# 331. *Isomorphous Replacement in Hydrated Salts. Part III.* The Systems* $CdCl_2$–$M^{II}Cl_2$–$H_2O$ ($M^{II}$ = Mg, Mn, $Fe^{II}$, Cu, *or* Ca), *with a Discussion of Certain Solid Solutions found in these Systems.*

By Henry Bassett and Robert N. C. Strain.

The systems indicated in the title have been examined at 25°, and the existence of the following double salts established: $2CdCl_2,MgCl_2,12H_2O$; $CdCl_2,2MgCl_2,12H_2O$; $4CdCl_2,MnCl_2,10H_2O$; $CdCl_2,CuCl_2,4H_2O$; $CdCl_2,2CaCl_2,12H_2O$; and that of $2CdCl_2,FeCl_2,12H_2O$ has been confirmed qualitatively. Each of these systems shows in addition one or more series of solid solutions. They appear to belong to several types and their nature is discussed. Most interest is attached to the solid solutions crystallising in thin negative hexagonal plates which appears to be a layer-lattice structure between $(Cd,M^{II})Cl_2,2{\cdot}5H_2O$ and $CdCl_2,2NaCl,3H_2O$ as end members. In some cases the $(Cd,M^{II})Cl_2,2{\cdot}5H_2O$ is stable enough to be isolated by itself; in other cases only intergrowths with $CdCl_2,2NaCl,3H_2O$ are obtainable.

When investigating the system $CdCl_2$–$NiCl_2$–$H_2O$ at 25° Bassett and others (Parts I and II, *locc. cit.*) discovered a solid solution crystallising in thin negative hexagonal plates which could be represented by the formula $(Cd,Ni)Cl_2,2{\cdot}5H_2O$, where Cd and Ni can replace one another and where there are 2·5 molecules of water for each atom of metal. This solid solution was observed over only a limited region, which is not surprising, since one end member, $NiCl_2,2{\cdot}5H_2O$, is not known to exist and the other, $CdCl_2,2{\cdot}5H_2O$, which is monoclinic, belongs to a different crystal system.

The ionic radii of cadmium and nickel are 1·03 and 0·78 Å, respectively (Evans, "Crystal Chemistry," Cambridge Univ. Press, 1938), which differ by 32% calculated on the smaller radius. Goldschmidt (*Trans. Faraday Soc.*, 1929, **25**, 253) has shown that isomorphous replacement of atoms does not occur unless the ionic radii differ by less than 15% and their polarisability is about the same, so that in the system $CdCl_2$–$NiCl_2$–$H_2O$ such solid solution is unexpected. When sodium chloride was added to this sytem it was found that it could enter isomorphously into the solid solution $(Cd,Ni)Cl_2,2{\cdot}5H_2O$ replacing the nickel and some of the cadmium. This new solid solution has a wide range of existence starting with the sodium-free $(Cd,Ni)Cl_2,2{\cdot}5H_2O$ and ending with the hexagonal $CdCl_2,2NaCl,3H_2O$. Evidence was brought forward to suggest that solid solution occurs by a replacement of $[Ni(H_2O)_4]^{\cdot\cdot}$ by $[Na_2(H_2O)_2]^{\cdot\cdot}$. A similar solid solution containing sodium chloride was observed in the system $CdCl_2$–$CoCl_2$–$H_2O$ but the sodium-free compound could not be obtained.

The present investigation was undertaken to determine if similar solid solutions with or without sodium chloride occur in other systems containing cadmium chloride and a

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* Parts I and II, *J.*, 1939, **646**, **653**.

bivalent metal chloride. The chlorides investigated were $MgCl_2$, $MnCl_2$, $CuCl_2$, $FeCl_2$ (qualitatively), and $CaCl_2$, chosen for their position in the Periodic Table, their ionic radii, and their different hydrates at 25°. With the exception of the system $CdCl_2$–$FeCl_2$–$H_2O$ these systems have been examined fully at 25° with particular reference to solid solutions, and in all cases sodium chloride was added to the system and a search made for a negative hexagonal phase.

None of the systems dealt with in this paper has been examined previously in detail, though some of the double salts which form congruent solutions had been prepared. Von Hauer recorded $CdCl_2,2MgCl_2,12H_2O$; $2CdCl_2,MnCl_2,12H_2O$; $2CdCl_2,FeCl_2,12H_2O$; $2CdCl_2,CaCl_2,7H_2O$; $CdCl_2,2CaCl_2,12H_2O$, and $CdCl_2,CuCl_2,4H_2O$ (*J. pr. Chem.*, 1856, **68**, 385) and $2CdCl_2,MgCl_2,12H_2O$ (*Sitzungsber. Akad. Wiss. Wien*, 1855, **17**, 331). We have been unable to get the manganese double salt and $2CdCl_2,CaCl_2,7H_2O$ at 25°, though the latter corresponds to the most $CaCl_2$-rich sample of an orthorhombic solid solution represented by ($CdCl_2,H_2O$–$CaCl_2,4H_2O$) obtained by us.

Table 1 shows the double salts and solid solutions we have identified, together with their optical characteristics.

TABLE 1. *Optical properties of solid phases.*

| Compound | Crystal habit | Extinction | System | Optical sign |
|---|---|---|---|---|
| $2CdCl_2,MgCl_2,12H_2O$ | Needles with pyramidal ends | All straight | Orthorhombic | Negative |
| $CdCl_2,2MgCl_2,12H_2O$ | Six-sided prisms | Straight or isotropic | Pseudo-hexagonal | Positive |
| $4CdCl_2,MnCl_2,10H_2O$ | Thin needles with poorly formed ends | Straight and a few possibly oblique | Orthorhombic? or monoclinic | Negative |
| $CdCl_2,CuCl_2,4H_2O$ | Thin green needles | Straight and slightly oblique | Monoclinic | Positive |
| $CdCl_2,2CaCl_2,12H_2O$ | Prisms | Straight and oblique | Monoclinic | Negative |
| Solid solution represented as ($CdCl_2,H_2O$–$CaCl_2,4H_2O$) | Needles | All straight | Orthorhombic | Negative |
| Metastable solid solution in all systems | Thin hexagonal plates | Isotropic | Hexagonal or pseudo-hexagonal | Negative |

The experimental results for the several systems are summarised in Tables 2—11 and shown graphically in Figs. 1—6.

The system $CdCl_2$–$FeCl_2$–$H_2O$ was examined only qualitatively. The solid phases over the whole range of solutions between those saturated with respect to hydrated cadmium chloride and hydrated ferrous chloride were examined under the polarising microscope. Only one new phase was observed, which crystallised in long needles of the negative orthorhombic class. As $2CdCl_2,MgCl_2,12H_2O$ and $2CdCl_2,NiCl_2,12H_2O$ are also negative orthorhombic, it is probable that this new phase is the $2CdCl_2,FeCl_2,12H_2O$ recorded by von Hauer (*loc. cit.*).

## EXPERIMENTAL

All solid phases (usually mounted in their own mother-liquor) were examined according to the usual methods with a polarising microscope with rotating stage, before chemical analyses were undertaken (Hartshorne and Stuart, "Crystals and the Polarising Microscope," 1934). Such examination is particularly useful when metastable phases are being investigated, as it can, in most cases, positively confirm that the stable phase is absent, thus guarding against confusing results being obtained by analysing mixtures not in equilibrium with their mother-liquor. Microscopic examination is also invaluable when definite mixtures of two solids are required in order to find an invariant point.

