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ON THE FORMATION OF DOUBLE SALTS.

[SECOND PAPER.]

THE DOUBLE CAESIUM MERCURIC CHLORIDES FORMING FROM ACETONE.

BY H. W. FOOTE AND F. L. HAIGH.

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In a previous article,[1] we considered the effect of a change in solvent on the formation of double salts which yield hydrates when crystallized from water. It was shown that the substitution of alcohol or acetone for water as solvent may produce salts of an entirely different type from those crystallizing from water, or may entirely prevent the formation of a double salt. Thus, there are three hydrated potassium mercuric chlorides which form, at 25°, from water while there is but one double salt formed from alcohol and two from acetone and all are different in type from the hydrates. The conclusion was drawn that when a double salt is formed containing the solvent, the latter is an essential constituent of the salt and is as important in determining the type of double salt formed as are the individual salts.

The case appears to be very different when double salts are formed which do not combine with the solvent. In general, it is to be expected that two single salts capable of forming an anhydrous double salt from one solvent should form the same salt from any other solvent unless the latter also enters into the compound. This can be demonstrated theoretically in a number of ways. If, for instance, the reverse is assumed, that a double salt AB forms from one solvent, while the single salts A and B are deposited by another, then the salt AB could be brought into contact with the second solvent in equilibrium with the single salts, and it would decompose into A and B. The latter could then be brought into contact with the first solvent in equilibrium with double salt and

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[1] THIS JOURNAL, 32, 618 (1910).

would form double salt, thus bringing about a perpetual motion. We have tested this conclusion in the present investigation by determining experimentally the double salts formed from a non-aqueous solution and comparing them with the anhydrous salts forming from water.

An unusual series of such anhydrous double salts is formed from water by caesium and mercuric chlorides. They were first described by Wells[1] and were again investigated by one of us[2] by the solubility method. They have the following formulas: $CsCl.5HgCl_2$, $CsCl.2HgCl_2$, $CsCl.HgCl_2$, $2CsCl.HgCl_2$, $3CsCl.HgCl_2$. We chose this series for investigation partly because one component, at least, mercuric chloride, is readily soluble in many organic solvents and partly because the series is the longest of any we know.

The same solubility method was applied which was previously used in investigating these salts. Absolute alcohol was first tried as a solvent. Double salts formed without question, as was shown by variable solubility, but the time required to reach equilibrium was too great, due to the low solubility of caesium chloride, and conflicting results were obtained. We then tried acetone. The salts were ground in a mortar and the solubility of mixtures determined. Here, again, we met with difficulty as equilibrium was reached very slowly and the results were irregular. The solubilities were, in general, greater than where alcohol was used, however, and the method appeared practicable, if the original caesium chloride were sufficiently fine. In all subsequent work, this salt was first ground and then sifted through the finest silk bolting cloth we could obtain. Mercuric chloride offered no special difficulty in reaching equilibrium as it is very soluble and it was accordingly ground in a mortar and not sifted. Weighed quantities of the salts, in varying proportions, were placed in glass-stoppered bottles and a measured volume of acetone added from a pipet. The mixtures were at once shaken vigorously to prevent lumps from forming, the bottles were sealed with paraffin and rotated in a thermostat at 25°. All mixtures were shaken at this temperature for at least forty-eight hours. A sample of the solution was then removed through a filter of glass wool into a weighed specimen tube for analysis. The residues were dried as rapidly as possible on filter papers. They were somewhat contaminated with salts from the solutions as the solvent is very volatil, and the analyses, in consequence, show a somewhat high percentage of mercuric chloride. Mercury was determined in both solution and residue by precipitating as sulfide, filtering on a Gooch crucible and drying at 110–120°. In the case of solutions, the filtrate from mercuric sulfide was evaporated to dryness and caesium weighed as chloride. In analyzing residues, caesium chloride

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[1] *Am. J. Sci.*, 44, 221 (1892).

[2] *Am. Chem. J.*, 30, 339 (1903).

was determined by difference, as tests in a closed tube showed in every case that there was no solvent of crystallization.

The results obtained, using sifted caesium chloride, are given below in the table. One result only, of all that were obtained on sifted material, is not given, as it was obviously in error.

SOLUBILITY OF CAESIUM AND MERCURIC CHLORIDES IN ACETONE AT 25°.

