76·18	97·53	0·75	33·03	,,
9	80·63	98·00	1·10	34·86	,,
10	95·62	96·81	0·74	33·05	,,
11	95·61	96·78	1·76	29·42	$HgCl_2.2HgO + HgCl_2.4HgO$
12	95·92	96·23	2·81	23·10	$HgCl_2.4HgO$
13	98·21	84·10	2·64	22·07	,,
14	98·20	71·34	3·02	21·86	,,
15	98·81	72·03	4·76	19·34	$HgCl_24HgO + HgO$
16	99·22	62·24	6·01	20·72	,, ,,
17	99·42	59·92	2·96	10·58	,, ,,
18	99·38	51·81	2·33	6·27	,, ,,
19	99·45	46·08	2·19	1·05	HgO
20	99·67	23·31	1·26	0·31	,,
21	100·00	0·00	—	—	,,

The above results are graphically shown in Fig. 1, in a square

diagram, measuring water (N) on the vertical side and molarpercentages of the chloride (x) on the horizontal side.

Fig. 1.



From this figure, it may be easily seen that we have only two definite oxychlorides represented by the points B and C, corresponding to the formula, $HgCl_2.2HgO$ and $HgCl_2.4HgO$, respectively. The oxychloride, $HgCl_2.4HgO$, forms probably some solid solution with the oxide, but the data are insufficient to say much about it.[1]

Now, some remarks will be made above the external appearance of the two compounds, obtained in the present investigation.

The oxychloride, $HgCl_2 2HgO$, is dark purple-reddish, needle shaped crystals. Judged from the color tone it may be the same

[1] The writer had only a limited period of time for the investigation and could not work out more completely.

compound as has been prepared by Volhard[1] from mercuric chloride and sodium acetate or by Millon[2], Thuemmel[3] and Schoch[4] from mercuric chloride and potassium carbonate.

The oxychloride, $HgCl_2.4HgO$, is a brownish yellow substance, amorphous to the naked eye. There are some points of resemblance between this compound and that which has been obtained by Thuemmel[3] and Schoch[5] from mercuric chloride and potassium bicarbonate; but it seems to differ from what has been prepared by Millon[2] from mercuric chloride and potassium carbonate.

As is remarked in Abegg's Handbuch der anorganischen Chemie[5], it seems the external appearances of these compounds vary according to the condition of formation.

Summary.

The equilibrium of a system consisting of mercuric chloride, yellow mercuric oxide and water was studied at 35°C.

The solubility of mercuric chloride was determined to be 8·58 grams per 100 grams solution or 9·39 grams in 100 grams water, and that of the yellow mercuric oxide to be 0·0014 grams per 100 grams solution or water.

Under the condition of the experiments, that is, from a system composed of mercuric chloride, yellow mercuric oxide and water at 35° only two oxychlorides, $HgCl_2.2HgO$ and $HgCl_2.4HgO$, were found to exist.

The oxychloride, $HgCl_2.4HgO$, probably forms some solid solution with the yellow mercuric oxide, HgO.

In conclusion the writer wishes to express his sincere thanks to Prof. Y. Osaka for his interest and advice throughout the experiment.

1, 2, 3, 4 Loc. cit.

5 Vol. II, 2, p. 623.