The procedure followed in examining the systems has been previously reported (Bassett, Henshall, Sergeant, and Shipley, *J.*, 1939, 649). As an alternative to the asbestos-coated filter plate in the phase-separation tube previously used, a detachable sintered-glass disc was employed when it was desired to wash crystals free from mother-liquor. A sintered-glass disc 18 mm. in diameter was fitted tightly into a soft rubber ring cut from rubber tubing having a wall thickness of 4—5 mm.: the disc and rubber ring were then wedged into the lower end of the separation tube, which had a slight taper. This assembly was found most reliable and afforded a quick and easy method for the removal of samples for analysis, the disc, rubber ring, and sample being pushed out of the tube by means of a glass rod.

The cadmium chloride used was purified by recrystallisation from water and the other salts were of A.R. quality. The components used in the sodium-free systems were free from sodium.

*Analytical Methods.*—Total chloride was determined in all cases as a check on the accuracy of the metal determinations. The silver chloride was weighed on a sintered-glass Gooch crucible.

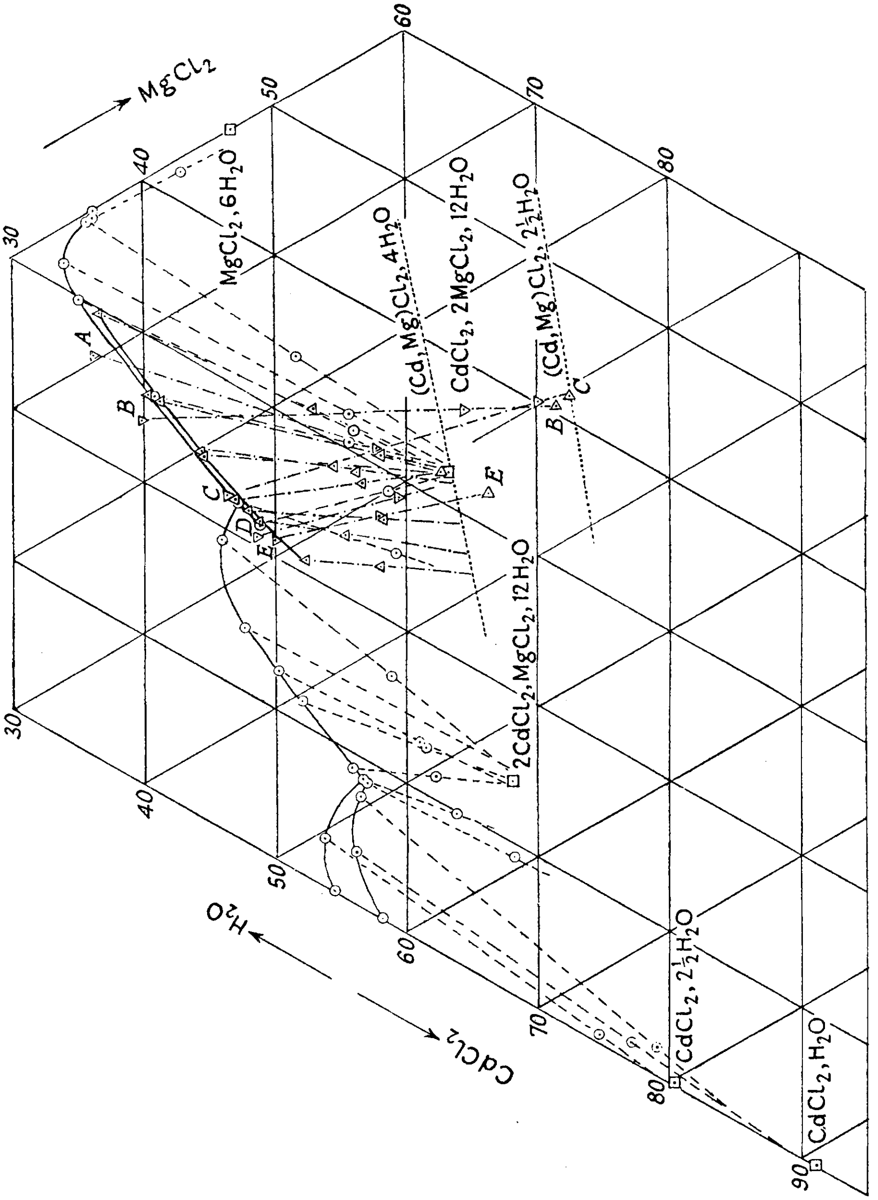


FIG. 1. *System* $CdCl_2$-$MgCl_2$-$H_2O$ (25°). (*See Tables* 2 *and* 6.)

◁ *Metastable negative hexagons.*
▷ ,, ,, ,, *(with indicator present).*
△ ,, ,, ,, *(calculated dry solid).*

(i) Cadmium was separated from magnesium or manganese by precipitation as sulphide from weakly acid solution. After being washed with dilute ammonium nitrate saturated with hydrogen sulphide, the precipitate was dissolved immediately in a minimum amount of concentrated hydrochloric acid. The cadmium was then precipitated and weighed as $NH_4CdPO_4,H_2O$ by the procedure described by Bassett *et al.* (*loc. cit.*, p. 650). As the weight of cadmium sulphide recovered from the $NH_4CdPO_4,H_2O$ filtrate varied from 0·1 to 1·0 mg. depending upon the conditions of the experiment, it was normally weighed as such after being washed and dried at 97° on a Gooch crucible. It is known that cadmium is not precipitated as sulphide of constant composition, but the error introduced is negligible as it only affects a small correction to the main cadmium estimation.

In dealing with cadmium chloride and calcium chloride mixtures, the cadmium was separated by precipitation as the anthranilate, which was weighed after drying at 105° (Funk and Ditt, *Z. anal. Chem.*, 1933, **91**, 332).

(ii) Calcium was precipitated as oxalate in the filtrate from the cadmium anthranilate (Funk

TABLE 2 (see Fig. 1). *System* $CdCl_2$–$MgCl_2$–$H_2O$ *at* 25°.

| Solution | | Moist solid | | | Equilibrium time (min.) given to metastable negative hexagons | Solution | | Moist solid | | | Equilibrium time (min.) given to metastable negative hexagons |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CdCl_2$, % | $MgCl_2$, % | $CdCl_2$, % | $MgCl_2$, % | Solid present * | | $CdCl_2$, % | $MgCl_2$, % | $CdCl_2$, % | $MgCl_2$, % | Solid present * | |
| 0 | 36·2 † | — | — | *a* | — | 27·1 | 21·8 | 31·2 | 24·1 | *f*(*m*) | 15 |
| 0·4$_2$ | 35·7 | 0·9$_0$ | 42·1 | *a* and *b* | — | 31·4 | 21·0 | 34·7 | 23·4 | *f*(*m*) | 30 |
| 0·4$_2$ | 35·3 | 17·5 | 34·2 | *b* | — | 26·6 | 19·2 | 42·3 | 16·7 | *c* | — |
| 2·3 | 31·6 | 23·3 | 30·4 | *b* | — | 33·4 | 14·2 | 41·1 | 14·5 | *c* | — |
| 5·4 | 30·0 | 24·6 | 31·5 | *b* | — | 37·7 | 12·6 | 47·9 | 13·1 | *c* | — |
| 14·7 | 26·2 | 25·1 | 30·4 | *b* | — | 40·7 | 11·5 | 48·4 | 13·2 | *c* | — |
| 24·9 | 22·4 | 34·4 | 24·8 | *b* and *c* | — | 47·0 | 8·9 | 50·9 | 11·3 | *c* | — |
| 27·2 | 21·9 | 29·9 | 28·8 | *b*(*m*) | — | 48·1 | 8·6 | 54·0 | 9·7 | *c* and *d* | — |
| 7·0 | 29·6 | 21·5 | 29·9 | *f*(*m*) | 20 | 50·6 | 3·2 | 74·3 | 0·3$_7$ | *d* | — |
| 14·5 | 26·1 | 27·1 | 30·7 | *f*(*m*) | 5 | 54·62 ‡ | 0 | — | — | *d* | — |
| 15·1 | 26·1 | 27·2 | 30·8 | *f*(*m*) | 10 | 48·5 | 8·8 | 59·1 | 9·2 | *c* and *e*(*m*) | — |
| 20·0 | 24·2 | 27·6 | 28·9 | *f*(*m*) | 20 | 49·2 | 7·2 | 77·1 | 1·7 | *e*(*m*) | — |
| 20·4 | 24·1 | 26·1 | 28·3 | *f*(*m*) | 25 | 52·8 | 3·5 | 75·9 | 1·1 | *e*(*m*) | — |
| 24·8 | 22·3 | 28·5 | 28·2 | *f*(*m*) | 35 | 58·10 ‡ | 0 | — | — | *e*(*m*) | — |
| 26·0 | 22·3 | 31·6 | 26·6 | *f*(*m*) | 30 | | | | | | |

