

147. Isomorphous Replacement in Hydrated Salts. Part I. The Systems $\text{CoCl}_2\text{-CuCl}_2\text{-H}_2\text{O}$; $\text{CdCl}_2\text{-NiCl}_2\text{-H}_2\text{O}$; $\text{CdCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$.

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The system $\text{CoCl}_2\text{-CuCl}_2\text{-H}_2\text{O}$ at 25° shows only the two simple hydrates $\text{CoCl}_2, 6\text{H}_2\text{O}$ and $\text{CuCl}_2, 2\text{H}_2\text{O}$. The system $\text{CdCl}_2\text{-NiCl}_2\text{-H}_2\text{O}$ is very complex at 25° with three hydrates of simple salts and six double salts of which two at least must be regarded as representing series of solid solutions. The system $\text{CdCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ is generally similar to the corresponding nickel system but only three of the types of double salt found in that system could be obtained at 25° in the cobalt system; a fourth is obtainable with the help of sodium chloride (see following paper).

THE system $\text{CoCl}_2\text{-CuCl}_2\text{-H}_2\text{O}$ has not been examined previously. We have studied it in case it might throw any light on the cobalt chloride colour change. The results are given in Table I and show that the only solid phases to occur at 25° are $\text{CoCl}_2, 6\text{H}_2\text{O}$ and $\text{CuCl}_2, 2\text{H}_2\text{O}$. The system $\text{CdCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ was examined for the same reason, and also because Benrath's results for this system (*Z. anorg. Chem.*, 1927, **163**, 396) were so different from those of Bassett and Croucher (J., 1930, 1796) for the system $\text{ZnCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$, to which some similarity might be expected, as to make a re-examination necessary. The system $\text{CdCl}_2\text{-NiCl}_2\text{-H}_2\text{O}$ has now been examined for the first time, as we found this essential in order to understand properly the system $\text{CdCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$.

In both these systems $\text{CdCl}_2, 2.5\text{H}_2\text{O}$ and $\text{CdCl}_2, \text{H}_2\text{O}$ are found at 25° , but the monohydrate is metastable towards the 2.5 hydrate over most of the range in which it can occur as solid phase. The hydrates $\text{CoCl}_2, 6\text{H}_2\text{O}$ and $\text{NiCl}_2, 6\text{H}_2\text{O}$ are found in the appropriate systems. The double salts which also occur are of great interest. In the nickel system

the compounds $4\text{CdCl}_2, \text{NiCl}_2, 10\text{H}_2\text{O}$; $2\text{CdCl}_2, \text{NiCl}_2, 12\text{H}_2\text{O}$; $2\text{CdCl}_2, \text{NiCl}_2, 6\text{H}_2\text{O}$; and $3\text{CdCl}_2, 2\text{NiCl}_2, 14\text{H}_2\text{O}$ appear to have an invariable composition.

In addition to these there are two series of solid solutions. One of these has almost exactly the composition required by the formula $\text{CdCl}_2, 2\text{NiCl}_2, 12\text{H}_2\text{O}$ over the extensive range in which it occurs as the stable solid phase. When it is followed into the region of solutions containing a larger proportion of cadmium chloride, where it is metastable, it becomes progressively richer in cadmium. This does not mean that $\text{CdCl}_2, 2\text{NiCl}_2, 12\text{H}_2\text{O}$ is one member of a series of solid solutions of which $2\text{CdCl}_2, \text{NiCl}_2, 12\text{H}_2\text{O}$ is the other member, for the latter compound has an entirely different crystalline form and the two solubility curves cut each other sharply. This matter is discussed in the following paper.

The second series of solid solutions is more difficult to define for, unlike the one just considered, its composition varies throughout the range over which we have been able to study it. The method of residues by itself is thus unable to give a definite solution to the problem, so we have used two other methods to supplement it. Mercuric chloride has been added as an indicator substance, as the mercuric ion was unlikely to replace either nickel or cadmium in the solid phase. On this assumption, the amount of mercury found in the equilibrium solution and moist solid enabled the amount of solution present in the latter to be calculated, and hence the composition of the dry solid. This method suffers from the disadvantage that the result obtained is very sensitive to small analytical errors.

