47. *The Ternary Systems constituted by Mercuric Chloride, Water, and an Alkaline-earth Chloride or Cupric Chloride.*

By Henry Bassett, Geoffrey W. Barton, Albert R. Foster, and Cyril R. J. Pateman.

In three-component systems derived from water and two electrolytes it is usual for the solubility curves to be convex towards the water point when plotted as weight percentages on triangular diagrams. This is due to a depressing effect of small quantities of the one electrolyte on the solubility of the other which gradually becomes less effective with increasing additions and is often followed by an enhancement of the solubility in more concentrated solutions owing to complex formation.

In the system $HgCl_2$–$CoCl_2$–H_2O (Bassett and Croucher, J., 1930, 1784), the solubility curve of mercuric chloride is markedly concave towards the water point. The only other case of the same kind then on record was in the system $HgCl_2$–$CuCl_2$–H_2O (Schreinemakers and Thonus, *Proc. Acad. Amsterdam*, 1912, **15**, 472), the isothermal of which at 35° consisted of a very concave solubility curve for mercuric chloride and a normal, slightly convex one for cupric chloride dihydrate. Other cases of concave solubility curves have since been reported, *e.g.*, in the system KCNS–AgCNS–H_2O (Occleshaw, J., 1932, 2404).

The present paper is the outcome of a wish to re-examine the $HgCl_2$–$CuCl_2$–H_2O system and to obtain additional cases of concave solubility curves. The mercuric chloride curve is concave in all of the systems examined except that containing calcium chloride, where it is a straight line. The barium chloride dihydrate curve is also concave.

The curves for mercuric chloride probably owe their form to the fact that this substance is practically a non-electrolyte, so that its marked tendency to form complexes with the added salt is the factor which determines the solubility influence from the first small additions of the latter. There is no initial depressing effect by the added chloride ion.

The curves for $CaCl_2,6HgCl_2,6H_2O$, $SrCl_2,3HgCl_2,8H_2O$, and for mercuric chloride in the $HgCl_2$–$CuCl_2$–H_2O system have a point of inflexion and are partly convex and partly concave.

Our experimental results are given in the tables and figures.

Earlier Work on the Systems, and Discussion of Results.

All the systems now dealt with were examined a hundred years ago by von Bonsdorff (*Pogg. Annalen*, 1829, **17**, 115, 247). He prepared a number of double salts and analysed them, but, as it is not possible to obtain them quite free from mother-liquor, it is not surprising that his formulæ are not always correct. His observations were very accurate, and his results excite admiration when one considers the difficulty in dealing with such systems before the discovery of the phase rule.

To the two magnesium compounds he gave the formulæ $MgCl_2,3HgCl_2,5H_2O$ and $MgCl_2,HgCl_2,6H_2O$, the former wrong only by $1H_2O$ and the latter correct. In the calcium chloride system, instead of the compound $CaCl_2,6HgCl_2,6H_2O$, he found $CaCl_2,5HgCl_2,8H_2O$, a formula which corresponds fairly closely with the average composition of the moist samples which we analysed. He also mentions another compound $CaCl_2,2HgCl_2,6H_2O$, but found it difficult to get pure and was doubtful about its composition : it is actually $CaCl_2,HgCl_2,4H_2O$ and its appearance is exactly as described by him ; his preparations may have contained some $CaCl_2,6HgCl_2,6H_2O$.

With strontium and barium chlorides Bonsdorff found $SrCl_2,2HgCl_2,2H_2O$ and $BaCl_2,2HgCl_2,2H_2O$ instead of $SrCl_2,3HgCl_2,8H_2O$ (solid solutions, see p. 154) and $BaCl_2,3HgCl_2,6H_2O$. He also says that a complex cupric mercuric chloride can be obtained in the form of prismatic needles or groups of needles, but gives no analysis or formula, nor is there anything to show that the needles did not consist of copper chloride dihydrate. Harth (*Z. anorg. Chem.*, 1897, **14**, 323) claims to have obtained $CuCl_2,HgCl_2$ as short greenish needles easily soluble in water, but gives no analytical or other details. It is clear from the context of his paper that he did not mean to imply that his supposed compound was anhydrous, but only that it contained the constituent salts in equimolecular proportion. We consider it very doubtful whether any compound of these two chlorides can separate from aqueous solutions. There is certainly no compound at 35° or 25° and, qualitatively, we could obtain no indications of any compound other than the two salts separating even at temperatures as low as − 15°.

Swan (*Amer. Chem. J.*, 1898, **20**, 613) repeated a few of Bonsdorff's preparations and said that there was only one magnesium compound $MgCl_2,3HgCl_2,6H_2O$ (and not $5H_2O$). He thought that Bonsdorff's $MgCl_2,HgCl_2,6H_2O$ was only a mixture, and also that the strontium compound was $SrCl_2,3HgCl_2,xH_2O$. Foote and Bristol (*ibid.*, 1904, **32**, 246) examined the system $HgCl_2$–$BaCl_2$–H_2O and showed by dilatometer experiments that a complex salt became stable below 17·2°. They made some solubility determinations at 10·4° and showed that the complex salt had the formula $BaCl_2,3HgCl_2,6H_2O$. We have entered their results on Fig. 1.

Further phase-rule investigation of these systems was clearly desirable on account of the remarkable nature of some of the compounds. It was advisable to settle the correct formulæ of these in connexion with our attempts to construct reasonable and consistent structural formulæ for a number of complex salts. Our results have been, in some respects, more striking than was anticipated.

Three types of complex salt are formed between mercuric chloride and the other bivalent metal chlorides examined: (i) $MCl_2,HgCl_2,xH_2O$, (ii) $MCl_2,3HgCl_2,xH_2O$, and (iii) $MCl_2,6HgCl_2,xH_2O$.

Compounds of type (i) were obtained with magnesium and calcium, as also, previously, with cobalt (Bassett and Croucher, *loc. cit.*). The double compound formed by manganese is also of this type (Bonsdorff, *loc. cit.*). Compounds of type (ii) were formed by magnesium, strontium, and barium, while calcium and strontium also yielded compounds of type (iii). These statements refer to a temperature of 25° (except in the case of barium). It is possible that other compounds may appear at lower temperatures, but no observations have been made in the course of our work which indicate any other compounds above about 12°, at any rate.

It seems highly probable that in all these compounds the whole of the mercury is in the complex anion of double salts in which M (=Mg, Ca, Sr, Ba, Co, Mn) functions as kation. This view of their constitution is supported very strongly by their water content, which is just sufficient to cause a reasonable hydration of the M kations. Thus, in compounds of type (i), x is 6 for the magnesium compounds and 4 for that of calcium (and also of cobalt and manganese), corresponding to the formulæ