* *a* = $MgCl_2,6H_2O$; *b* = $CdCl_2,2MgCl_2,12H_2O$; *c* = $2CdCl_2,MgCl_2,12H_2O$; *d* = $CdCl_2,2{\cdot}5H_2O$; *e* = $CdCl_2,H_2O$; *f* = Negative hexagons. (*m*) = Metastable.

† Seidell, " Solubilities of Inorganic and Metal Organic Compounds," 3rd edtn. (1940).

‡ Bassett *et al.*, *J.*, 1939, 646.

TABLE 3 (see Fig. 2). *System* $CdCl_2$–$MnCl_2$–$H_2O$ *at* 25°.

| Solution | | Moist solid | | | Solution | | Moist solid | | |
|---|---|---|---|---|---|---|---|---|---|
| $CdCl_2$, % | $MnCl_2$, % | $CdCl_2$, % | $MnCl_2$, % | Solid present * | $CdCl_2$, % | $MnCl_2$, % | $CdCl_2$, % | $MnCl_2$, % | Solid present * |
| 0 | 43·55 † | — | — | *a* | 45·5 | 11·3 | 73·8 | 2·3 | *c* |
| 7·7 | 40·4 | 2·6 | 55·9 | *a* | 51·6 | 2·9 | 74·3 | 0·8$_6$ | *c* |
| 16·5 | 36·6 | 6·8 | 53·7 | *a* | 54·62 ‡ | 0 | — | — | *c* |
| 27·5 | 31·1 | 37·4 | 32·9 | *a* | 43·0 | 15·3 | 69·0 | 7·7 | *b* and *d*(*m*) |
| 31·6 | 27·5 | 55·9 | 18·2 | *a* and *b* | 43·7 | 14·8 | 70·6 | 6·5 | *d*(*m*) |
| 36·5 | 22·2 | 58·6 | 15·9 | *b* | 44·3 | 13·0 | 65·0 | 7·4 | *d*(*m*) |
| 37·1 | 21·9 | 58·0 | 15·9 | *b* | 47·3 | 8·6 | 74·3 | 3·6 | *d*(*m*) |
| 40·9 | 18·0 | 65·5 | 11·5 | *b* and *c* | 58·10 ‡ | 0 | — | — | *d*(*m*) |

* *a* = $MnCl_2,4H_2O$; *b* = $4CdCl_2,MnCl_2,10H_2O$; *c* = $CdCl_2,2{\cdot}5H_2O$; *d* = $CdCl_2,H_2O$. (*m*) = Metastable.

† Seidell (*op. cit.*). ‡ Bassett *et al.* (*loc. cit.*).

TABLE 4 (see Fig. 3). *System* $CdCl_2$–$CuCl_2$–$H_2O$ *at* 25°.

| Solution | | Moist solid | | | Solution | | Moist solid | | |
|---|---|---|---|---|---|---|---|---|---|
| $CdCl_2$, % | $CuCl_2$, % | $CdCl_2$, % | $CuCl_2$, % | Solid present * | $CdCl_2$, % | $CuCl_2$, % | $CdCl_2$, % | $CuCl_2$, % | Solid present * |
| 0 | 43·6 | — | — | *a* | 31·8 | 25·1 | 41·8 | 31·0 | *b* |
| 8·2 | 39·4 | 4·2 | 64·0 | *a* | 36·4 | 22·6 | 42·6 | 28·3 | *b* |
| 13·7 | 36·8 | 4·5 | 68·2 | *a* | 38·8 | 21·1 | 60·8 | 15·7 | *b* and *d* |
| 21·4 | 32·4 | 11·9 | 53·9 | *a* | 39·7 | 18·8 | 75·7 | 5·4 | *c* and *d* |
| 22·4 | 32·0 | 28·1 | 45·3 | *a* and *b* | 47·4 | 7·1 | 75·9 | 1·0 | *c* |
| 23·7 | 31·4 | 38·6 | 33·0 | *b* | 54·62 † | 0 | — | — | *c* |
| 24·4 | 30·7 | 38·4 | 32·8 | *b* | 38·6 | 20·6 | 69·6 | 8·8 | *d*(*m*) |
| 28·1 | 27·6 | 40·0 | 32·1 | *b* | 46·5 | 11·0 | 71·2 | 4·0 | *d*(*m*) |
| 30·5 | 26·2 | 38·3 | 30·3 | *b* | 53·5 | 4·3 | 80·3 | 1·6 | *d*(*m*) |
| 30·7 | 26·4 | 41·0 | 31·3 | *b* | 58·10 † | 0 | — | — | *d*(*m*) |

* *a* = $CuCl_2,2H_2O$; *b* = $CdCl_2,CuCl_2,4H_2O$; *c* = $CdCl_2,2{\cdot}5H_2O$; *d* = $CdCl_2,H_2O$. (*m*) = Metastable.

† Bassett *et al.* (*loc. cit.*).

and Ditt, *loc. cit.*), and, after being washed with a saturated solution of calcium oxalate (Bassett, *J.*, 1934, 1273), it was determined volumetrically with 0·1N-potassium permanganate.

(iii) Copper was precipitated and weighed as cuprous thiocyanate in the presence of sulphur dioxide. The ammonium thiocyanate in the filtrate from the latter does not intefere with the precipitation and weighing of the cadmium as $NH_4CdPO_4,H_2O$. Sulphur dioxide was removed by boiling before precipitation of the cadmium.

(iv) Magnesium and manganese were precipitated by standard procedure as $NH_4MgPO_4,xH_2O$ and $NH_4MnPO_4,H_2O$. The former was weighed as $Mg_2P_2O_7$, and the latter was weighed as such.

FIG. 2. *System* $CdCl_2$–$MnCl_2$–$H_2O$ (25°).

