CCXXXIV.—*A Phase-rule Study of the Cobalt Chloride Colour Change.*

By Henry Bassett and (in part) Herbert Harry Croucher.

It was shown in 1902 by Donnan and H. Bassett (J., **81**, 939) that the well-known and striking colour changes, red $\rightleftharpoons$ blue, of cobalt chloride solutions are associated with fundamental ionic changes. Red kations are present in the red solutions and blue anions in the blue solutions. The colour changes were accordingly explained on the basis of some such equilibrium as $Co^{\cdot\cdot} + 4Cl' \rightleftharpoons CoCl_4''$, but the precise nature of either of the coloured ions was not actually determined.

Most of the work done on the subject prior to 1902 is discussed in the paper quoted. Numerous investigators have studied the problem since that date but, in a sense, it still remains where it was left in 1902. Many of the later workers ignore the perfectly definite results of Donnan and Bassett, and endeavour to explain the colour changes entirely in terms of varying hydration of the cobalt chloride. This applies to papers by Lewis (*Z. physikal. Chem.*, 1905, **52**, 224), Jones and H. P. Bassett (*ibid.*, p. 231), and by Hulbert, Hutchinson, and Jones (*J. Physical Chem.*, 1917, **21**, 150). Hartley (J., 1903, **83**, 401) considered that $CoCl_2,2H_2O$, not $CoCl_2$, was formed on heating aqueous solutions of cobalt chloride, and that the effect of zinc chloride in keeping cobalt solutions pink could be explained by supposing that a double salt was formed which was not converted into a dihydrate on heating the solution. Moore (*Z. physikal. Chem.*, 1906, **55**, 641) considered that his spectroscopic measurements on various cobalt chloride solutions lent no support to the hydrate theory of the colour change, but rendered the existence of complex ions containing cobalt very probable. Brown (*Proc. Roy. Soc. Edin.*, 1912, **32**, 50), on the other hand, interpreted his measurements of light absorption by cobalt chloride solutions in terms of varying hydration of the cobalt chloride.*

Denham (*Z. physikal. Chem.*, 1909, **65**, 641), from measurements of transport numbers, concluded that "autocomplexes" (*i.e.*, negative ions containing cobalt) were present in solutions of cobalt bromide. Benrath (*Z. anorg. Chem.*, 1907, **54**, 328), by boiling-point determinations on aqueous solutions, found that chlorides, such as mercuric chloride, which favour the red colour form complexes with cobalt chloride, whereas those which favour the blue colour do not.

Gróh (*ibid.*, 1925, **146**, 305) measured molecular extinction coefficients of solutions of cobalt chloride in various alcohols and in water, and noted the effect of addition of lithium chloride. He considered that the results were in complete accord with the assumption of an equilibrium $CoCl_2 + 2Cl' \rightleftharpoons CoCl_4''$, the blue colour of the solutions being due to the complex ion $CoCl_4''$. Gróh and Schmid (*ibid.*, 1927, **162**, 321) came to the same conclusion from observations on the solubility of lithium chloride in acetone solutions of cobalt chloride. Hantzsch (*ibid.*, p. 237) attempted to account for the colour changes in terms of red and blue pseudo-salts and blue true salts, also suggesting that solid, purple $CoCl_2,2H_2O$ gives a blue form in solution which is unstable in the solid state.

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* Vaillant (*Compt. rend.*, 1929, **189**, 747) concludes that the only light absorbent is the $Co^{\cdot\cdot}$ ion, the activity of which varies according to the concentration, solvent, etc.

Kotschubei (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1055) studied the water carried by the ions by Nernst's method, using phenol as the indicator substance. He found that the hydration of the cobalt ion and of undissociated cobalt chloride molecules diminished with increase of concentration and rise of temperature, and considered that the change was probably from $Co(H_2O)_6^{\cdot\cdot}$ to $Co(H_2O)_4^{\cdot\cdot}$ and $\left[Co{}^{(H_2O)_2}_{Cl_2}\right]$, and not to $CoCl_4''$. He states that, although the formation of $CoCl_4''$ by the action of hydrochloric acid or ammonium, potassium, magnesium, or aluminium chloride on aqueous cobalt chloride solutions is not yet definitely established, the red solutions obtained by addition of zinc, cadmium, mercuric, stannous, or antimony chloride contain complex ions of the probable composition $\left[Co{}^{Cl_4}_{(ZnCl_2)_2}\right]''$, $\left[Co{}^{Cl_4}_{(HgCl_2)_2}\right]''$, etc., but it does not appear that either Kotschubei or anyone else has provided any evidence in support of such complexes.