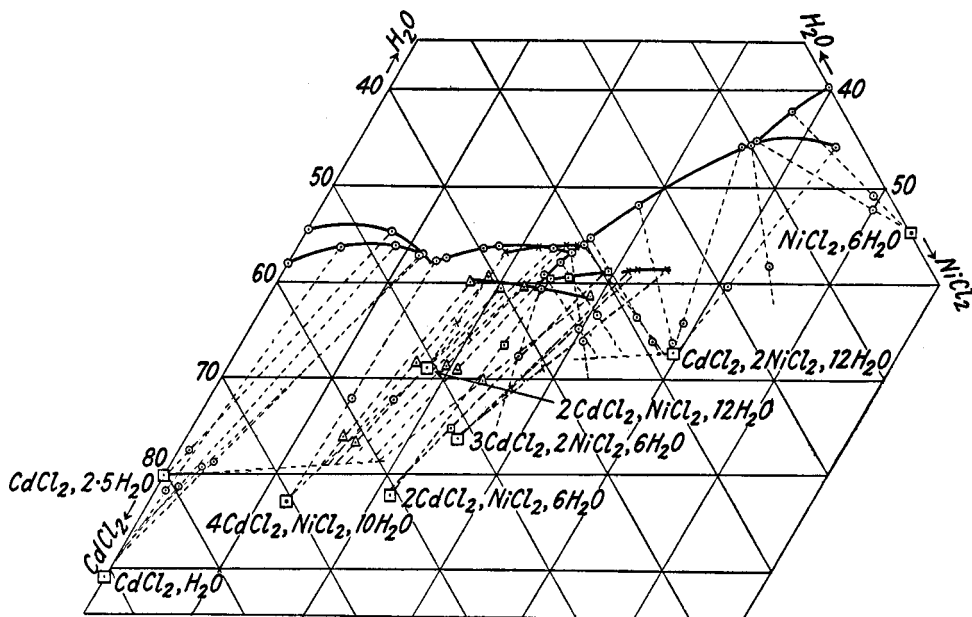
The nitrate ion also was tried as an indicator (see following paper), but this too was not very satisfactory, and no really satisfactory indicator has been found.

The best method of all is to obtain the solid phase in a dry state and analyse it in that condition. The solid in question crystallises in hexagonal plates and, in spite of the fact that it is always in a metastable condition at 25° , it was possible to obtain it in plates of several mm. diameter. These were too thin and small, however, to be obtained quite dry by means of filter papers, but they could be dried, without decomposition or precipitation of solid from adhering mother-liquor, by washing with alcohol, or, better, acetone. All the above methods agreed in indicating that the hexagonal series of solid solutions could be represented as $(\text{Cd}, \text{Ni})\text{Cl}_2, 2.5\text{H}_2\text{O}$, in which there was an average of 2.5 water molecules for each atom of metal. The ordinary hydrate of cadmium chloride, $\text{CdCl}_2, 2.5\text{H}_2\text{O}$, is not one constituent of this series of solid solutions, however, as it is crystallographically entirely different. The above conclusion is abundantly confirmed by the results obtained for the solid solutions which contained sodium chloride in addition (see following paper).

It is reasonable to suppose that in the system $\text{CdCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$, double salts corresponding to all the above nickel salts should be obtainable. It would seem, however, that some of them are too unstable at 25° for this to be possible. The two compounds $4\text{CdCl}_2, \text{CoCl}_2, 10\text{H}_2\text{O}$ and $2\text{CdCl}_2, \text{CoCl}_2, 12\text{H}_2\text{O}$ have definite ranges of stable existence at 25° , whereas $\text{CdCl}_2, 2\text{CoCl}_2, 12\text{H}_2\text{O}$ was obtained as a very metastable form by inoculation with $\text{CdCl}_2, 2\text{NiCl}_2, 12\text{H}_2\text{O}$, but it was not possible to decide whether this was to be regarded, like the nickel compound, as an end member of a series of solid solutions.