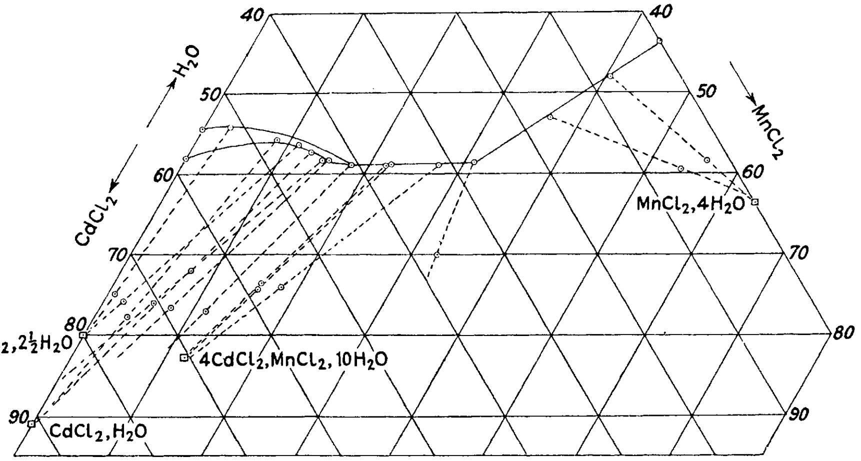
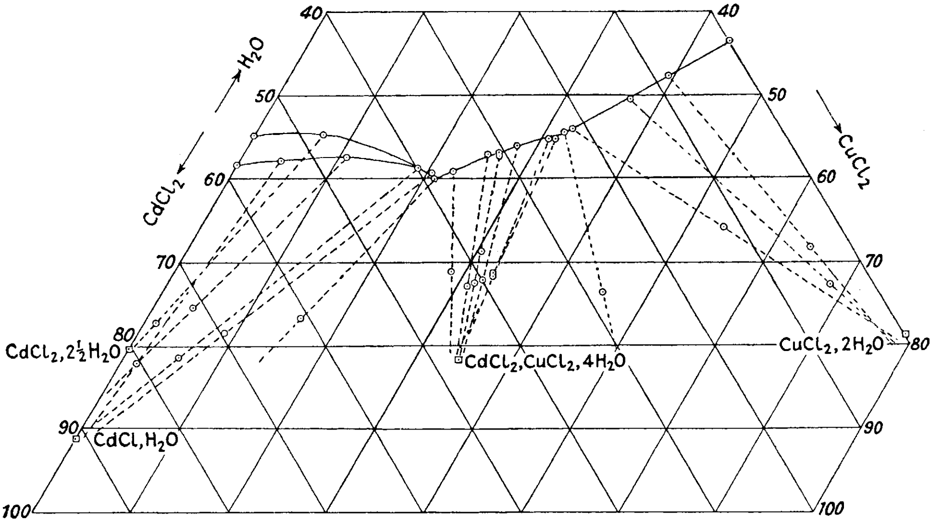


FIG. 3. *System* $CdCl_2$–$CuCl_2$–$H_2O$ (25°).



(v) Sodium was precipitated as $NaZn(UO_2)_3(C_2H_3O)_9,6H_2O$ in the presence of the other metals and weighed as such, standard procedure being followed.

(vi) Bromate was determined iodometrically by Kolthoff's method (*Pharm. Weekblad*, 1919, **56**, 393) in acid solution, ammonium molybdate being used as catalyst.

Since the two double salts $CdCl_2,2MgCl_2,12H_2O$ and $2CdCl,MgCl_2,12H_2O$ form congruent solutions, the methods of preparation given by von Hauer (*loc. cit.*) are satisfactory.

The one double salt, namely, $4CdCl_2,MnCl_2,10H_2O$, does not form a congruent solution. The double salt $2CdCl_2,MnCl_2,12H_2O$ reported by von Hauer could not be obtained at 25° even after seeding with the corresponding cadmium magnesium double salt, nor was there any indication from optical examinations that this double salt exists at higher temperatures. Its existence is clearly open to doubt.

The tie lines in Fig. 3 scarcely enable a clear decision to be made as to whether the double salt has three or four molecules of water of crystallisation. As the salt forms a congruent solution, the matter could be settled by analysis of the crystals obtained at 25° from a solution containing the constitutent salts in exact equimolar proportion. The crystals were well dried between hardened filter-paper and air-dried at room temperature, reaching constant weight after 24 hours. Analysis of the air-dry double salt to give indirectly the amount of water of crystallisation gave $H_2O$, 17·8% (Calc. for $CdCl_2,CuCl_2,4H_2O$ : $H_2O$, 18·2%).

*The Solid Solutions found in the Several Systems.*—A solid forming thin negative hexagonal plates has been observed in all the systems dealt with in the present communication. In all cases this is metastable at 25° towards other crystalline phases and is a solid solution with variable composition. The ease with which the negative hexagonal plates can be obtained varies according to the system. In some cases they can be obtained from the pure systems, but in others the presence of sodium chloride is necessary and some of it is found in the hexagonal plates. The evidence suggests that the negative hexagons are of two types, one of which is truly hexagonal and can be regarded as having $(Cd,M^{II})Cl_2,2{\cdot}5H_2O$ and $CdCl_2,2NaCl,3H_2O$ as its end members, and a second which is only pseudo-hexagonal, being biaxial with a small optical axial angle, and which can be regarded as a solid solution represented by $(Cd,M^{II})Cl_2,4H_2O$. It would appear that sodium chloride can enter into the latter solid solution but the evidence is conflicting. In the case of the $CdCl_2$–$MgCl_2$–$H_2O$ system, addition of sodium chloride is unfavourable to the formation of the pseudo-hexagonal plates, whereas in the $CdCl_2$–$CaCl_2$–$H_2O$ system such addition appears to be necessary. There is no analytical evidence for the presence of sodium chloride in any of the pseudo-hexagonal plates such as there is for the truly hexagonal forms.

TABLE 5 (see Fig. 4). *System* $CdCl_2$–$CaCl_2$–$H_2O$ *at* 25°.

| Solution |  | Moist solid |  |  | Solution |  | Moist solid |  |  |
|---|---|---|---|---|---|---|---|---|---|
| $CdCl_2$, % | $CaCl_2$, % | $CdCl_2$, % | $CaCl_2$, % | Solid present * | $CdCl_2$, % | $CaCl_2$, % | $CdCl_2$, % | $CaCl_2$, % | Solid present * |
| 0 | 45·05 † | — | — | *a* | 38·3 | 19·3 | 57·7 | 19·2 | *c* |
| 1·6 | 44·6 | 6·6 | 47·4 | *a* and *b* | 43·1 | 16·7 | 61·1 | 14·5 | *c* |
| 4·5 | 39·8 | 24·6 | 36·9 | *b* | 46·8 | 14·9 | 62·2 | 10·9 | *c* |
| 8·7 | 37·5 | 27·3 | 35·7 | *b* | 47·8 | 11·3 | Not sufficient for analysis |  | *d* and *e* |
| 12·0 | 35·0 | 26·1 | 36·5 | *b* |  |  |  |  |  |
| 16·5 | 32·5 | 28·6 | 35·2 | *b* | 48·6 | 8·3 | 77·7 | 0·8$_7$ | *d* |
| 17·8 | 32·2 | 27·9 | 36·0 | *b* | 50·0 | 6·1 | 73·0 | 1·3 | *d* |
| 21·8 | 30·5 | 27·9 | 34·5 | *b* | 54·62 ‡ | 0 | — | — | *d* |
| 24·8 | 29·1 | 28·6 | 35·3 | *b*(*m*) | 48·6 | 10·0 | 72·6 | 4·1 | *e*(*m*) |
| 24·3 | 28·8 | 39·4 | 27·2 | *b* and *c* | 48·9 | 8·9 | 72·5 | 4·4 | *e*(*m*) |
| 25·0 | 28·3 | 55·3 | 22·2 | *c* | 51·8 | 5·6 | 78·1 | 1·5 | *e*(*m*) |
| 32·8 | 21·7 | 51·3 | 20·9 | *c* | 58·10 ‡ | 0 | — | — | *e*(*m*) |

* *a* = $CaCl_2,6H_2O$ ; *b* = $CdCl_2,2CaCl_2,12H_2O$ ; *c* = Solid solution ($CdCl_2,H_2O$–$CaCl_2,4H_2O$) ; *d* = $CdCl_2,2{\cdot}5H_2O$ ; *e* = $CdCl_2,H_2O$. (*m*) = Metastable.