Hill and Howell (*Phil. Mag.*, 1924, **48**, 833) put forward a new idea and suggested that whether cobalt compounds are red or blue depends upon the state of co-ordination of the cobalt atom : if this is surrounded by six other groups or atoms a red colour results, whilst if there are only four groups or atoms, the colour is blue. In several later papers by Howell (J., 1927, 158, 2039, 2843; 1928, 162), this point of view has been consistently developed, but it does not seem easy to reconcile it with the electrical evidence as to the nature of the red and blue solutions. One of Howell's arguments is based on the fact that in crystals of magnesium oxide each magnesium atom is surrounded by six oxygen atoms, and that when some magnesium is replaced by cobalt a red or pink substance results (cobalt pink). He concludes that in red aqueous solutions of cobalt compounds the cobalt atom is surrounded by six water molecules.

To conclude from these facts that the red or pink colour of aqueous cobalt solutions is due to the presence of cobalt ions *co-ordinated* with these six molecules is quite unjustified, for magnesium oxide has an ionic lattice similar to that of sodium chloride (Grimm and Sommerfeld, *Z. Physik*, 1926, **36**, 36) and the magnesium atoms are ionised with a co-ordination number zero,* although surrounded in

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* In Werner's notation there is no doubt that such an ion would be said to have a zero co-ordination number. Chemists by the expression " co-ordination " imply a special kind of covalency linkage, and it is unfortunate that crystallographers use it in a broader sense to indicate the number of other atoms surrounding a central atom in a crystal lattice whether these other atoms are ionised or attached by covalencies. Howell confuses the two uses of the term.

the crystal lattice by six oxygen ions. In the cobalt pink, where some magnesium has been replaced by cobalt, the latter would also be in the ionic state, from which it may be deduced that the unco-ordinated cobalt ion $Co^{\bullet\bullet}$ is pink (or red). In the crystal lattice of the cobalt pink, the cobalt is not co-ordinated in the Wernerian sense (*i.e.*, attached by covalencies) to the six oxygen atoms which surround it. It may be readily granted that in red aqueous solutions the cobalt may normally be co-ordinated with six molecules of water, but the only justifiable conclusion to draw from the fact that the colour is similar to that of cobalt pink would seem to be that the colour is independent of the state of co-ordination. There can be little doubt that conditions in the concentrated solutions which show the colour changes are very complex, which renders it extremely difficult to interpret any physical measurements, whether spectroscopic or otherwise, made on the actual solutions. We have therefore attacked the problem in another way, by studying the solid phases which can be in equilibrium with various red or blue cobalt chloride solutions. From the nature of the solids which separate, more or less reasonable deductions may be made as to the ions or molecules present in the solutions.

EXPERIMENTAL.

The experimental procedure consisted of a phase-rule examination, carried out at 25°, of a series of three-component systems. The systems chosen were two of the blue ones, $CoCl_2$–HCl–H_2O and $CoCl_2$–$MgCl_2$–H_2O, and two of the red ones, $CoCl_2$–$HgCl_2$–H_2O and $CoCl_2$–$ZnCl_2$–H_2O, and they will be considered in this order.