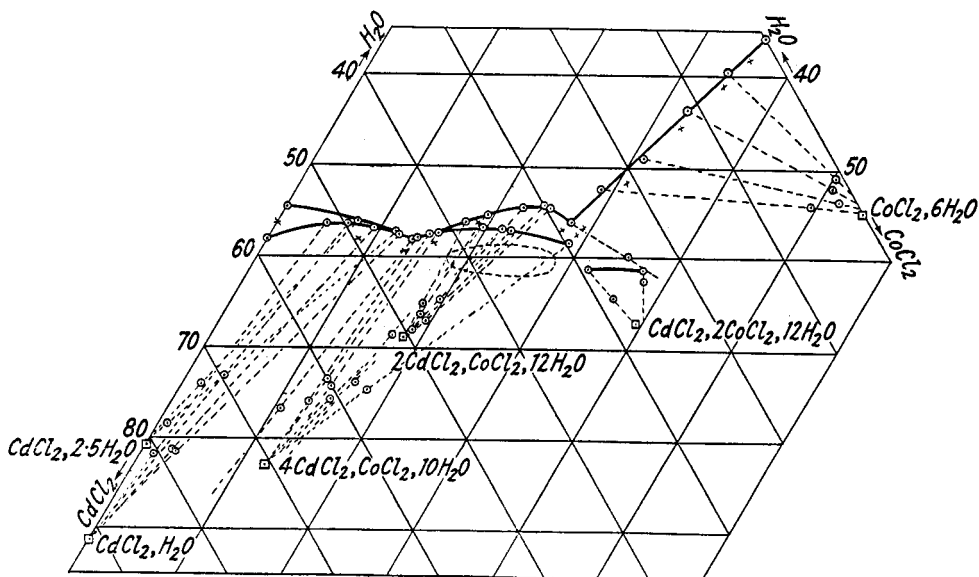
The investigation of the $\text{CdCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ system was started before that of the nickel system, and we were greatly puzzled by the erratic way in which, over a certain range of concentrations, a substance separated which crystallised in hexagonal plates. It was noticed that it could only be obtained when a certain sample of anhydrous cadmium chloride was used in making up the mixtures. It was then found that this sample contained 1.3% of sodium chloride, and that the presence of a small amount of the latter is essential for the formation of the red hexagonal plates which contain sodium chloride. The nature of these could not be cleared up satisfactorily until the $\text{CdCl}_2\text{-NiCl}_2\text{-H}_2\text{O}$ system had been studied, but the investigation of that system and the work described in the following paper show that the red hexagonal plates consist of a solid solution $(\text{Cd}, \text{Co})\text{Cl}_2, 2.5\text{H}_2\text{O}$ in which some of the cobalt has been replaced by sodium. In the case of nickel, the pure solid solution $(\text{Cd}, \text{Ni})\text{Cl}_2, 2.5\text{H}_2\text{O}$, free from sodium, can be obtained, but this does not appear to be possible in the cobalt series. The results for the systems $\text{CdCl}_2\text{-NiCl}_2\text{-H}_2\text{O}$ and $\text{CdCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ are shown in Tables II and III and Figs. 1 and 2.

FIG. 1.

I. The system $\text{CdCl}_2\text{-NiCl}_2\text{-H}_2\text{O}$.

| | |
|---|-----------------------|
| Points relating to $\text{NiCl}_2, 6\text{H}_2\text{O}$ | } shown by \odot . |
| " " $\text{CdCl}_2, 2\text{NiCl}_2, 12\text{H}_2\text{O}$ | |
| " " $4\text{CdCl}_2, \text{NiCl}_2, 10\text{H}_2\text{O}$ | |
| " " $\text{CdCl}_2, \text{H}_2\text{O}$ | |
| " " $\text{CdCl}_2, 2.5\text{H}_2\text{O}$ | } shown by \times . |
| " " $2\text{CdCl}_2, \text{NiCl}_2, 12\text{H}_2\text{O}$ | |
| " " $3\text{CdCl}_2, 2\text{NiCl}_2, 14\text{H}_2\text{O}$ | |
| " " $2\text{CdCl}_2, \text{NiCl}_2, 6\text{H}_2\text{O}$ | |
| " " $(\text{Cd}, \text{Ni})\text{Cl}_2, 2.5\text{H}_2\text{O}$ solid solution, shown by \triangle . | |

FIG. 2.



The region in which the red hexagonal plates of $(\text{Cd},\text{Co})\text{Cl}_2 \cdot 2.5\text{H}_2\text{O}$ were first obtained in presence of very small amounts of sodium chloride is included within the oval dotted line in Fig. 2. The compound $2\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$ had been obtained by von Hauer (*Sitzungsber. Akad. Wien*, 1855, 17, 331) and by Benrath (*loc. cit.*).

The crystallographic examination of the solid phases is extremely important when dealing with such complex systems as $\text{CdCl}_2 \cdot \text{NiCl}_2 \cdot \text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot \text{H}_2\text{O}$. Such examinations have been made in all cases, and have been most useful both in distinguishing different compounds and in recognising similar compounds in the two systems.