† Bassett, Gordon, and Henshall, *J.*, 1937, 971. ‡ Bassett *et al.*, *J.*, 1939, 646.

In the system $CdCl_2$–$CaCl_2$–$H_2O$ there is in addition an entirely different type of solid solution. This forms long thin needles of the negative orthorhombic class and can be regarded as having $CdCl_2,H_2O$ and $\beta$-$CaCl_2,4H_2O$ as its end members. It is a stable form and its solubility curve covers a considerable range between those of $CdCl_2,H_2O$ and $CdCl_2,2CaCl_2,12H_2O$.

The determination of the actual composition of solid solutions of these types is a matter of extreme difficulty. In some cases we have removed adhering mother-liquor from the crystals by means of organic solvents; in other cases we have added suitable substances in small amounts to the system which would enable the composition of the dry solid, free from mother-liquor, to be calculated. The results obtained are considered to be reasonably reliable. The experimental results are shown in Tables 6—11 and Figs. 1, 4, 5, and 6. The double salt $2CdCl_2,CaCl_2,7H_2O$ recorded by von Hauer (*loc. cit.*) would have a calculated composition of $CdCl_2$, 60·7% and $CaCl_2$, 18·4%. This corresponds to the composition found for the most $CaCl_2$-rich sample of this solid solution (see Fig. 4) and would be expected from the ratio of salts used by von Hauer ($CdCl_2 : CaCl_2 = 4 : 3$).

The theoretical explanation of these peculiar solid solutions must clearly pay great attention to the best-defined case of all, namely, that found in the systems $CdCl_2$–$NiCl_2$–$H_2O$ and $CdCl_2$–$NiCl_2$–NaCl–$H_2O$ (Bassett *et al.*, *loc. cit.*). The suggestion made there was that the process involved was a gradual replacement of $[Ni(H_2O)_4]^{\cdot\cdot}$ or $[Cd(H_2O)_4]^{\cdot\cdot}$ by $[Na_2(H_2O)_2]^{\cdot\cdot}$.

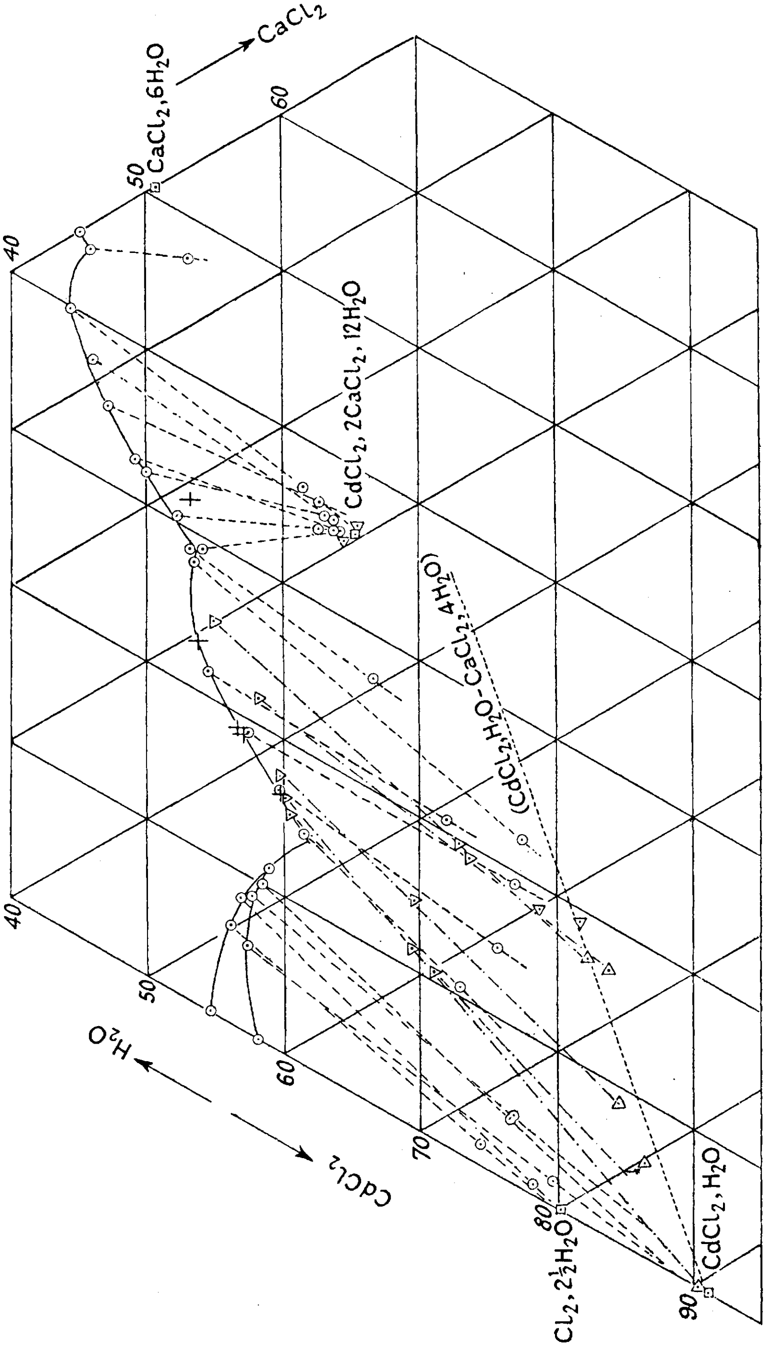


FIG. 4. *System* $CdCl_2$–$CaCl_2$–$H_2O$ (25°). (*See Table 5.*)

+ *Metastable negative hexagons in presence of NaCl only* (*Table* 9).
▷ *Orthorhombic solid solution* ($CdCl_2,H_2O$–$CaCl_2,4H_2O$), *with indicator present* (*Table* 10).
△ ,, ,, *calculated dry solid* (*Table* 10).
▽ ,, *Washed dry solids*'' (*Table* 11).

It is perhaps more probable that a layer-lattice structure is built up with layers of $CdCl_2,2NaCl,3H_2O$ and layers of $(Cd,M^{II})Cl_2,2{\cdot}5H_2O$. It is quite possible that the structure of $(Cd,M^{II})Cl_2,2{\cdot}5H_2O$ and $CdCl_2,2NaCl,3H_2O$ might be sufficiently similar for the formation of layer-lattice intergrowths. The additional stability introduced by the $CdCl_2,2NaCl,3H_2O$ might enable a hexagonal form of $(Cd,M^{II})Cl_2,2{\cdot}5H_2O$ to occur which is not capable of existing in the free state. In a similar way the pseudo-hexagonal compound when it contains sodium might be made up of layers of $(Cd,M^{II})Cl_2,4H_2O$ and $CdCl_2,2NaCl,3H_2O$.