No.	Per cent. $HgCl_2$ in solution.	Per cent. CsCl in solution.	Per cent. $HgCl_2$ in residue.	Residue contains.
1	57.74	0	100	$HgCl_2$
2	57.79	0.13	98.91	$HgCl_2$ and $CsCl.5HgCl_2$
3	57.74	0.14	95.98	
4	57.74	0.20	89.16	$CsCl.5HgCl_2$
5	52.54	0.22	89.36	
6	49.83	0.32	89.32	
	Calculated for $CsCl.5HgCl_2$		88.94	
7	44.32	0.50	87.35	$CsCl.5HgCl_2$ and $CsCl.2HgCl_2$
8	44.46	0.44	79.90	
9	39.65	0.48	77.30	$CsCl.2HgCl_2$
10	28.48	0.48	76.99	
	Calculated for $CsCl.2HgCl_2$		76.29	
11	26.96	0.52	72.63	$CsCl.2HgCl_2$ and $CsCl.HgCl_2$
12	27.32	0.61	63.48	
13	21.50	0.46	62.15	$CsCl.HgCl_2$
14	13.08	0.45	62.24	
	Calculated for $CsCl.HgCl_2$		61.67	
15	0.16	0.19	54.02	Mixtures of several salts
16	0.17	0.25	37.88	
17	0.02	0.11	18.17	
18	0	0.032	0	CsCl

In the table, Nos. 1 and 18, respectively, show the solubility of pure mercuric chloride and caesium chloride. Excluding Nos. 15–17 for the time, the results are grouped, each group representing (1) constant solubility and varying residue where a mixture of two salts was present or (2) varying solubility and constant residue showing a pure salt. The relation of the solutions to each other is better shown by the mercuric chloride than by caesium chloride as the latter is so small in every case that the errors of analysis hide the regularities. It is evident from the results that three, at least, of the five salts which form from water also form from acetone. The residues in Nos. 15–17 correspond respectively in composition to mixtures of the 1 : 1 and 2 : 1, the 2 : 1 and 3 : 1 and the 3:1 and caesium chloride. The solubilities in these cases are exceedingly small and no conclusions can be drawn from them as to what salts were present in the mixtures. We were therefore forced to rely on microscopic examination of the residues to determin what salts were present.

The crystals of all the caesium mercuric chlorides have been investigated by Penfield,[1] so that his descriptions were available for comparison. We also prepared the pure 2 : 1 and 3 : 1 salts from water. The proportions of salts and water used in preparing these double salts were calculated from solubility results obtained in a previous article.[2] The solutions were cooled rapidly to form small crystals for comparison with the small crystals obtained from acetone. Finally, duplicates of Nos. 15–17 were prepared as before, shaken at 25° for three days and then allowed to rest for several days, the object being to obtain as well-formed crystals as possible. Shaking in the thermostat injures the crystals but is necessary in order to make the salts form. Standing at rest sharpened the crystal forms considerably. The 3 : 1 salt prepared from water showed crystals of the form figured by Penfield, slender crystals with unsymmetrical terminations. The 2 : 1 salt was not figured by Penfield but our specimen showed flat plates with characteristic cleavage at right angles. Both salts are birefringent. From acetone, No. 17 showed the best crystals. In this, there were three perfectly distinct substances, (1) rounded masses of isotropic material, evidently caesium chloride, (2) crystals identical in appearance with the 3 : 1 salt with characteristic unsymmetrical terminations, and (3) flat plates like the 2 :1 salt prepared by us and described by Penfield. There could be no question of identity of the two anisotropic substances with the 2 : 1 and 3 : 1 double salts from water. Nos. 15 and 16 showed similar crystals of these two double salts and also more or less of the 1 : 1 salt. The latter is isotropic like caesium chloride so that it could be readily distinguished under crossed Nicols from the other forms. No indication of salts other than those mentioned was obtained. Of course a system containing three salts, as in No. 17, is unstable and one salt should disappear. The slight solubility of the salts, however, makes it a difficult matter to reach complete equilibrium.

We consider the evidence complete that from water, acetone, or in general from any solvent, the same anhydrous double salts are formed.

SHEFFIELD CHEMICAL LABORATORY,
YALE UNIVERSITY, NEW HAVEN, CONN.

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[1] *Am. J. Sci.*, [3] 44, 311 (1892).

[2] *Loc. cit.*