The cobalt chloride used for the investigation was nickel- and iron-free, obtained from British Drug Houses, Ltd., and the other salts and the hydrochloric acid used were the purest which could be purchased. Great care was paid to the analytical work, for it was only by so doing that reproducible and intelligible results could be obtained. Many of the solutions dealt with were very concentrated and viscous, and in order to avoid unnecessary duplication of results it was necessary to make them up by careful weighing. Mixtures were usually calculated so as to give 10—20 g. of equilibrium solution and about 1 g. of solid phase, and it was found best to dissolve all the solid phase to begin with by heating the mixture. The solutions so obtained usually crystallised spontaneously, but some of the zinc solutions required suitable inoculation. The mixtures were contained in thin, hard-glass bottles, in which the solutions could be boiled if necessary. The bottles were closed with corks which had been soaked in ceresin wax, the corks and neck of the bottles being then well coated over with more wax. This method of closure was found entirely satisfactory. The bottles were rotated in the thermostat at 25° until solid and solution had come into equilibrium, for which 2 days were found to be ample, even with the most viscous solutions. In the case of the $CoCl_2$–HCl–H_2O system, the mixtures were allowed to settle before some of the solution was removed with a pipette to a weighing bottle (which for the stronger solutions contained some water). The moist solid was rapidly drained on a porous plate before transference to another weighing bottle. Sometimes this draining was omitted to minimise loss of hydrogen chloride. With the other three systems, solution and solid were separated by filtration on the pump in a jacketed filter tube with an asbestos pad, back diffusion of water vapour from the pump being prevented by a calcium chloride tower. The moist solid was rapidly pressed between filter paper, and suitable amounts of equilibrium solution and moist solid were weighed out for analysis, all these operations being carried out as rapidly as possible so as to minimise absorption of moisture from the air. The appearance of the crystals under the microscope was always noted and found to be very helpful, as each compound met with in the course of the work had a perfectly distinctive form and appearance.

The compositions of equilibrium solution and moist solid obtained by analysis were entered on triangular graph paper and the nature of the solid phase was obtained in the usual way, without any ambiguity. The analytical results are given in Tables I—IV and have been plotted in Figs. 1—4.

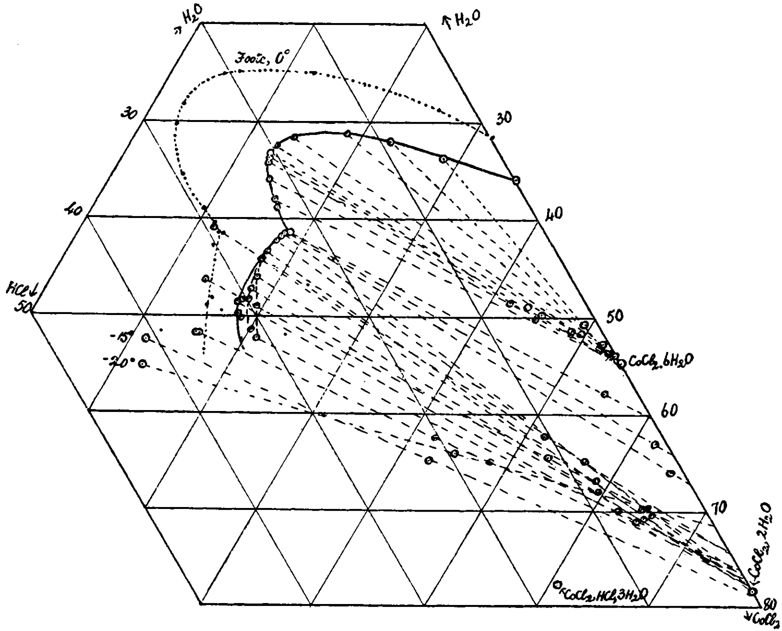
The System $CoCl_2$–HCl–H_2O.

Sabatier in 1888 (*Compt. rend.*, **107**, 42) made some qualitative observations on the solubility of cobalt chloride in dilute hydrochloric acid, and the system has been examined in detail at 0° by Foote (*J. Amer. Chem. Soc.*, 1923, **45**, 663) with hydrogen chloride concentrations ranging from 0 to 40%. The solid phases found were $CoCl_2,6H_2O$ and $CoCl_2,2H_2O$—no compound with hydrogen chloride could be obtained, although with cupric chloride a compound, $CuCl_2,HCl,3H_2O$, was found which was stable over a considerable range of solutions.

The results we have obtained at 25° are analogous and are shown in Table I and Fig. 1. Analyses were made for this system by determining total chloride gravimetrically and cobalt as pyrophosphate.