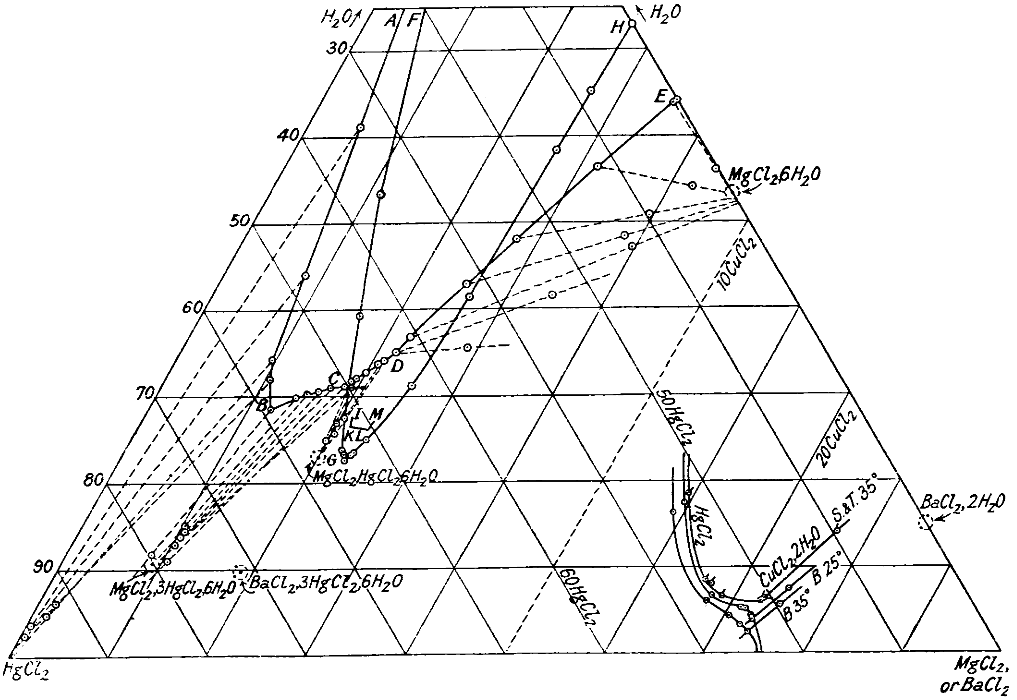
$$[Mg(H_2O)_6]^{\cdot\cdot}[HgCl_4]'' \text{ and } [Ca(H_2O)_4]^{\cdot\cdot}[HgCl_4]''.$$

For magnesium and barium compounds of type (ii), *x* has the value 6, and for that of strontium it is 8, corresponding to the formulæ

$$[(\text{Mg or Ba})(H_2O)_6]^{\cdot\cdot}[Cl_2HgCl_2HgCl_2HgCl_2]'' \text{ and } [Sr(H_2O)_8]^{\cdot\cdot}[Cl_2HgCl_2HgCl_2HgCl_2]''.$$

According to Sidgwick's covalency rule, the maximum co-ordination number of magnesium and calcium is six, and it is eight for strontium. For barium also it is not less than eight, but it is well known that with elements of high atomic number the more highly co-ordinated conditions tend to be unstable. For the two compounds of type (iii) the value of *x* is 6. Here again a long-chain anion appears to be formed, and we give the calcium and the strontium compound the formulæ

Fig. 1.



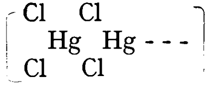
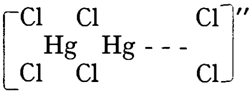
In Fig. 1. AB *is solubility curve of* $HgCl_2$.
BC ,, ,, ,, $MgCl_2,3HgCl_2,6H_2O$.
CD ,, ,, ,, $MgCl_2,HgCl_2,6H_2O$.
DE ,, ,, ,, $MgCl_2,6H_2O$.
FG ,, ,, ,, $HgCl_2$.
GH ,, ,, ,, $BaCl_2,2H_2O$.
IKLM *Foote and Bristol's results at* 10·4°.
KL *is solubility curve of* $BaCl_2,3HgCl_2,6H_2O$.

Fig. 1A.

In Fig. 1A. *Portions of three isothermals are shown of the system* $HgCl_2$–$CuCl_2$–H_2O *in the neighbourhood of the points of intersection of the solubility curves of* $HgCl_2$ *and* $CuCl_2,2H_2O$. *The upper curve shows Schreinemakers and Thonus's results at* 35°. *The intermediate curve shows our results at* 25°, *and the lower curve those at* 35°. *The scale of Fig.* 1A *is twice that of Fig.* 1. *The* $BaCl_2,2H_2O$ *point refers to Fig.* 1.

$$[\text{Ca(or Sr)}(H_2O)_6]^{\cdot\cdot}[Cl_2HgCl_2HgCl_2HgCl_2HgCl_2HgCl_2HgCl_2]''.$$

The large anion makes large hydration of the kation possible in spite of the fact that these compounds only separate from solutions containing not more than 20—30% of total water. This anion containing six atoms of mercury is the longest chain ion of this type with which we are acquainted. Some of our reasons for postulating anions such as the above have already been given (Bassett and Croucher, *loc. cit.*; Bassett and Sanderson, J., 1932, 1855).

Chain anions are always subject to the disruptive tendency of their constituent ions to become free, and, from this point of view, mercuric chloride appears to be peculiarly well adapted to build up such ions. It is well known to be almost un-ionised in aqueous solution and even to show signs of being complex. The symmetry produced by the attachment of two chlorine ions at one end of a neutral molecule  $\left[\begin{array}{cc}\mathrm{Cl} & \mathrm{Cl} \\ \mathrm{Hg} & \mathrm{Hg}\,--- \\ \mathrm{Cl} & \mathrm{Cl} \end{array}\right]$ to form the chain anion  $\left[\begin{array}{ccc}\mathrm{Cl} & \mathrm{Cl} & \mathrm{Cl}\\ \mathrm{Hg} & \mathrm{Hg}\,--- & \\ \mathrm{Cl} & \mathrm{Cl} & \mathrm{Cl}\end{array}\right]''$ would probably greatly enhance the stability of the structure. Such chlorine ions must be provided by another chloride, however, since mercuric chloride is insufficiently ionised to provide them itself.

In view of the non-electrolytic character of mercuric chloride, it was just conceivable that some of these complexes might have an entirely different constitution from that proposed above and contain complex kations in which molecules of mercuric chloride were co-ordinated to the other metal atom in the same sort of way as molecules of water or ammonia in hydrates or ammines. On this basis the compound $\mathrm{CaCl_2,6HgCl_2,6H_2O}$ might have been regarded as $[\mathrm{Ca(HgCl_2)_6}]^{\cdot\cdot}\mathrm{Cl_2}'$, but it would be difficult to place the water molecules in such a structure. Their presence, in just the amount required by the calcium, etc., shows, in our view, that the idea of a complex kation containing mercuric chloride is quite untenable.

The compound $\mathrm{SrCl_2,3HgCl_2,8H_2O}$, *i.e.*, $[\mathrm{Sr(H_2O)_8}]^{\cdot\cdot}[\mathrm{(HgCl_2)_3Cl_2}]''$, is remarkable in being the limit of a series of solid solutions of which the other constituent is strontium chloride dihydrate. This shows in a striking way that the dihydrate must really be complex and have the quadrimolecular formula $\mathrm{(SrCl_2,2H_2O)_4}$ with a structure analogous to that of the mercuric chloride double salt, *viz.*, $[\mathrm{Sr(H_2O)_8}]^{\cdot\cdot}[\mathrm{Cl_2SrCl_2SrCl_2SrCl_2}]''$.

This result affords strong support for our view that with bivalent metals there is a great tendency to assume the 0-, 4-, 6-, or 8-co-ordinated condition rather than any intermediate values. Polymerisation is frequently necessary to render this possible. The zero-co-ordinated condition is normally only assumed in extreme cases where the higher values 4, 6, or 8 are impossible. Since strontium chloride dihydrate is complex, it is highly probable that the dihydrates of calcium chloride and of barium chloride are also complex, but there is no direct proof of this at present and we can only guess at the probable degree of complexity. In the calcium compound a quadrimolecular formula is unlikely, since, according to Sidgwick's rule, calcium cannot have a higher co-ordination number than six. The only possibility would thus seem to be $\mathrm{(CaCl_2,2H_2O)_3}$ or $\mathrm{(CaCl_2,2H_2O)_2}$, corresponding to $[\mathrm{Ca(H_2O)_6}]^{\cdot\cdot}[\mathrm{Cl_2CaCl_2CaCl_2}]''$ or $[\mathrm{Ca(H_2O)_4}]^{\cdot\cdot}[\mathrm{CaCl_4}]''$. The barium compound could be either quadri-, ter-, or bi-molecular.

Crystallographically, the three dihydrates look very similar and probably they are all monoclinic. According to Mugge (*Jahrb. Min.*, 1888, **1**, 145), $\mathrm{SrCl_2,2H_2O}$ is not isomorphous with $\mathrm{BaCl_2,2H_2O}$, although it probably is with $\mathrm{BaBr_2,2H_2O}$; the last is monoclinic but not isomorphous with its chloride and not of a related form.