EXPERIMENTAL.

Amounts of the various chlorides were weighed out and dissolved in sufficient water by heating to give, on subsequent cooling to 25° , about 1—2 g. of solid to 10 g. of solution. The mixtures were placed in hard-glass bottles which were closed by corks soaked in paraffin wax and finally sealed by applying the melted wax. The bottles were rotated mechanically in an electrically controlled thermostat for a few hours to allow equilibrium between solid phase and solution to be established. In cases where the solid phase was metastable, it was usually advisable to replace mechanical shaking of the bottle by occasional hand shaking over a period of time the length of which depended upon the degree of metastability of the solid.

Cadmium chloride monohydrate persists very tenaciously under conditions where it is metastable with respect to the 2.5 hydrate, so inoculation with the latter was often necessary. Once the main outlines of the phase-rule diagram had been settled and samples of the various solid phases secured, much time could be saved in filling in the details by inoculation of suitably chosen solutions with the appropriate solid. This applies, of course, to all phase-rule investigations of the type described in this paper.

The contents of the solubility bottles, when ready for analysis, were filtered with the aid of the pump in a jacketed filter-tube through an asbestos pad. Liquid was expressed as completely as possible from the moist solid whilst still in the jacketed tube by means of a flattened glass rod, and samples of solution and moist solid were weighed out for analysis. It is important that only one lot of material should be weighed out for the analysis of the moist solid, since the proportion of solid and solution may vary widely in different lots. The one lot is diluted to a suitable volume, and portions taken for the several estimations which have to be made. Of the materials used in preparing the mixtures, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was "nickel and iron free"; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was "cobalt and iron free"; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and HgCl_2 were A.R. products, and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, the purest obtainable, was shown to be free from sodium. As an additional precaution to ensure absence of sodium, the $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were recrystallised before use.

Analytical Methods.—Chloride was weighed as silver salt after precipitation from nitric acid solution.

Copper was precipitated as sulphide by means of sodium thiosulphate from solutions strongly acidified with sulphuric acid. It was weighed as cuprous sulphide after ignition in hydrogen.

Cobalt was usually weighed as Co_3O_4 after precipitation by means of α -nitroso- β -naphthol, but in the analyses for the system $\text{CoCl}_2 \cdot \text{CuCl}_2 \cdot \text{H}_2\text{O}$ it was estimated electrolytically, in the manner described for nickel, in the filtrate from the copper sulphide. The filtrate was first concentrated to the stage at which fumes of sulphuric acid appeared. It was then cooled, diluted with water, and filtered from sulphur which had separated owing to decomposition of polythionates. After the removal of the electrodes at the conclusion of the electrolysis, the electrolyte was treated with a few drops of ammonium sulphide, and any precipitated cobalt sulphide filtered off, ignited, the residue dissolved in aqua regia, evaporated to dryness with sulphuric acid and weighed as cobalt sulphate, the appropriate correction being applied to the weight of metallic cobalt. The cobalt deposit, unlike that of nickel, was invariably dark, and sometimes incoherent, so the method cannot be recommended.

Nickel. The separation and estimation of nickel by the dimethylglyoxime method is, in our experience, liable to give low results for various reasons (see Nuka, *Z. anal. Chem.*, 1932, 91, 29), and we found the electrolytic method to be much more reliable. The filtrate from the cadmium sulphide, containing not more than 0.1 g. of nickel, was evaporated with sulphuric acid to remove hydrogen chloride. 1 G. of ammonium sulphate was added to the residue, which was made up to 120 c.c. with water. After addition of 40 c.c. of concentrated ammonia, the solution was electrolysed overnight with platinum electrodes at a potential difference of about

2.5 volts. This method gave a hard deposit which showed no tendency to flake when being washed with water and alcohol prior to weighing.

Cadmium was separated from nickel or cobalt by precipitation as sulphide from acid solution. The solution containing 0.1—0.2 g. of cadmium was diluted to 100 c.c., 2 c.c. of concentrated sulphuric acid were added, and hydrogen sulphide passed through until precipitation of cadmium sulphide was complete. The sulphide was filtered off, washed with water, dissolved in concentrated hydrochloric acid, and the solution evaporated to a small bulk with 0.5 c.c. of concentrated sulphuric acid. The concentrated liquid was transferred to a large porcelain crucible in which the evaporation was continued till the bulk was reduced to about 2 c.c. To avoid sputtering, the evaporation was completed by heating the rim of the crucible with a ring burner. The last traces of acid were removed by heating to constant weight just below redness, the cadmium being weighed as sulphate. As this is hygroscopic, weighing must be done expeditiously.