The salts $CdCl_2,H_2O$ and $\beta$-$CaCl_2,4H_2O$ are both negative orthorhombic and so is the solid solution which seems to be formed between them; this too might well have a layer-lattice structure. Structures akin to those suggested are well known among minerals—examples are the humite group and the staurolite group of silicates (see Wells, " Structural Inorganic Chemistry," pp. 470, 472). The solubility curve of the negative orthorhombic solid solution, were it not too unstable, would cut the side of the triangular diagram at about $CaCl_2$, 51·3% (Fig. 4), which is the solubility of $\beta$-$CaCl_2,4H_2O$ at 25°. This confirms other evidence that $\beta$-$CaCl_2,4H_2O$ could be an end member of the solid solution. The ordinary orthorhombic form of $CdCl_2,H_2O$ cannot, however, be the other end member, as the solubility curve of the monohydrate is quite distinct from that of the solid solution. We have observed nothing to suggest that sodium chloride can enter into the negative orthorhombic ($CdCl_2,H_2O$–$CaCl_2,4H_2O$) solid solution.

*Details of the Solid Solutions in the Several Systems.—System* $CdCl_2$–$MgCl_2$–$H_2O$. The forms crystallising in thin negative hexagonal plates exist in the same region as the compound $CdCl_2,2MgCl_2,12H_2O$, and since it is only just metastable to this salt its solubility curve could be followed for a considerable distance. At the $MgCl_2$-rich end of its range the tie lines converge very closely on to the point representing $CdCl_2,2MgCl_2,12H_2O$, so this would seem to represent the limit of solid-solution formation. In this region the compound $CdCl_2,2MgCl_2,12H_2O$ can be considered to exist in two polymorphic forms. In contact with solutions containing more than 25% by weight of $CdCl_2$ the solid phase becomes progressively richer in this salt as indicated by the tie lines failing to converge on a single point. The position of the solubility curve suggests that the limiting solid solution on the $CdCl_2$ side might correspond to a compound $CdCl_2,MgCl_2,8H_2O$. Over the complete range of existence the thin hexagons have very similar optical properties with edge angles of 120°, the face of the crystal plates showing long thin troughs etched parallel to the sides. Under favourable crystallising conditions the hexagons can have a thicker habit and display secondary faces. The hexagons are not truly uniaxial but show an interference figure which becomes biaxial with a small optical angle (pseudo-hexagonal) on rotation of the crystal, indicating a small divergence from the true hexagonal form. The $CdCl_2,2MgCl_2,12H_2O$ crystals are in the form of positive hexagonal columns which can show a hexagonal section which is also optically pseudo-hexagonal.

The negative hexagons were too thin to be dried mechanically between hardened filter-paper and too soluble in organic solvents for the mother-liquor to be removed by washing, though various mixtures were tried. Addition of sodium chloride to the system, in the hope that increase in stability and the presence of sodium chloride might make the crystals easier to wash free from mother-liquor, led to no satisfactory results.

Sulphuric acid was found to be a satisfactory " indicator " when added in small amounts to the mixtures. Analysis of solution and moist solid enables the composition of the pure dry solid to be calculated on the assumption that all the " indicator " found in the moist solid is present in the adhering solution. The metastable phase normally had an existence time of up to 30 minutes and could be separated by filtration during this period without precipitation of the stable phase.

Potassium bromate was tried as an indicator but it greatly increased the instabilty of the negative hexagons; even when only 5 minutes were allowed before separation of solid and solution, some stable phase was observed in the moist solid a few minutes after sampling had taken place.

The results obtained by the indicator technique are given in Table 6. Where sulphuric acid was used as an indicator all the results refer to samples which were observed to be thin negative hexagons both before and after filtration.

The results in Table 6 appear to be of considerable significance. The results for the solutions after correction for the amount of indicator present do not quite fall on the solubility curve of the negative hexagons as given by the results without indicator in Table 2; this is due to the short time allowed for equilibrium and the disturbance caused by the presence of the indicator especially when present in comparatively high concentration.

Experiment *A* gives a result for the dry solid which agrees exactly with the indications given by the convergence of the tie lines in that region of the diagram. This shows that the indicator method using sulphuric acid can be regarded as giving reliable results.

Experiment *E* gives a point falling close to, though somewhat below the line $(Cd,Mg)Cl_2,4H_2O$, but though it indicates an increase in the proportion of $CdCl_2$ relatively to that of $MgCl_2$ it cannot be regarded with much confidence for the reason mentioned above.

Experiments *B* and *C* give results which are especially interesting as they both give points for the dry solid lying almost exactly on the $(Cd,Mg)Cl_2,2{\cdot}5H_2O$ line. Both are close to the position represented by $2CdCl_2,5MgCl_2,17{\cdot}5H_2O$ (Calc.: $CdCl_2$, 31·7; $MgCl_2$, 41·2%). This seems to show that the metastable hexagons found in the system $CdCl_2{-}MgCl_2{-}H_2O$ are of two types: (*a*) biaxial (pseudo-hexagonal) solid solution—$(Cd,Mg)Cl_2,4H_2O$; (*b*) uniaxial, hexagonal, solid solution—$(Cd,Mg)Cl_2,2{\cdot}5H_2O$. Type (*a*) appears to be more stable and more readily obtained than type (*b*).

TABLE 6 (see Fig. 1). *Composition of* $CdCl_2,MgCl_2$ *negative hexagons* (25°).

| Equilibrium time (min.) | Solution * | | | | Moist solid * | | | | Calculated dry solid | | Ref. in Fig. 1 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $CdCl_2$, % | $MgCl_2$, % | $H_2SO_4$, % | $KBrO_3$, % | $CdCl_2$, % | $MgCl_2$, % | $H_2SO_4$, % | $KBrO_3$, % | $CdCl_2$, % | $MgCl_2$, % | |
| | (9·7) | (26·9) | | | (27·0) | (31·0) | | | | | |
| 25 | 9·6 | 26·7 | $0{\cdot}6_5$ | — | 26·9 | 31·0 | $0{\cdot}1_4$ | — | 31·9 | 32·2 | *A* |
| | (15·7) | (24·1) | | | (27·6) | (37·0) | | | | | |
| 30 | 14·7 | 22·6 | $6{\cdot}1_5$ | — | 27·2 | 36·5 | $1{\cdot}3_6$ | — | 30·7 | 40·5 | *B* |
| | (24·1) | (22·6) | | | (29·9) | (40·2) | | | | | |
| 30 | 24·0 | 22·5 | $0{\cdot}3_5$ | — | 29·9 | 40·2 | 0·03 | — | 30·5 | 42·0 | *C* |
| 20 | 27·8 | 21·0 | † | — | 31·7 | 28·9 | † | — | — | — | *D* |
| | (29·1) | (21·4) | | | (31·5) | (26·8) | | | | | |
| 5 | 28·8 | 21·1 | — | 1·13 | 31·3 | 26·7 | — | 0·57 | 33·9 | 32·4 | *E* |

* Figures in parentheses are calculated by neglecting amount of " indicator " present.

† Small amount, not determined.

It must be remembered that the tie lines relating to solid solutions are liable to be somewhat erratic, owing to the fact that, although the surface layers of the solid phase are in equilibrium with the solution, the composition will change with growth. The gross composition of the solid phase will therefore vary somewhat according to the relative proportions of the solid phase which have separated in different experiments. Poggiale (*Compt. rend.*, 1870, **70**, 1130) records a compound $MgCl_2,NaCl,2H_2O$, but Keitel (*Kali*, 1923, **17**, 248, 261) could not confirm this and says that $MgCl_2$ and NaCl form no double salts or solid solutions.