The system $\mathrm{CaCl_2}$–$\mathrm{HgCl_2}$–$\mathrm{H_2O}$ is of unusual complexity, but the results obtained are correspondingly interesting. The complexity is due to the occurrence at 25° of two double salts and three different hydrates of calcium chloride (hexa-, tetra-, and di-), of which one, the tetra-hydrate, occurs in no less than three distinct forms. Two of these modifications were already known, but the third has been obtained for the first time—it is intermediate as regards stability conditions between the other two. Calcium chloride solutions can be readily obtained in metastable states and it is this fact alone which has made it possible to examine many of the curves in this system, since four of them are entirely metastable.

The different behaviour of strontium chloride in this respect makes it almost impossible to realise any metastable conditions in the $\mathrm{HgCl_2}$–$\mathrm{SrCl_2}$–$\mathrm{H_2O}$ system. It was only just possible to get sufficient analytical data to fix the formula of the compound $\mathrm{SrCl_2,6HgCl_2,6H_2O}$, which is metastable at 25°, although the similarity of its crystalline form to that of $\mathrm{CaCl_2,6HgCl_2,6H_2O}$ was really sufficient for the purpose.

The general character of the compounds and conditions which occur in the several systems can be seen from the figures, and only a few points require further discussion. In some of the diagrams the tie-lines have been omitted to avoid confusion, but in all cases they run very close indeed to the appropriate points. Only in the $HgCl_2$–$SrCl_2$–H_2O system does the direction of the tie-lines cause any difficulty. The inflected curve which comes between those of the constituent salts corresponds to a series of more or less parallel tie-lines. At the mercury-rich end these run very close to the point for a compound $SrCl_2,3HgCl_2,8H_2O$, and the nature of the tie-lines can be satisfactorily accounted for if they correspond to a series of solid solutions which lie on a line joining the $SrCl_2,3HgCl_2,8H_2O$ point with that of $SrCl_2,2H_2O$. The degree of wetness of the various " moist solids " analysed, as judged by eye, agreed very well in each case with this view of the matter, whereas, if one had assumed that one constituent of the solid solutions was $SrCl_2,3HgCl_2,6H_2O$, the moist solids would have had to be much wetter than was probable from their appearance. Another very important point in favour of the above interpretation of the solid solutions is that the solubility curve of the solid solutions can be extrapolated quite naturally so as to run to the point corresponding to the solubility of strontium chloride dihydrate in pure water at 25°. This point cannot be determined directly, but by extrapolation from measurements at 70° and above (see Seidell, " Solubilities of Inorganic and Organic Substances," 1911, p. 317) it can be estimated to be about 40% $SrCl_2$. The uncertainty attaching to this figure is small, since the solubility curve is practically a straight line between 180° and 70°. The slope of the tie-lines in the region of solid solutions becomes more nearly vertical, corresponding to a larger proportion of strontium chloride in the solid solution the larger the proportion of solid phase which separates from the original homogeneous liquid solution. The more solid solution separates from a given mixture the greater is the initial concentration of the homogeneous liquid solution, the greater its $HgCl_2/SrCl_2$ ratio, and the smaller its water content. These changes correspond to a decrease in this ratio for the solid solution which separates. It is thus evident that an increase in the strontium chloride content of the solid solution depends, not on increasing the concentration of strontium chloride with reference to that of mercuric chloride in the liquid solution, but rather on a decrease in the water content of the mixture. It is mainly this, in all probability, which determines the proportion of $[(SrCl_2)_3Cl_2]''$ anions which are present. Their concentration appears to be quite low except in solutions of very small water content. This dependence of the slope of the tie-lines and the composition of the solid solution on the amount of solid separating from a liquid mixture is precisely similar to what was found in the system $CoCl_2$–$ZnCl_2$–H_2O (Bassett and Croucher, *loc. cit.*, p. 1804).

The point of inflexion in the solubility curves of $CaCl_2,6HgCl_2,6H_2O$ and of $SrCl_2,3HgCl_2,8H_2O$ (solid solutions) is a direct consequence of a portion of the curves being concave to the water point, for the metastable prolongation of these curves should bend round the points representing the composition of pure $CaCl_2,6HgCl_2,6H_2O$ and $SrCl_2,3HgCl_2,8H_2O$ respectively.

Several investigations in recent years have indicated a considerable tendency to association among salts of the alkaline-earth metals. Unmack, Murray-Rust, and Hartley (*Proc. Roy. Soc.*, 1930, *A*, **127**, 228), from conductivity measurements in methyl-alcoholic solution, found this to be the case for the thiocyanates. The conditions prevailing in aqueous solutions of the chlorides seem to be peculiar and the presence of complex ions might help to account for them (Hepburn, J., 1932, 550, 566, 575, 1284).

The concavity of the mercuric chloride curves does not always necessitate an inflexion, however, for the metastable prolongation of these curves would end somewhere on the side of the triangle opposite the water point and this would often be possible without such an inflexion. In the $HgCl_2$–$CuCl_2$–H_2O system, Schreinemakers and Thonus (*loc. cit.*) found the mercuric chloride curve to be so concave that it must show a point of inflexion in the metastable region or immediately before it. Those authors made no mention of the analytical methods they employed, and as this system offers difficulties in that respect, we re-examined it after developing what we believe to be a trustworthy method of analysis. We made this examination both at 25° and at 35°, the temperature used by Schreinemakers and Thonus. Both our isothermals correspond to considerably more concentrated solutions than were found by these authors at 35°, while the mercuric chloride curve on both of them shows the point of inflexion recognised to be necessary by them. One of the points on their curve for mercuric chloride—that at 49·5% $HgCl_2$ and 5·94% $CuCl_2$—is so out of line with their others that we think 49·5 must be a misprint for 39·5.

In Figs. 2 and 2A, the curves for $CaCl_2,6H_2O$, for the three forms of $CaCl_2,4H_2O$, and for $CaCl_2,2H_2O$ all show signs of doubling back, so that they would eventually cut the H_2O–$CaCl_2$ side of the triangle a second time. Fig. 2A is a 20-fold magnification of the region where the curves of $CaCl_2,6HgCl_2,6H_2O$, $CaCl_2,HgCl_2,4H_2O$, α-$CaCl_2,4H_2O$, and $CaCl_2,2H_2O$ intersect. Such a large scale is almost beyond the accuracy of the analytical work, but it makes the relationships clearer.

Fig. 2.

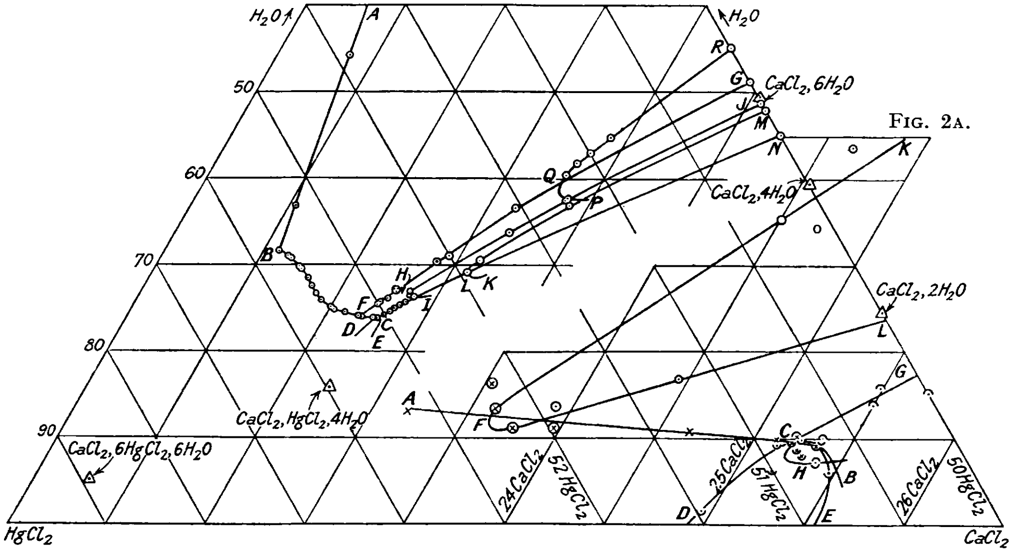


Fig. 2A.