An alternative method, estimation as $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, was sometimes used. This, though more rapid than the above, has the disadvantage of requiring a solubility correction. It was carried out as follows. The hydrochloric acid solution of the cadmium sulphide was boiled to remove hydrogen sulphide, neutralised with ammonia, and diluted to about 100 c.c. (if not more than 0.15 g. of cadmium was present). 2 G. of ammonium chloride were added, the solution heated to boiling, and 10 c.c. of 20% diammonium hydrogen phosphate solution added with stirring. On standing overnight the flocculent precipitate became completely crystalline, and was then filtered off on a Gooch crucible. It was washed with 50 c.c. of water saturated with respect to $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, followed by 10 c.c. of absolute alcohol, dried for 1 hour at 100° , and weighed. It was found necessary to estimate the cadmium still present in the filtrate (without the washings) by precipitation as sulphide, which was converted into and weighed as sulphate.

Optical Properties of the Double Salts and Solid Solutions found in the Systems $\text{CdCl}_2\text{--NiCl}_2\text{--H}_2\text{O}$ and $\text{CdCl}_2\text{--CoCl}_2\text{--H}_2\text{O}$.— $4\text{CdCl}_2 \cdot \text{NiCl}_2 \cdot 10\text{H}_2\text{O}$ forms pale green monoclinic needles which are optically negative and have an optic axial angle of about 60° . The optic axial plane is inclined at an angle of 7° to the direction of elongation.

$2\text{CdCl}_2 \cdot \text{NiCl}_2 \cdot 12\text{H}_2\text{O}$ crystallises in pale green needles, elongated in the direction of slow vibration, which are orthorhombic and positive with a large optic axial angle.*

$2\text{CdCl}_2 \cdot \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ forms pale green, tabular, orthorhombic crystals which are negative and have an optic axial angle of about 45° .

$3\text{CdCl}_2 \cdot 2\text{NiCl}_2 \cdot 14\text{H}_2\text{O}$ forms pale green monoclinic needles which are negative and have an optic axial angle of about 60° . The optic axial plane is inclined at an angle of 17° to the direction of elongation.

TABLE I.—The System $\text{CoCl}_2\text{--CuCl}_2\text{--H}_2\text{O}$.

| Solution. | | | Moist solid. | | | Solid phase. |
|----------------------|-------------------------------|----------------------------------|----------------------|-------------------------------|----------------------------------|---|
| CuCl_2 , %. | CoCl_2 , % (direct). | CoCl_2 , % (by diff.).* | CuCl_2 , %. | CoCl_2 , % (direct). | CoCl_2 , % (by diff.).* | |
| 44.0 † | nil | nil | — | — | — | $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 39.29 | 4.34 | 3.95 | 63.24 | 2.06 | 1.49 | " |
| 34.00 | 8.99 | 8.97 | 70.30 | 2.26 | 1.88 | " |
| 30.33 | — | 12.66 | 60.75 | — | 4.34 | " |
| 25.62 | — | 17.48 | 62.37 | 5.70 | 5.56 | " |
| 18.01 | 26.06 | 26.17 | 44.17 † | 21.53 | — | $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 15.08 | — | 27.48 | — | — | 48.43 | $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 9.99 | 30.50 | 30.33 | 2.49 † | 49.53 | — | " |
| 5.34 | 33.19 | 32.90 | 1.29 | 51.40 | 50.98 | " |
| nil | 35.87 | — | — | — | — | " |

* Calculated from total chlorine and copper estimations.

† From Seidell's "Solubilities of Inorganic and Organic Substances," 1911, p. 124.

‡ Calculated from total chlorine and cobalt estimations.

The solid solution of which one end member is $\text{CdCl}_2 \cdot 2\text{NiCl}_2 \cdot 12\text{H}_2\text{O}$ forms dark green hexagonal crystals, optically positive, which are not markedly extended in any direction.

The solid solution $(\text{Cd}, \text{Ni})\text{Cl}_2 \cdot 2.5\text{H}_2\text{O}$ crystallises in thin, pale green plates which are hexagonal and optically negative.