*System* $CdCl_2{-}MnCl_2{-}NaCl{-}H_2O$. No negative hexagons were obtained in the system $CdCl_2{-}MnCl_2{-}H_2O$ but in the presence of sodium chloride they appeared. With a molecular ratio $MnCl_2 : CdCl_2 = 2{\cdot}2 : 1$ they could not be obtained if the NaCl content was less than 0·5% (calculated on the total anhydrous salts). As the proportion of NaCl was increased to 15%, the stability of the hexagons was found to increase. Their appearance was identical with that of hexagons found in the $CdCl_2{-}MgCl_2{-}H_2O$ system but, unlike the latter, they always gave a true uniaxial interference figure.

The negative hexagons were too thin for mechanical drying, and although various substances were tried as indicators none was found suitable. The presence of sulphate caused the hexagons to become very unstable, whereas bromate caused oxidation trouble, and so on. A satisfactory washing technique was, however, developed which enabled a dry preparation to be obtained for analysis. Acetone or acetone–ether caused precipitation from the mother-liquor but it was found that a slightly warmed mixture of 90% acetone and 10% water (by vol.) was satisfactory as a first wash liquid and the following procedure gave crystals of the negative hexagons uncontaminated by the component salts or $4CdCl_2,MnCl_2,10H_2O$: the moist crystals were sucked as dry as possible on a sintered-glass crucible, then washed successively 3 times with the above warm mixture of acetone and water, 3 times with acetone, and twice with ether (dried over sodium), and finlly kept at room temperature for 15 minutes before sampling for analysis. Owing to the tendency of the thin plates to pack tightly under suction, only small quantities of the solid could be satisfactorily washed at one time.

The composition of a number of preparations of the dry negative hexagons separated in the above manner is given in Table 7 and shown graphically in Fig. 5.

It must be admitted that, whatever the care used, separation of solid from aqueous phases by washing with organic solvents is always subject to some uncertainty. The points for the solid solutions in Fig. 5 fall at some distance from the line joining the points $CdCl_2,2NaCl,3H_2O$ and $(Cd,Mn)Cl_2,2{\cdot}5H_2O$. However, as the results obtained in the $CdCl_2{-}NiCl_2{-}NaCl{-}H_2O$ system were much more definite because the negative hexagons were obtainable as much larger crystals, it is reasonable to conclude that, since the negative hexagons in both systems are optically completely similar, the manganese crystals are solid solutions between (Cd,Mn)$Cl_2$,2·5$H_2O$ and $CdCl_2$,2NaCl,3$H_2O$. The system $MnCl_2$–NaCl–$H_2O$ was examined qualitatively by observing the optical properties of the solid phases and no indication was obtained for the existence of any double salt.

TABLE 7 (see Fig. 5). *System* $CdCl_2$–$MnCl_2$–NaCl–$H_2O$ (25°) : *negative hexagons.*

| Composition, % (by wt.) | | | Composition, % (molar) | | | Composition, % (by wt.) | | | Composition, % (molar) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CdCl_2$ | $MnCl_2$ | NaCl | $CdCl_2$ | $MnCl_2$ | NaCl | $CdCl_2$ | $MnCl_2$ | NaCl | $CdCl_2$ | $MnCl_2$ | NaCl |
| 55·9 | 12·4 | 8·0 | 16·4 | 5·3 | 7·4 | 60·1 | 2·5 | 22·7 | 21·1 | 1·3 | 25·0 |
| 54·8 | 15·0 | 7·7 | 16·7 | 6·7 | 7·4 | 56·8 | 1·0 | 28·6 | 19·8 | 0·5 | 31·2 |
| 55·7 | 13·6 | 9·5 | 17·4 | 6·2 | 9·3 | 55·6 | 2·6 | 28·8 | 19·7 | 1·4 | 32·1 |

*System* $CdCl_2$–$CuCl_2$–$H_2O$. No negative hexagons were observed in this system in the absence of sodium chloride, but on addition of the latter small plates of this nature were obtained when the molecular ratio $CdCl_2$ : $CuCl_2$ ranged from 0·35 to 0·96. These plates, which were pseudo-hexagonal, were very unstable and were always observed in the presence of the stable phase. No detailed study of their chemical composition was possible.

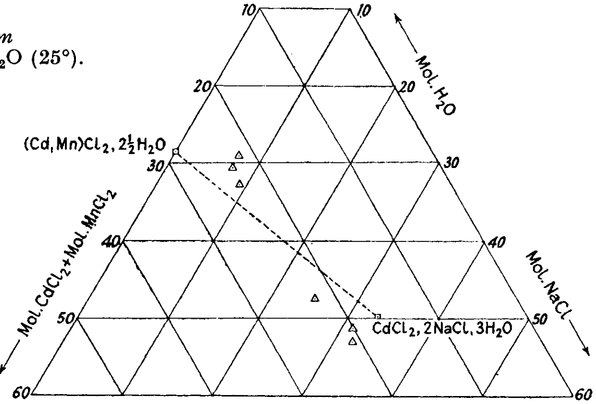


FIG. 5. *System* $CdCl_2$–$MnCl_2$–NaCl–$H_2O$ (25°).

No double salts have been observed in the system $CuCl_2$–NaCl–$H_2O$ at 30° (Schreinemakers and de Baat, *Z. physikal. Chem.*, 1909, **65**, 586).

*System* $CdCl_2$–$FeCl_2$–$H_2O$. In this system also the hexagons could only be obtained in the presence of sodium chloride and were observed when the molecular ratio $CdCl_2$ : $FeCl_2$ varied from 0·9 to 1·7. They were very unstable, were usually contaminated with the stable phase, and were not examined further.

*System* $CdCl_2$–$CaCl_2$–$H_2O$. When sodium chloride is added to this system, and in its presence only, a new phase occurs, crystallising in thin plates, which is metastable to the orthorhombic solid solution ($CdCl_2$,$H_2O$–$CaCl_2$,4$H_2O$). Under favourable conditions the plates can have a regular hexagonal outline, but this is generally irregular. The crystals are negative hexagonal but have been observed in a few instances to give a uniaxial interference figure in white light which becomes biaxial on rotation, so that in such cases the crystals are only pseudo-hexagonal. This is like the case of the negative hexagons in the system $CdCl_2$–$MgCl_2$–NaCl–$H_2O$ and may mean that there are two types of negative hexagonal phase—one uniaxial and truly hexagonal which is a layer lattice structure built up from (Cd,Ca)$Cl_2$,2·5$H_2O$ and $CdCl_2$,2NaCl,3$H_2O$, and a second, biaxial and pseudo-hexagonal which is the solid solution (Cd,Ca)$Cl_2$,4$H_2O$. It was found that the negative hexagons occurred over the range where the molecular ratio $CdCl_2$ : $CaCl_2$ was 0·5 to 1·8 provided that the NaCl content was from 2 to 10% of the total weight of the mixture. These were the most stable and easiest to handle of all the metastable hexagons observed in the present investigation.

Two series of preparations of the negative hexagons were separated in the dry condition by washing with mother-liquor–alcohol mixtures of increasing alcohol content and then with alcohol–ether mixtures of increasing ether content. The washed crystals were then air-dried. The compositions of one series are given in Table 8.