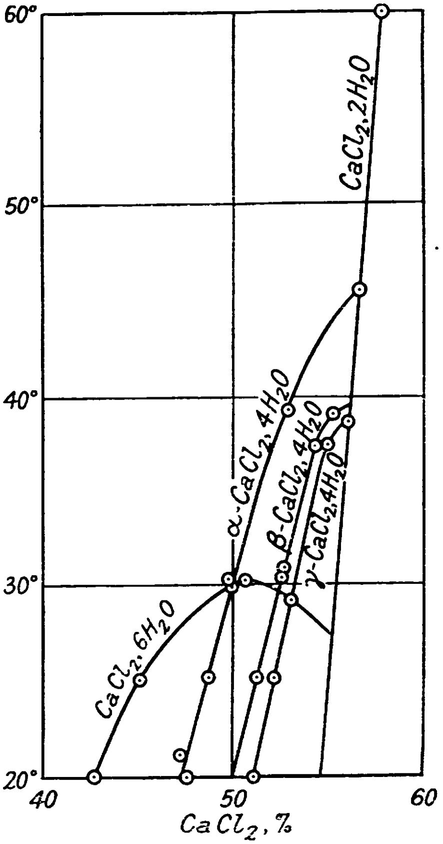
In Fig. 2. AB *is the solubility curve of* $HgCl_2$. IHJ *is the solubility curve of* β-$CaCl_2,4H_2O$.
BFC ,, ,, ,, $CaCl_2,6HgCl_2,6H_2O$. KLM ,, ,, ,, γ-$CaCl_2,4H_2O$.
DCE ,, ,, ,, $CaCl_2,HgCl_2,4H_2O$. CLN ,, ,, ,, $CaCl_2,2H_2O$.
FQG ,, ,, ,, α-$CaCl_2,4H_2O$. PQR ,, ,, ,, $CaCl_2,6H_2O$.
All curves below the lines ABFQR *represent metastable conditions.*

In Fig. 2A. AFCB *is part of solubility curve of* $CaCl_2,6HgCl_2,6H_2O$: *points on this curve shown thus,* ×.
KFL ,, ,, ,, ,, α-$CaCl_2,4H_2O$: ,, ,, ,, ,, ⊙.
GCH ,, ,, ,, ,, $CaCl_2,2H_2O$: ,, ,, ,, ,, ⊙.
DCE ,, ,, ,, ,, $CaCl_2,HgCl_2,4H_2O$: ,, ,, ,, ,, ⊙.
The $CaCl_2,4H_2O$ *and* $CaCl_2,2H_2O$ *points are on the scale of and refer to the main diagram.*
The scale of Fig. 2A *is* 20 *times that of Fig.* 2.

The three forms of calcium chloride tetrahydrate now call for special consideration. Two of these were already known and their solubilities in water had been determined by Roozeboom (*Z. physikal. Chem.*, 1889, **4**, 42), who designated them α- and β-, the α-form being the more stable in contact with aqueous solutions and having the smaller solubility. Our new form is intermediate between these two as regards stability and solubility, so its designation is a matter of some difficulty. As its solubility is nearer to that of Roozeboom's β-form than to that of his α-form it might be called the β′-form ; the alternative is to alter the name of the old β-form to γ-, and to call our new form β- : although this plan involves a possibility of confusion, we prefer to adopt it.

The three forms are absolutely distinct in appearance ; after a little experience they can be handled readily, and by inoculation with the correct form, solutions in equilibrium with any one variety are readily obtained. By inoculating a solution in equilibrium with the γ-form (old β-form) with a crystal of the new β-form, the γ-crystals are seen to be gradually replaced by those of the β-, and if the mixture is then inoculated with the α-form a complete change to this occurs. There can thus be no doubt about the existence of three distinct forms.

Fig. 3.



The α-$CaCl_2$,$4H_2O$ was first obtained by Hammerl (*Wien. Sitzungsber.*, 1875, **72**, 667), who merely describes the crystals as being " well formed." Roozeboom (*loc. cit.*) describes them as granular, apparently rhombic, and settling quickly. We obtained beautiful brilliant diamond-shaped rhombs, often much facetted and sometimes forming cross-like twins. The dimensions of the rhombs do not differ greatly in any direction, and hence the granular character to which Roozeboom refers.

Our new β-form occurs as square-ended prisms, some nearly square, others much longer than they are broad; the edges are often bevelled.

The γ- (old β-) $CaCl_2$,$4H_2O$ was first obtained by Lefebvre (*Compt. rend.*, 1870, **70**, 684), who describes its spontaneous separation in great plates from solutions containing about 55% $CaCl_2$. These plates are rhombohedral and readily cleave into long needles, the oblique ends of which often have the acute angle truncated.

We determined the solubility of all three forms in pure water at 25° in order to be quite sure which corresponded to Roozeboom's α- and β-forms. The solubility of our new β-form in pure water has been determined at several temperatures and its solubility curve is shown in Fig. 3.

When the separation of the tetrahydrate from pure aqueous solutions is entirely spontaneous, it nearly always comes out in the γ-form. We first obtained the new β-form by inoculation of a mercuric chloride–calcium chloride solution with partially dehydrated hexahydrate. This is not very reliable, however, as the α- or the γ-form may result. In time, either the γ- or the β-form changes into the α-form, but they may persist for months at 25°. The γ-form always seems to change spontaneously into the α-form directly, and only into the new β-form as an intermediate stage if inoculated with the latter.

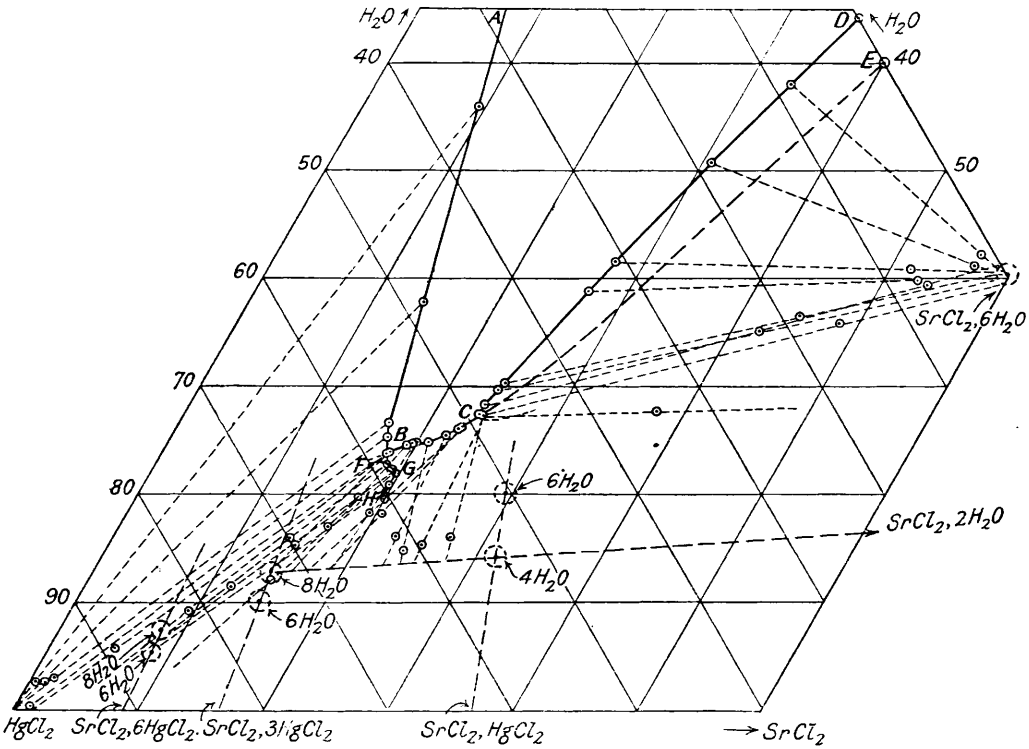
Calcium chloride dihydrate can also exist at 25° in metastable equilibrium with a certain range of solutions, containing a high proportion of mercuric chloride. Such mixtures were prepared by inoculating suitable solutions with crystals of dihydrate obtained by allowing pure calcium chloride solutions of appropriate concentrations to crystallise above about 60°. It forms large rhombohedral plates which float in the dense equilibrium solutions.