We have been unable to obtain any compound with hydrogen chloride; even in experiments at as low a temperature as — 20°, with the solution saturated with the gas at atmospheric pressure, the solid phase was $CoCl_2,2H_2O$, and we consider that conditions in this system at atmospheric pressure never allow of the separation of a compound $CoCl_2,HCl,3H_2O$, though possibly it might separate under high pressures of hydrogen chloride. Sabatier (*loc. cit.*) thought he had obtained this compound, but provided no analytical evidence in support of it; moreover, his account of what happens agrees exactly with what we observed, and the crystals he saw were almost certainly those of the dihydrate. That a compound $CoCl_2,HCl,3H_2O$ is potentially capable of existence, we do not doubt, but whether any individual compound can separate from solution in the solid state is determined by a diversity of solubility relationships, and in the present case the insolubility of the dihydrated cobalt chloride under the conditions prevailing does not allow the acid compound to form. The lithium salt of the acid, $CoCl_2,LiCl,3H_2O$, was prepared and analysed by Chassevent (*Ann. Chim. Phys.*, 1894, **30**, 5) and appears to be a well-defined compound of a deep blue colour. Both the cupric and the cobalt hydrochloric acid solutions contain the metal in the anions (Donnan and Bassett, *loc. cit.*), and the cupric compound $CuCl_2,HCl,3H_2O$ presumably has the structure $[H,(H_2O)_2]^{\bullet}\left[Cu{}^{Cl_3}_{H_2O}\right]'$, in which the co-ordination

FIG. 1.



number of the hydrogen is two—its maximum value according to Sidgwick and Callow (J., 1924, **125**, 532)—and that of the copper, four. The lithium cobalt salt would similarly be

$$[\mathrm{Li(H_2O)_2}]^{\cdot}\left[\mathrm{Co}^{\mathrm{Cl_3}}_{\mathrm{H_2O}}\right]',$$

and it seems fair to conclude that a blue anion $\left[\mathrm{Co}^{\mathrm{Cl_3}}_{\mathrm{H_2O}}\right]'$ is a chief constituent of the blue hydrochloric acid–cobalt chloride solutions. In this ion, the cobalt has a co-ordination number of four, and the water molecule is probably attached to the cobalt by the oxygen atom, although when water is present in negative ions the co-ordination is commonly through the hydrogen atoms (Sidgwick, " Electronic Theory of Valency," 1927, p. 194). According to Benrath (*Z. anorg. Chem.*, 1927, **163**, 396), there is a lithium compound $CoCl_2,4LiCl,10H_2O$, but the existence of this seems unlikely for the reasons given on pp. 1791, 1795, 1807.

Our data for solubilities (g. per 100 g. of solution) in the system $CoCl_2$–HCl–H_2O carried out at 0°, and below, are as follows (see also Fig. 1) :

	Solution.		Moist solid.			Solution.		Moist solid.	
Temp.	$CoCl_2$.	HCl.	$CoCl_2$.	HCl.	Temp.	$CoCl_2$.	HCl.	$CoCl_2$.	HCl.
0°	15·85	36·04	47·89	17·05	0°	11·55	29·39	51·15	10·95
0	15·54	36·24	41·84	20·47	−15	11·40	41·10	42·35	22·33
0	13·68	32·80	52·84	11·68	−20	12·52	42·78	44·62	19·74

For the experiments at 0°, suitably prepared mixtures were contained in tightly stoppered bottles which were shaken at intervals in the powdered ice by which they were surrounded. After about 4 hours, the mixtures were allowed to settle and some of the solution was removed by means of a cooled pipette to a weighing bottle containing water in which it was weighed. After decanting the rest of the solution, the very moist solid was also transferred as rapidly as possible to a weighing bottle containing water. The figures obtained at 0° confirm in a general way those of Foote (*loc. cit.*) for the $CoCl_2,2H_2O$ region.