* The compound $2\text{CdCl}_2 \cdot \text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ is also stated to be rhombic (Rimbach, *Ber.*, 1897, **30**, 3073).

4CdCl₂.CoCl₂.10H₂O forms fine pink needles, elongated in the direction of slow vibration, which are orthorhombic (or possibly monoclinic) and negative with an optic axial angle of about 60°. The corresponding nickel compound is monoclinic. The two differ only in so far as the acute bisectrix section of the nickel compound shows oblique extinction. The angle is 7°, which does not indicate any fundamental difference between the two compounds, in view of the indefinite extinction of that section of the cobalt compound (it is probably straight but is imperfect).

2CdCl₂.CoCl₂.12H₂O crystallises in red needles elongated in the slow direction, which are orthorhombic and positive and have an optic axial angle of 65—75°. Grailich (*Sitzungsber. Akad. Wien*, 1858, 27, 13) states that this compound is rhombic (see footnote, p. 650).

TABLE II.—*The System CdCl₂-NiCl₂-H₂O.*

| | Solution. | | | Moist solid. | | | Solid phase. |
|-----|---------------------------------------|------------------------------------|------------------------|---------------------------------------|------------------------------------|------------------------|--------------|
| | CdCl ₂ , % (by diff.).* | CdCl ₂ , % (direct). | NiCl ₂ , %. | CdCl ₂ , % (by diff.).* | CdCl ₂ , % (direct). | NiCl ₂ , %. | |
| B | nil | nil | 39.58 | — | — | — | a |
| | 4.58 | — | 37.39 | 1.50 | — | 49.20 | a |
| | 9.44 | — | 35.73 | 2.07 | — | 49.91 | a |
| | 9.96 | — | 35.56 | 14.40 | — | 43.26 | a, b |
| m † | 2.33 | 2.47 | 43.31 | 19.63 | 19.88 | 40.97 | b |
| | 11.01 | — | 34.91 | 25.50 | — | 38.73 | b |
| | 23.35 | — | 28.55 | 27.42 | — | 38.79 | b |
| | 29.40 | — | 25.93 | 29.24 | — | 34.36 | b |
| | 30.30 | — | 25.72 | 28.96 | — | 36.96 | b |
| | 31.37 | — | 25.01 | 38.00 | — | 26.76 | b, e |
| m | — | 31.81 | 25.02 | — | 35.23 | 30.69 | b, f |
| m † | 33.28 | 33.28 | 24.47 | 32.93 | 32.75 | 30.45 | b |
| m † | 35.74 | 35.94 | 23.55 | 35.19 | 35.08 | 29.66 | b |
| m † | 36.58 | 36.64 | 24.04 | 42.03 | 41.73 | 25.46 | b, g |
| m | 24.09 | — | 34.50 | 40.23 | — | 28.43 | c |
| m | 26.72 | — | 31.82 | 42.90 | — | 27.12 | c |
| m | 27.70 | — | 31.11 | 44.36 | — | 26.56 | c |
| m | 29.54 | — | 29.23 | 52.45 | — | 23.74 | d |
| m | 29.84 | — | 29.10 | 51.91 | — | 23.40 | d |
| m | 33.52 | — | 25.96 | 55.38 | — | 21.75 | d |
| m | 35.07 | — | 24.85 | 42.80 | — | 23.74 | d |
| m | 36.30 | — | 23.91 | 48.10 | — | 21.05 | d, g |
| | 32.05 | — | 24.23 | 45.56 | — | 20.23 | e |
| E | 33.8 | — | 22.3 | — | — | — | e, f |
| m | 34.51 | — | 21.69 | 47.71 | — | 18.97 | e |
| m | 37.83 | — | 19.13 | 45.80 | — | 18.55 | e |
| m | 33.21 | — | 23.18 | 55.52 | — | 16.74 | f |
| | 38.16 | 38.35 | 18.09 | 58.01 | 57.90 | 14.45 | f |
| | 39.64 | 39.85 | 16.83 | 52.81 | — | 17.45 | f |
| | 43.45 | — | 13.99 | 61.36 | — | 13.07 | f |
| | 44.51 | — | 13.26 | 59.24 | — | 12.78 | f |
| E | 45.2 | — | 12.7 | — | — | — | f, h |
| m | — | 32.20 | 29.13 | — | 46.32 | 23.90 | g |
| m | 37.67 | 37.69 | 22.68 | 48.96 | — | 19.67 | g |
| m | 40.05 | — | 20.41 | 61.23 | — | 15.30 | g |
| m | 40.62 | — | 19.00 | 51.55 | — | 16.85 | g |
| m | 42.54 | — | 17.52 | 61.60 | — | 14.31 | g |
| | 45.34 | 44.91 | 11.84 | 76.91 | 77.00 | 3.52 | h, i |
| m | 45.85 | — | 11.37 | — | 75.34 | 3.72 | h |
| m | — | 47.68 | 8.56 | — | 79.67 | 1.89 | h |
| m | 52.64 | — | 3.97 | 80.91 | — | 1.10 | h |
| m | 58.10 | — | nil | — | — | — | h |
| | — | 46.98 | 7.61 | — | 76.65 | 1.20 | i |
| | — | 54.62 | nil | — | — | — | i |