Crystals of the dihydrate are rather similar in appearance to those of γ-tetrahydrate, but the latter are not so well formed and have a marked tendency to be six-sided, whereas the former—especially from mercuric chloride solutions—separate as clear well-formed rhombohedral plates of which the acute angles are only occasionally truncated by small faces.

The solubility of the dihydrate in pure water at 25° can be obtained by extrapolation from Roozeboom's figures (*loc. cit.*). It does not seem to be realisable experimentally. We could not follow the curve very far into the region of low mercuric chloride content, but its probable course is indicated in Fig. 2.

In view of the behaviour of strontium chloride dihydrate, it is important to note that no evidence of any solid solution formation could be detected in the case of the corresponding calcium salt, although it was specially sought. The very hygroscopic nature of the latter and the horizontal position of the tie-lines make them very sensitive to small changes in water content of the moist solid. They run as near to the $CaCl_2,2H_2O$ point as can be expected. There was no solid solution formation in the case of $BaCl_2,2H_2O$ either.

FIG. 4.



AB *is the solubility curve of* $HgCl_2$.
BCE „ „ „ *solid solutions* $SrCl_2,3HgCl_2,8H_2O$–$SrCl_2,2H_2O$.
CD „ „ „ $SrCl_2,6H_2O$.
FGH „ „ „ $SrCl_2,6HgCl_2,6H_2O$.

EXPERIMENTAL.

Solubility determinations were made in all cases at 25°, the procedure used being as described by Bassett and Croucher (*loc. cit.*). A.R. Compounds were used in all cases where obtainable; $SrCl_2,6H_2O$ was a purchased sample which analysis showed to be perfectly satisfactory. The time of shaking at 25° was seldom less than 24 hr., which was found to be adequate, but was often several weeks even in the case of metastable $CaCl_2$ systems.

When dealing with $SrCl_2,6HgCl_2,6H_2O$ great care had to be exercised, however, owing to its instability. Suitable mixtures had to be well heated and then cooled rapidly and allowed to stand quietly at 25°, whereupon the octahedral crystals separated. The mixtures could only be left for 15—30 min. with gentle shaking before separation for analysis, otherwise they set to a nearly solid mass of $SrCl_2,3HgCl_2,8H_2O$. This was liable to occur if any attempt was made to filter off the solid phase, and as a rule the clear solution had to be removed with a warm pipette and the dense solid separated by decantation and weighed in the solubility bottle; consequently, the moist solid retained a very high proportion of mother-liquor. In one case the mixture was successfully filtered for analysis.

In one expt., where both solid solution and $SrCl_2,6H_2O$ were in equilibrium with solution, the solid solution had slowly formed large crystals at the expense of the floating crystals of $SrCl_2,6H_2O$—the mixture having been kept stationary. As the crystals of solid solution remained attached to the bottom of the tube it was possible to separate them for analysis in a moist but otherwise pure state. The tie-line shows their composition to be 58·4% $HgCl_2$, 27·6% $SrCl_2$. This is richer in $SrCl_2$ than any other solid solution we obtained, and corresponds to the presence of 20·5% of the $(SrCl_2,2H_2O)_4$ constituent.

In Table II, owing to the complexity of the system, the curve for each compound has been treated as a single unit so that the points corresponding to the coexistence of two solid phases appear twice—once on each curve. For the compound $CaCl_2,HgCl_2,4H_2O$ the times for which each mixture was shaken at 25° have been given to show how little a variation in the time affects the results obtained. The chief difficulties in fixing the exact position of the solubility curve are due to the excessively small range of concns. over which the compound can be obtained, to the great readiness with which $CaCl_2,6HgCl_2,6H_2O$ separates, and to the limitations of the analytical methods. $CaCl_2,HgCl_2,4H_2O$ separates readily on cooling hot solutions made up with care so as to come within the region of existence of the compound. It is a matter of some difficulty, however, to get a prepn. which is entirely free from either $CaCl_2,2H_2O$ or $CaCl_2,6HgCl_2,6H_2O$.

The fact that in the 3-weeks expt. $CaCl_2,6HgCl_2,6H_2O$ had changed completely into $CaCl_2,HgCl_2,4H_2O$ definitely shows that at 25° the curve for the latter compound cuts that for the former. In the region of the $\frac{3}{4}$-hr. and 17-hr. expts. $CaCl_2,HgCl_2,4H_2O$ is relatively very unstable towards $CaCl_2,6HgCl_2,6H_2O$ and even in the short times allowed considerable change had occurred, so that the solid phases were actually mixtures.

The $2\frac{1}{2}$-day and 8-day expts. are similar in the sense that no conversion of $CaCl_2,HgCl_2,4H_2O$ into $CaCl_2,6HgCl_2,6H_2O$ had occurred. This suggests that there is only a slight instability of the former towards the latter in the positions corresponding to these two expts., and this is our chief reason for making the curve for $CaCl_2,6HgCl_2,6H_2O$ bend round in the manner shown: it must bend round somewhere, as it should form a closed curve round the point representing pure $CaCl_2,6HgCl_2,6H_2O$.

Methods of Analysis.—Great attention was paid to these. Except in presence of Cu, Hg was estimated as HgS after pptn. with H_2S and drying at 100—110°. It has been shown by Fenimore and Wagner (*J. Amer. Chem. Soc.*, 1931, **53**, 2453) that this method is subject to a small error due to chloride carried down by the HgS. We, too, found that the wt. of HgS obtained is about 0·3% too great, and that it made little difference whether the solution from which pptn. occurred was free from added acid or was 2*N* with respect to HCl. The HgS is somewhat hygroscopic and should be weighed quickly. We have not considered it necessary to correct our results for the above small error. Mg was estimated as $Mg_2P_2O_7$ and Sr and Ba as sulphate after separation by standard procedure from the evaporated Hg filtrate. Ca was separated from the latter as CaC_2O_4: in some cases this was titrated with $KMnO_4$, but in others it was ignited and weighed as CaO. Preference was given to the latter procedure—especially in critical or difficult regions of the $CaCl_2$ system, as it was considered more reliable. A special method of analysis was devised for the $HgCl_2$–$CuCl_2$–H_2O system, since ordinary methods for separating mercury and copper appear to be most unsatisfactory.

In our hands the method of Krauss (*Z. angew. Chem.*, 1927, **40**, 354) gave high results for Cu and low results for Hg. We found that the most satisfactory procedure was to determine Cu as the salicylaldoxime compound (Ephraim, *Ber.*, 1930, **63**, *B*, 1928), and then to determine total Cl in another portion of the mixture and to calculate the Hg by means of these two determinations. Hg cannot be satisfactorily estimated by pptn. with H_2S in the Cu filtrate, partly because the org. matter present interferes with the pptn., and partly because the HgS absorbs the org. matter. Cl cannot be estimated directly in presence of Hg owing to the solvent action of $Hg(NO_3)_2$ on AgCl (see Ephraim, "Text Book of Inorganic Chemistry," 1926, p. 225; Winkler, "Ausgewählte Untersuchungsverfahren," 1931, p. 129). The method we adopted was to remove Hg from solution with Cu turnings and then to ppt. total Cl with $AgNO_3$. Our standard procedure was as follows.