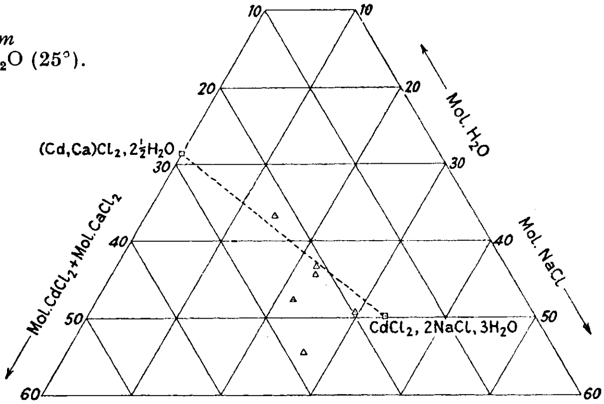
TABLE 8 (see Fig. 6). *System* $CdCl_2$–$CaCl_2$–NaCl–$H_2O$ (25°) : *negative hexagons.*

(Mol. ratio $CdCl_2 : CaCl_2 = 1{\cdot}33$.)

| | Composition of washed dry solid, % | | | | | | |
|---|---|---|---|---|---|---|---|
| Concn. of NaCl in | By analysis | | | Calculated molecular proportions | | | |
| (mixture (%) | $CdCl_2$ | $CaCl_2$ | NaCl | $CdCl_2$ | $CaCl_2$ | NaCl | $H_2O$ |
| 2 | 61·7 | 4·8 | 14·1 | 19·8 | 2·6 | 14·2 | 63·4 |
| 2½ | 59·5 | 2·4 | 21·3 | 19·7 | 1·3 | 22·2 | 56·8 |
| 3 | 60·4 | 2·2 | 21·3 | 20·5 | 1·2 | 22·7 | 55·6 |
| 4 | 54·2 | 2·8 | 28·1 | 18·2 | 1·6 | 29·6 | 50·6 |

These results are shown in Fig. 6 and can certainly be regarded as showing that the negative hexagons were solid solutions covering the range (Cd,Ca)$Cl_2$,2·5$H_2O$ to $CdCl_2$,2NaCl,3$H_2O$. The agreement is as good as can be expected from the method.

FIG. 6. *System* $CdCl_2$–$CaCl_2$–NaCl–$H_2O$ (25°).



The results of another series examined earlier are shown in Table 9.

TABLE 9 (see Figs. 4 and 6). *System* $CdCl_2$–$CaCl_2$–NaCl–$H_2O$ (25°) : *negative hexagons.*

(Sodium chloride concentration constant at 2%.)

| Mol. ratio | | | | | | | Washed dry solid | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CdCl_2$ | Liquid, % | | | Moist solid, % | | | By analysis, % | | | Mol. proportions, % (calc.) | | | |
| $CaCl_2$ | $CdCl_2$ | $CaCl_2$ | NaCl | $CdCl_2$ | $CaCl_2$ | NaCl | $CdCl_2$ | $CaCl_2$ | NaCl | $CdCl_2$ | $CaCl_2$ | NaCl | $H_2O$ |
| 0·48 | 21·1 | 32·0 | 0·4 | — | — | — | — | — | — | — | — | — | — |
| 0·61 | 30·5 | 23·0 | 0·7 | 46·4 | 18·1 | 7·0 | 57·7 | 8·9 | 21·8 | 22·3 | 5·7 | 26·4 | 45·6 |
| 1·33 | 37·6 | 19·2 | 1·0 | — | — | — | — | — | — | — | — | — | — |
| 1·33 | 38·3 | 19·0 | 1·0 | 51·3 | 13·7 | 6·9 | 61·7 | 4·8 | 14·1 | 19·8 | 2·6 | 14·2 | 63·4 |
| 1·82 | 43·6 | 16·3 | 0·9 | 53·5 | 12·8 | 6·4 | 61·7 | 5·4 | 18·9 | 22·6 | 3·2 | 21·7 | 52·4 |

These results are useful because, owing to the small percentage of NaCl in the solution, this salt can be treated as an inert constituent and plotted in Fig. 4 to show the approximate relationship which the metastable negative hexagonal solid solution (Cd,Ca)$Cl_2$,2·5$H_2O$ would have to the other solid phases if realisable in the absence of sodium chloride. The data for the three dry solid phases are plotted in Fig. 6. The compositions of two of the solids only appear explicable on the assumption that appreciable contamination of the metastable negative hexagons had occurred. Contamination with the stable phase ($CdCl_2$,$H_2O$–$CaCl_2$,4$H_2O$) which can have about 1—2 mols. of $H_2O$ per mol. of (Cd,Ca)$Cl_2$ would not alone produce these results, but the anhydrous bivalent salts would, and although these were not detected optically, much practical difficulty had been experienced with these particular experiments.

Two methods have been used for determining the composition of the negative orthorhombic solid solution. At the $CdCl_2$-rich end of the series, the indicator method with potassium bromate was found to be satisfactory. The results seem to show definitely that the solid solution is between some form of $CaCl_2$,4$H_2O$ (possibly the β-form) and $CdCl_2$,$H_2O$. The presence of the indicator ($KBrO_3$) is bound to cause some disturbance of the equilibrium conditions between the solid and liquid. Probably for this reason the solution points of the bromate experiments do not always fall quite on the solubility curve of the solid solutions, while the solution–moist solid tie-lines slope at a different angle from those in the absence of bromate.

TABLE 10 (see Fig. 4). *Negative orthorhombic solid solution* ($KBrO_3$ *indicator method*).

| Liquid, % | | | Moist solid, % | | | Dry solid composition, % (calc.) | |
|---|---|---|---|---|---|---|---|
| $CdCl_2$ | $CaCl_2$ | $KBrO_3$ | $CdCl_2$ | $CaCl_2$ | $KBrO_3$ | $CdCl_2$ | $CaCl_2$ |
| 29·8 | 25·0 | 0·171 | 53·1 | 19·8 | 0·059 | 65·3 | 17·1 |
| 36·5 | 21·7 | 0·137 | 54·6 | 19·0 | 0·055 | 66·9 | 17·2 |
| 42·0 | 17·9 | 0·124 | 55·1 | 14·4 | 0·076 | 75·6 | 9·0 |
| 45·0 | 15·4 | 0·258 | 60·4 | 10·7 | 0·127 | 80·3 | 6·1 |
| 43·8 | 16·4 | 0·136 | 58·1 | 11·2 | 0·094 | 90·3 | Nil or very small |

In the $CaCl_2$-rich region of ($CdCl_2,H_2O$–$CaCl_2,4H_2O$) and for $CdCl_2,2CaCl_2,12H_2O$ the crystals could be obtained free from mother-liquor by the washing technique already described for the negative hexagons. Table 11 shows several results obtained in this manner and also one for crystals dried by hand pressure between filter-paper.

TABLE 11 (see Fig. 4). *System* $CdCl_2$–$CaCl_2$–$H_2O$ : *composition of washed dry solid.*

| Estimated approximate composition of mother-liquor, % | | Composition of washed solid, % | | | |
|---|---|---|---|---|---|
| $CdCl_2$ | $CaCl_2$ | $CdCl_2$ | $CaCl_2$ | Solid | Washing technique |
| 16 | 33 | 29·0 | 36·6 | $CdCl_2,2CaCl_2,12H_2O$ | EtOH–mother-liquor |
| 22 | 30 | 29·5 | 34·9 | ,, | ,, ,, |
| 29 | 24 | 62·6 | 19·2 | Orthorhombic solid solution ($CdCl_2,H_2O$–$CaCl_2,4H_2O$) | EtOH–$Et_2O$ |
| 33 | 22 | 60·1 | 18·5 | ,, ,, | Hand-dried |

The two results obtained with the double salt $CdCl_2,2CaCl_2,12H_2O$ are important as they show that the method gives reliable results for the double salt and should do the same for the solid solutions.

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