B. Value obtained by Benrath (*Z. anorg. Chem.*, 1932, 205, 417).

m. Metastable.

E. Values estimated from the diagram.

a. NiCl₂.6H₂O.

b. CdCl₂.2NiCl₂.12H₂O.

c. 3CdCl₂.2NiCl₂.14H₂O.

d. 2CdCl₂.NiCl₂.6H₂O.

e. 2CdCl₂.NiCl₂.12H₂O.

f. 4CdCl₂.NiCl₂.10H₂O.

g. (Cd,Ni)Cl₂.2.5H₂O solid solution.

h. CdCl₂.H₂O.

i. CdCl₂.2.5H₂O.

* Calculated from total chlorine and nickel estimations.

† In these cases cadmium was weighed as CdNH₄PO₄.H₂O, and in all other cases as CdSO₄.

$\text{CdCl}_2 \cdot 2\text{CoCl}_2 \cdot 12\text{H}_2\text{O}$ crystallises in thick, red, six-sided plates which are optically positive and belong to the hexagonal system.

The solid solution $(\text{Cd}, \text{Co})\text{Cl}_2 \cdot 2 \cdot 5\text{H}_2\text{O}$ (only obtainable in the cobalt series with a small sodium content) crystallises in thin, red, six-sided plates which are optically negative and belong to the hexagonal system.

The two compounds $4\text{CdCl}_2 \cdot \text{NiCl}_2 \cdot 10\text{H}_2\text{O}$ and $3\text{CdCl}_2 \cdot 2\text{NiCl}_2 \cdot 14\text{H}_2\text{O}$ are optically very similar and not easily distinguished under the microscope. The regions of the equilibrium diagram in which they occur, are, fortunately, well separated.

It should be especially noted that, both in the nickel and in the cobalt series, there are two compounds crystallising in six-sided plates belonging to the hexagonal system. These are readily distinguished by a determination of the optical sign.

The sizes of the optic axial angles were estimated either from the curvature of the isogyres in the axial interference figures or from the distance between the melatopes in acute bisectrix figures, both methods giving a possible error of about 20% with the equipment available.

In the system $\text{CoCl}_2 - \text{CuCl}_2 - \text{H}_2\text{O}$, the CoCl_2 percentages obtained by difference (Table I) are regarded as the more trustworthy and give excellent results when plotted in a triangular diagram. The cobalt estimations by the electrolytic method were not very satisfactory especially with small amounts of cobalt, probably on account of oxidation of the electro-deposit.

Notes on Table II.—The absence of a figure for CdCl_2 in the column headed "by diff." means that no chloride estimation was made, usually because of shortage of material.

The data for "CdCl₂, % (by diff.)" have been plotted in Fig. 1 when available. They can be regarded as more reliable than the "direct" figures owing to the rather troublesome nature of the cadmium estimations. Some "moist solid" points and tie lines have been omitted from the figure so as to avoid congestion.

$\text{CdCl}_2 \cdot 2\text{NiCl}_2 \cdot 12\text{H}_2\text{O}$ is the only one of the double salts b—g which can form a stable congruent solution at 25°.

The Composition of the Dry Solid Phase $(\text{Cd}, \text{Ni})\text{Cl}_2 \cdot 2 \cdot 5\text{H}_2\text{O}$, which crystallises in Optically Negative Hexagons.—Analysis of crystals obtained free from mother-liquor by washing with alcohol gave CdCl_2 , 65.46; NiCl_2 , 13.87%, which corresponds very closely to a hydrate $(\text{Cd}, \text{Ni})\text{Cl}_2 \cdot 2 \cdot 5\text{H}_2\text{O}$.