The solution, containing sufficient material to yield 0·2—0·5 g. of AgCl, was diluted to about 60 c.c., treated with 0·5 c.c. of 2*N*-HNO_3 and 2 g. of small Cu turnings. Immediately before use these had been boiled for a few min. with about 0·05*N*-HNO_3 to remove oil and surface contaminations, and well rinsed with cold distilled H_2O. It was found best to let the Cu act first at a relatively low temp. by heating the mixture over quite a small flame or else on top of an oven at about 110°; after several hours of such heating, the mixture was just raised to the boil and kept rather below it for about 2 hr. Any Hg_2Cl_2 which might have separated initially should by then have completely disappeared. The amalgamated Cu was then filtered off and washed with two 5-c.c. portions of 2*N*-NH_3 aq., followed by H_2O. (The NH_3 was used to dissolve any basic salts which might have formed.) Cl was pptd. as AgCl in the filtrate after acidification with HNO_3.

With A.R. $CuSO_4,5H_2O$ the salicylaldoxime method gave results about 0·3% too high, and in mixtures containing known amounts of $CuSO_4$ and $HgCl_2$ comparable to those in the solutions being studied, the Cu results were about 0·7% too high. In all our analyses of the $HgCl_2$–$CuCl_2$–H_2O system, we have accordingly reduced the weight of copper salicylaldoxime by 0·7% before calculating the percentages of $CuCl_2$ and $HgCl_2$ present. We believe the results so obtained to be very trustworthy. The copper salicylaldoxime was always pptd. from the neutral solution. Addition of NH_4OAc and HOAc made no difference to the results and was therefore omitted. The method described gave excellent values for the chloride content of known mixtures of A.R. $CuSO_4,5H_2O$ and $HgCl_2$.

Properties of the Several Complex Salts.—All the complex salts found in these systems form incongruently satd. solutions and are consequently decomp. by pure H_2O. When $CaCl_2,6HgCl_2,6H_2O$ or $SrCl_2,6HgCl_2,6H_2O$ is treated with H_2O, a preliminary separation of $HgCl_2$ can be observed. Both of these compounds form well-developed regular octahedra which always sink in their equilibrium solutions.

The $SrCl_2,3HgCl_2,8H_2O$ solid solutions form rhombohedral plates which appear as needle-like crystals, or aggregates of such, when they separate rapidly. In some of our expts., metastable $SrCl_2,3HgCl_2,8H_2O$ at one end of the solid solution range, or metastable $SrCl_2,6H_2O$ at the other end, slowly changed into the $SrCl_2,3HgCl_2,8H_2O$ solid solution which under these conditions formed large rhombohedral plates, the acute angles of which were often truncated to give hexagonal plates.

Crystals of $SrCl_2,2H_2O$, prep. by crystn. from pure solutions of $SrCl_2$ above 70°, had a precisely similar appearance to that of these solid solutions. In the region near the point of intersection of the solubility curves of $SrCl_2,6H_2O$ and solid solution, the two solids can be readily distinguished since the prisms of $SrCl_2,6H_2O$ float, whilst the crystals of solid solution sink in the equilibrium solutions.

$MgCl_2,3HgCl_2,6H_2O$ also forms large rhombohedral plates with good rhombohedral cleavages.

$MgCl_2,HgCl_2,6H_2O$ crystallises in prisms which appear to be monoclinic. Both the complex $MgCl_2$ salts sink in their equilibrium solutions, while $MgCl_2,6H_2O$ floats in the solution which is in equilibrium with both it and $MgCl_2,HgCl_2,6H_2O$.

$CaCl_2,HgCl_2,4H_2O$ forms prisms which are apparently isomorphous with those of $CoCl_2,HgCl_2,4H_2O$. When formed rapidly, the prisms are needle-like, but when formed slowly, as by the slow change of previously separated but metastable $CaCl_2,6HgCl_2,6H_2O$, fine six-sided prisms with pyramidal ends are obtained which have a superficial resemblance to crystals of quartz. The crystals of this compound sink in their equilibrium solutions.

Numbers in italics in Tables I—VI correspond to metastable conditions.

TABLE I.

System $HgCl_2$–$MgCl_2$–H_2O.

Solution.		Moist solid.			Solution.		Moist solid.		
$HgCl_2$.	$MgCl_2$.	$HgCl_2$.	$MgCl_2$.		$HgCl_2$.	$MgCl_2$.	$HgCl_2$.	$MgCl_2$.	
* 6·90	nil	—	—	A	48·95	19·22	53·71	19·52	C
33·47	5·40	97·36	0·30	,,	48·78	19·45	55·51	19·95	,,
47·72	8·28	96·07	0·60	,,	47·32	20·01	53·35	19·86	,,
56·03	9·86	93·76	1·49	,,	45·45	20·90	54·26	20·16	,,
57·46	10·68	92·08	1·64	,,	44·93	21·12	52·11	20·32	,,
59·23	12·48	79·84	8·68	A, B	† 43·25	21·97	24·03	34·43	C, D
55·90	14·44	74·70	10·32	B	43·14	21·92	35·76	28·83	,,
55·78	14·38	76·65	10·13	,,	41·66	22·43	13·23	39·68	D
54·53	15·24	76·67	10·43	,,	31·92	25·29	13·14	38·34	,,
53·15	16·30	74·91	10·68	,,	24·29	27·64	9·61	39·60	,,
51·88	17·27	76·84	10·32	,,	11·76	31·72	3·51	42·40	,,
50·08	18·77	78·29	10·53	B, C	0·58	35·48	0·11	43·84	,,
49·85	*19·23*	*75·53*	*10·54*	B	nil	35·70 ‡	—	—	,,
49·47	19·07	55·40	19·82	C					

* Foote and Levy, *Amer. Chem. J.*, 1906, **35**, 238.

† Independent results at different times by different workers.

‡ Interpolated from van 't Hoff and Meyerhoffer's results (*Z. physikal. Chem.*, 1898, **27**, 74).

Symbols used for solid phases : A = $HgCl_2$; B = $[Mg(H_2O)_6][Hg_3Cl_8]$; C = $[Mg(H_2O)_6][HgCl_4]$; D = $[Mg(H_2O)_6]Cl_2$.

TABLE II.

System $HgCl_2$–$CaCl_2$–H_2O.

	Solution.		Moist solid.		
	$HgCl_2$.	$CaCl_2$.	$HgCl_2$.	$CaCl_2$.	
	6·90	nil	—	—	A
	38·50	7·25	97·53	1·01	,,
	52·66	10·53	94·27	1·42	,,
	56·71	11·35	85·36	5·07	* A, B
	56·87	11·43	89·04	4·87	
	56·85	11·61	85·09	6·83	B
	56·31	12·60	83·79	7·25	,,
	56·20	13·09	84·46	7·86	,,
	55·70	14·80	82·62	7·36	* ,,
	55·68	14·70	83·65	7·74	
	55·50	16·04	82·89	7·59	,,
	55·63	16·90	83·30	8·47	,,
	55·58	17·81	82·46	8·62	,,
	55·42	18·77	81·36	7·90	,,
	54·96	19·98	79·66	9·19	,,
	54·87	20·40	85·64	8·33	,,
	53·86	21·67	83·92	8·15	,,
	52·67	23·19	82·12	8·79	,,
	52·21	23·62	44·04	31·97	B, α
	52·15	23·53	45·14	31·72	
	51·97	23·96	51·57	28·08	
	51·31	*24·66*	*84·52*	*8·19*	B
	50·90	*25·13*	*84·10*	*8·46*	,,
†	*50·84*	*25·19*	*79·20*	*10·43*	B, ? C
	50·81	*25·25*	*73·79*	*13·87*	,,
	50·81	*25·30*	*66·92*	*19·69*	B, C
	50·78	*25·22*	*74·00*	*14·39*	B, D
	50·76	*25·24*	*66·80*	*19·63*	
	50·72	*25·33*	*61·27*	*22·47*	B, C
¾ hr.	*51·47*	*24·92*	*57·81*	*23·87*	C, some B
17 hr.	*50·99*	*25·21*	*60·03*	*23·41* ‡	,,
8 days	*50·90*	*25·14*	*59·56*	*24·39*	C
2 ,,	*50·84*	*25·19*	*79·20*	*10·43*	C, B
3¾ ,,	*50·81*	*25·25*	*73·79*	*13·87*	
1 month	*50·81*	*25·30*	*66·92*	*19·69*	
3 weeks	*50·77*	*25·25*	*58·74*	*24·84* §	C
24 hr.	*50·76*	*25·38*	*26·26*	*51·20*	C, D
3 days	*50·67*	*25·35*	*53·11*	*29·42*	
3½ ,,	*50·72*	*25·33*	*61·27*	*22·57*	C, B
2½ ,,	*50·72*	*25·48*	*57·63*	*24·88*	C
	50·78	*25·22*	*74·00*	*14·39*	D, B
	50·76	*25·24*	*66·80*	*19·63*	
	50·76	*25·38*	*26·26*	*51·20*	D, C
	50·67	*25·35*	*53·11*	*29·42*	
	50·30	*25·50*	*15·21*	*60·57*	D
	50·21	*25·48*	*15·56*	*60·00*	,,
	49·99	*25·74*	*20·41*	*55·29*	,,
	49·21	*26·04*	*20·46*	*55·40*	,,
	49·16	*26·17*	*15·21*	*60·35*	D
	48·50	*26·33*	*8·72*	*65·55*	,,
	47·77	*26·81*	*14·07*	*60·65*	,,
	47·01	*27·22*	*18·92*	*56·30*	,,
	46·06	*27·77*	*15·42*	*60·48*	,,
	45·82	*27·90*	*15·91*	*51·21*	D, β
	45·71	*27·81*	*17·10*	*49·53*	
	39·24	*31·61*	*8·45*	*55·24*	D, γ
	nil	*55·00* ‖	—	—	D
	39·24	*31·61*	*8·45*	*55·24*	D, γ
	37·14	*32·36*	*11·48*	*52·60*	γ
	25·10	*37·99*	*12·29*	*49·71*	,,
	24·25	*38·50* ¶	—	—	γ, E
	nil	*52·13*	—	—	γ
	45·82	*27·90*	*15·91*	*51·21*	β, D
	45·71	*27·81*	*17·10*	*49·53*	
	46·03	*27·15*	*23·48*	*43·26*	β
	32·73	*33·65*	*8·81*	*54·07*	,,
	25·24	*37·39*	*10·29*	*51·98*	,,
	24·71	*37·73*	*8·14*	*49·96*	β, E
	0·14	*51·14*	—	—	β
	nil	*51·30*	—	—	,,
	51·20	*24·46*	*3·55*	*58·80*	α
	51·90	*23·93*	*7·16*	*55·66*	,,
	51·97	*23·96*	*51·57*	*28·08*	α, B
	52·16	*23·77*	*18·11*	*48·29***	,,
	52·21	23·62	44·04	31·97	,,
	52·15	23·53	45·14	31·72	
	50·24	24·50	12·59	52·07	α
	50·08	24·71	11·76	52·58	,,
	49·68	24·65	5·81	57·13	,,
	48·65	25·35	12·55	51·95	,,
	47·53	25·54	7·92	54·83	,,
	47·37	25·74	12·75	51·75	,,
	47·19	25·65	8·52	53·83	,,
	41·62	27·99	5·19	56·70	,,
	39·97	29·01	6·79	55·70	,,
	30·70	32·72	2·30	59·70	,,
	24·00	36·00 ††	—	—	α, E
	nil	*48·85* ††	—	—	α
	23·00	*39·30* ††	—	—	E, γ
	24·71	*37·73*	*8·14*	*49·80*	E, β
	24·00	36·00 ††	—	—	E, α
	23·73	35·95	0·88	51·41	E
	22·10	36·32	1·07	50·98	,,
	20·08	37·04	4·73	48·26	,,
	17·04	38·36	2·51	49·23	,,
	nil	45·05	—	—	,,

* Independent experiments by different workers at different times.

† The moist solid analysed was $[Ca(H_2O)_6][(HgCl_2)_6Cl_2]$, but a few prisms of $[Ca(H_2O)_4][HgCl_4]$ were seen sticking to the sides of the solubility bottles.

‡ This point clearly lies slightly off the correct, very unstable part of the $[Ca(H_2O)_4][HgCl_4]$ curve, though it serves to indicate the approx. position of the curve.

§ In this experiment large crystals of $[Ca(H_2O)_4][HgCl_4]$ had grown at the expense of crystals of $[Ca(H_2O)_6][(HgCl_2)_6Cl_2]$ which were originally present.

‖ Extrapolated from Roozeboom's curve.

¶ Estimated from curves.

** Very little B.

†† Estimated from curves.

Symbols used for solid phases: A = $HgCl_2$; B = $[Ca(H_2O)_6][(HgCl_2)_6Cl_2]$; C = $[Ca(H_2O)_4][HgCl_4]$; D = $CaCl_2,2H_2O$; E = $CaCl_2,6H_2O$; α = α-$CaCl_2,4H_2O$; β = β-$CaCl_2,4H_2O$; γ = γ-$CaCl_2,4H_2O$.

Formation of Unstable $SrSO_4,2H_2O$.—In the course of the numerous estimations of Sr, it was noticed that the $SrSO_4$ when pptd. at room temp. almost always separated, in the first instance, in a very bulky form which rapidly became dense and granular. The latter crystals—small diamond-shaped rhombs and derived forms—consist of $SrSO_4$. It seemed probable that the bulky solid was $SrSO_4,2H_2O$, for, under the microscope, it was seen to consist of groups of needle-like prisms. These were too fine for satisfactory optical examination, but there was nothing in their behaviour so far as it could be examined which was incompatible with a crystal form analogous to that of gypsum $CaSO_4,2H_2O$. The following expts. make it highly probable that the unstable compound really is the dihydrate. It changes so rapidly into the stable $SrSO_4$ that separation for analysis has to be done quickly. The change is much faster whilst the solid is in the mother-liquor than after it has been washed and dried.

Only small quantities could be prepared at a time. These were filtered rapidly on a small Buchner funnel, well washed with H_2O, abs. EtOH, and Et_2O, and air-dried for a few mins. The loss of wt. (in g.) under various conditions was then determined :

	(*a*).	(*b*).	(*c*).
Preparation.	0·5 G. $SrCl_2,6H_2O$ in 5 c.c. cold H_2O + 4 c.c. $2N$-H_2SO_4.	0·5 G. $SrCl_2,6H_2O$ in 5 c.c. cold H_2O + 5 c.c. $2N$-H_2SO_4, followed at once by 50 c.c. abs. EtOH.	As in (*b*), but with 15 c.c. H_2O, and carried out at 0°.
Wt. of $SrSO_4,xH_2O$ taken	0·1885	0·4060	0·3540
Loss after ¾ hr. in the air	0·0048	—	—
Loss at 110° after ¼ hr.	0·0037 *	0·0249 †	0·0163
Extra loss at 110° over-night ...	0·0015	0·0028	—
,, ,, on ignition	0·0041	0·0087	0·0122
Total loss of wt.	0·0141	0·0364	0·0285
,, ,, %	7·48	8·97	8·05

* Extra loss in this case. † After 3½ hr. at 110°.

The microscopic appearance of all three prepns. indicated that approx. half had changed into $SrSO_4$, and as the H_2O content of $SrSO_4,2H_2O$ should be 16·40%, it is considered that the above results agree with the view that the unstable hydrate is the dihydrate.

Needles of $SrSO_4,xH_2O$ had been previously noticed by Lambert and Hume-Rothery (J., 1926, 2637), who made a careful examination of the conditions under which they were formed. Owing to the instability of the hydrate they were unable to determine, or to suggest any value for, x.