TABLE III.—*The System $\text{CdCl}_2 - \text{CoCl}_2 - \text{H}_2\text{O}$.*

| Solution. | | Moist solid. | | Solid phase. | Solution. | | Moist solid. | | Solid phase. |
|----------------------|----------------------|----------------------|----------------------|--------------|----------------------|----------------------|----------------------|----------------------|--------------|
| CdCl_2 , %. | CoCl_2 , %. | CdCl_2 , %. | CoCl_2 , %. | | CdCl_2 , %. | CoCl_2 , %. | CdCl_2 , %. | CoCl_2 , %. | |
| nil | 35.87 | — | — | a | m 29.82 | 28.63 | 56.86 | 17.81 | d |
| 5.39 | 34.06 | 0.83 | 50.10 | a | m 33.24 | 24.00 | 58.74 | 16.20 | d |
| 11.20 | 32.45 | 1.74 | 50.25 | a | m 34.51 | 22.43 | 57.64 | 16.18 | d |
| 17.99 | 31.00 | 1.84 | 51.67 | a | m 35.10 | 21.62 | 60.75 | 14.95 | d |
| 23.71 | 28.66 | 4.75 | 49.31 | a | m 37.07 | 19.72 | 51.39 | 17.09 | d |
| 28.22 | 27.75 | 24.92 | 35.06 | a, c | m 41.30 | 16.01 | 60.46 | 13.75 | d |
| m 24.15 | 37.11 | 24.53 | 37.96 | b | 42.43 | 15.16 | 60.63 | 13.63 | d |
| (24.22) | | (25.10) | | | 42.57 | 15.02 | 60.14 | 13.40 | d |
| m 29.21 | 31.96 | 28.36 | 35.99 | b | 43.95 | 14.01 | 62.89 | 13.04 | d |
| (29.03) | | (28.35) | | | 44.25 | 13.74 | 66.00 | 10.82 | d, e |
| 29.61 | 25.00 | 47.50 | 19.62 | c | 45.20 | 12.23 | 78.35 | 3.45 | e, f |
| 30.02 | 24.33 | 49.43 | 18.81 | c | m 47.36 | 9.30 | 78.50 | 2.81 | e |
| 32.10 | 22.33 | 44.94 | 19.84 | c | m 49.66 | 6.77 | 69.71 | 3.50 | e |
| 35.95 | 19.26 | 47.74 | 18.65 | c | m 51.78 | 4.71 | 80.60 | 1.31 | e |
| 38.25 | 17.71 | 46.80 | 18.20 | c | m 58.10 | nil | — | — | e |
| 41.57 | 15.80 | 59.98 | 13.92 | c, d | 45.40 | 11.71 | 77.70 | 0.95 | f |
| | | | | | 48.73 | 7.38 | 72.07 | 1.95 | f |
| | | | | | 54.62 | nil | — | — | f |

m. Metastable.
a. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.
b. $\text{CdCl}_2 \cdot 2\text{CoCl}_2 \cdot 12\text{H}_2\text{O}$.
c. $2\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$.
d. $4\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 10\text{H}_2\text{O}$.
e. $\text{CdCl}_2 \cdot \text{H}_2\text{O}$.
f. $\text{CdCl}_2 \cdot 2 \cdot 5\text{H}_2\text{O}$.

The data in Table III are plotted in Fig. 2. They are based on estimations of total chloride and cobalt (as Co_2O_3), the cadmium being obtained by difference. Only in the case of the two mixtures where $\text{CdCl}_2 \cdot 2\text{CoCl}_2 \cdot 12\text{H}_2\text{O}$ was the solid phase were cadmium estimations carried out. The results of the direct estimations are shown in parentheses below the values obtained indirectly. In these two experiments cadmium was separated as sulphide and weighed as

$\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, and the cobalt was determined electrolytically in the filtrate from the cadmium sulphide.

Benrath's results (*loc. cit.*) recalculated to our units are indicated by small crosses in Fig. 2. They are stated by Benrath to correspond to the three solid phases $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $2\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$, and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$. No analyses of moist solids are given and no information about the appearance of the double salt except that it is red. His double-salt region really covers that of the two compounds $2\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$ and $4\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 10\text{H}_2\text{O}$. His values for the concentrations are in every case considerably higher than those found by us. Neither of the double salts can give a stable congruent solution at 25° , although $2\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$ only just fails to do so.

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