TABLE III.

Solubilities of Hydrates of Calcium Chloride.

% $CaCl_2$ in solution. (B = Present authors; R = Roozeboom.)

		Forms of $CaCl_2,4H_2O$.			
Temp.	$CaCl_2,6H_2O$.	α.	β (new).	γ.	$CaCl_2,2H_2O$.
60·0°	—	—	—	—	(R) *57·80*
45·3	—	(R) 56·6	—	—	(R) *56·6*
* 39·2	—	—	*56·1*	—	*56·1*
39·0	—	(B) 52·90	—	—	—
38·9	—	—	(B) *55·38*	—	—
38·4	—	—	—	(R) *56·0*	(R) *56·0*
37·2	—	—	(B) *54·30*	(B) *54·84*	—
30·7	—	—	(B) *52·67*	—	—
30·25	—	—	(B) *52·52*	—	—
30·2	(R) 50·7	—	—	—	—
30·1	—	(B) 49·87	—	—	—
29·8	(R) 50·1	(R) 50·1	—	—	—
* 29·5	52·4	—	*52·4*	—	—
29·2	—	—	—	(R) *53·0*	—
25·0	(R) 45·05	(B) *48·85* *48·68*	(B) *51·30*	(B) *52·13*	*55·0* †
		(R) *48·85*		(R) *52·15*	—
21·05	—	(B) *47·32*	—	—	—
20·0	—	(R) *47·6*	—	(R) *51·1*	—

* Temperature and concentrations estimated from the curves.
† By extrapolation.

TABLE IV.

System $HgCl_2$–$SrCl_2$–H_2O.

Solution.		Moist solid.		
$HgCl_2$.	$SrCl_2$.	$HgCl_2$.	$SrCl_2$.	
6·90	nil	—	—	A
34·70	9·30	96·87	0·51	,,
48·21	13·93	96·36	1·07	,,
56·62	16·65	95·23	1·73	,,
57·17	17·34	98·67	1·12	,,
58·30	18·04	81·12	9·50	A, B (S)
58·46	18·01	89·00	5·35	
58·68	*18·47*	*69·80*	*14·05*	A, C
58·49	*19·42*	*76·99*	*11·64*	C
58·46	*19·53*	*73·27*	*14·55* *	,,
59·49	*19·66*	*66·15*	*16·61*	,,
58·13	18·00	69·77	14·91	B (S)
56·20	19·20	62·40	17·80	,,
55·95	19·52	66·16	16·54	,,
55·45	19·82	62·22	19·35	,,
54·33	20·88	61·44	23·87	,,
52·70	21·90	61·20	22·60	B (S)
51·20	22·50	60·40	20·00	,,
50·87	22·98	61·37	20·33	,,
48·90	23·69	15·79	48·39	B (S), E
48·81	24·01	34·53	37·80	‡ ,,
		56·88	26·93	
48·77	*23·90*	*59·60*	*25·04*	B (S)
nil	*40·00*	—	—	D
48·20	23·60	7·00	53·50	E
46·25	24·02	22·56	42·35	,,
45·32	24·26	18·85	44·82	,,
34·52	26·78	7·61	52·65	,,
31·02	27·50	7·76	51·58	,,
18·82	30·50	2·42	56·51	,,
8·55	33·42	1·11	56·58	,,
nil	35·84 †	—	—	,,

* This solid phase was largely converted into the solid solution, but the solution point seems to be on the $[Sr(H_2O)_8][(HgCl_2)_6Cl_2]$ curve.

† Benrath (*Z. anorg. Chem.*, 1927, **163**, 398) found 35·70%.

‡ Large crystals of solid solution separating from a similar mixture.

Symbols used for solid phases : A = $HgCl_2$; B = $[Sr(H_2O)_8][(HgCl_2)_3Cl_2]$; C = $[Sr(H_2O)_8][(HgCl_2)_6Cl_2]$; D = $[Sr(H_2O)_8][(SrCl_2)_3Cl_2]$ = $SrCl_2,2H_2O$; E = $SrCl_2,6H_2O$; (S) = Solid solution.

TABLE V.

System $HgCl_2$–$BaCl_2$–H_2O.

Solution.		Moist solid.		
$HgCl_2$.	$BaCl_2$.	$HgCl_2$.	$BaCl_2$.	
6·90	nil	—	—	A
15·07	3·28	95·91	trace	,,
35·36	11·19	96·92	0·68	,,
44·58	16·23	94·32	1·62	,,
54·43	21·96	94·26	2·56	,,
54·41	22·55	91·54	3·84	,,
54·74	22·91	60·17	28·56	A, B
54·93	22·80	70·06	23·68	
53·83	23·11	11·48	71·06	B
53·69	23·23	12·88	70·15	,,
51·34	23·82	10·67	73·21	,,
43·51	25·22	7·74	75·04	,,
32·45	26·07	1·99	81·12	,,
14·98	26·73	—	—	,,
8·10	26·54	—	—	,,
nil	27·08 *	—	—	,,

* Compare 27·09 found by Jelissejew (*Ber. Inst. Phys. Chem. Anal., Leningrad*, 1926, **3**, 443) and 27·10 found by Wolkow (*ibid.*, p. 704).

Symbols used for solid phases : A = $HgCl_2$; B = $BaCl_2,2H_2O$.

TABLE VI.

System $HgCl_2$–$CuCl_2$–H_2O.

25° *Isothermal.*

Solution.		Moist solid.		
$HgCl_2$.	$CuCl_2$.	$HgCl_2$.	$CuCl_2$.	
6·90	nil	—	—	A
51·47	14·86	96·39	1·28	,,
52·89	18·86	96·25	1·79	,,
51·83	20·64	97·83	1·00	,,
51·57	20·95	94·65	2·42	,,
51·50	21·35	96·70	1·28	,,
51·68	21·46	39·55	43·92	A, B
48·75	22·53	10·22	68·03	B
nil	43·32 *	—	—	,,

35° *Isothermal.*

Solution.		Moist solid.		
$HgCl_2$.	$CuCl_2$.	$HgCl_2$.	$CuCl_2$.	
8·51 †	nil	—	—	A
52·36	14·51	97·50	0·86	,,
53·28	18·70	98·25	0·72	,,
52·60	20·27	97·00	1·28	,,
52·35	21·09	97·73	1·03	,,
52·13	21·69	27·73	56·21	A, B
49·71	22·50	8·84	69·15	B
nil	44·47 †	—	—	,,

* Foote, *J. Amer. Chem. Soc.*, 1912, **34**, 880.

† Figure quoted by Schreinemakers and Thonus (*loc. cit.*).

Symbols used for solid phases : A = $HgCl_2$; B = $CuCl_2,2H_2O$.

SUMMARY.

The systems $HgCl_2$–Mg(Ca, Sr, Ba, Cu)Cl_2–H_2O have been examined at 25° and that containing copper also at 35°. Several complex salts have been found, corresponding to the three types $MCl_2,HgCl_2,xH_2O$, $MCl_2,3HgCl_2,xH_2O$, and $MCl_2,6HgCl_2,xH_2O$. Some of the solubility curves are of unusual type in being either concave to the water point or partly convex and partly concave.

The strontium chloride system is remarkable in containing a region of solid solutions which are based upon $SrCl_2,3HgCl_2,8H_2O$ and $SrCl_2,2H_2O$. The latter compound is thus shown to be $(SrCl_2,2H_2O)_4$. The probable structures of the various complex salts have been considered, as well as some of the factors which determine the form of the solubility curves.

A new form of $CaCl_2,4H_2O$ has been obtained which is intermediate as regards stability between the two forms previously known.

The unstable hydrate of strontium sulphate is probably a dihydrate.

With bivalent metals there is a great tendency to assume the 0-, 4-, 6-, or 8-co-ordinated condition rather than any intermediate value.

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