In the experiments carried out at − 15° and − 20°, the solutions were contained in weighed test-tubes, and were kept saturated with hydrogen chloride for several hours while immersed in the freezing mixture. After standing for some time, the solution was decanted into another weighed test-tube. Both solution and moist solid were again saturated with the gas whilst standing in the freezing mixture. The current of gas was then stopped, a known volume of cold water added to the contents of each test-tube, and the tubes were removed from the freezing mixture, corked, and weighed. A known weight of solution and moist solid was thus secured and analysed as usual.

Although the solution point so obtained would be somewhat on the solid side of the true solution point owing to the presence of a small amount of solid phase in the solution used for analysis, yet the tie line should run to the point corresponding to the solid phase actually present. This was found to be $CoCl_2,2H_2O$ * and not $CoCl_2,HCl,3H_2O$, and the appearance of the crystals under the microscope was quite characteristic and like all other preparations of the dihydrate. The crystals of this compound are slender purple prisms with oblique ends, and appear always to have precisely the same form and colour, whether prepared by melting and dehydrating the hexahydrate over a small flame or by the action of hydrogen chloride on cobalt chloride solution at − 20°. We were anxious to be sure of this, for, at one time, we thought that in the 25° isotherm there were indications of two distinct solubility curves for $CoCl_2,2H_2O$ at the higher concentrations of hydrogen chloride. We think there can be little doubt that the variable results obtained in this region, however, are due to the difficulty of avoiding some loss of hydrogen chloride during separation of the strongly fuming solutions. The partial pressure of the gas in some of these was considerable, as was indicated by the pressure inside the bottles when they were opened, the sudden release of pressure sometimes causing the solution to effervesce momentarily. The solubility curve of $CoCl_2,2H_2O$ must be regarded as being only approximately determined. The points lying nearest to the H_2O–HCl side of the triangular diagram are most likely to be correct.

A restricted number of observations might lead one to think that two distinct solubility curves existed corresponding to two different solid phases. This, we suggest, is a more likely explanation of the two solubility curves found by Carter and Megson (J., 1928, 2954) in the system $CuBr_2$–HBr–H_2O than the one put forward by those authors. They considered that their metastable curve probably corresponded to a compound $3CuBr_2,2HBr,6H_2O$. We think that this is very unlikely and that the solid phase corresponding to both the stable and the metastable curve was anhydrous copper bromide. This interpretation of the results agrees quite well with the diagrams in Carter and Megson's paper.

The System $CoCl_2$–$MgCl_2$–H_2O.

This was examined by Benrath (*loc. cit.*) at 25°, but he made very few observations, which, moreover, seem to have been inaccurate;

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* The tie line for the solubility at −20° runs rather wide of the $CoCl_2,2H_2O$ point. This is because, after decanting the solution, some of the moist solid remained near the top of the test-tube so that on resaturation with hydrogen chloride this small portion of the total moist solid used for analysis was not properly saturated.

also no analyses of the solid phases were recorded. It is not surprising, therefore, that he failed to find the blue compound

$$CoCl_2,MgCl_2,8H_2O.$$

Our results are given in Table II and Fig. 2. The analyses in this system were rather troublesome. The cobalt was separated as sulphide, ammonium chloride being added and the current of hydrogen sulphide started before the solution was made weakly ammoniacal. Even then, however, a small amount of magnesium (up to 1% of that present) was carried down with the cobalt. The cobalt sulphide was filtered, washed with hydrogen sulphide water, and ignited while moist with the filter paper in a porcelain crucible. The product of the ignition, which appears to be a basic sulphate, was moistened with concentrated sulphuric acid, and several c.c. of concentrated hydrochloric acid were added. The crucible was covered with a small watch-glass and heated on a silica plate so that the acid boiled gently. When all the solid had dissolved, which took a considerable time, the contents of the crucible were evaporated to dryness over a very small flame and finally with a special ring-burner which allowed the sulphuric acid to be removed without spurting. The cobalt was weighed as sulphate. The ignition of the sulphate at a dull red heat was carried to such a point that it became slightly grey owing to incipient decomposition. If this were not done, there was danger of some pyrosulphate remaining undecomposed and giving high results for the cobalt. The sulphate was then dissolved in boiling water, and the small amount of cobalt oxide filtered off and weighed as Co_3O_4. The rest of the cobalt was then again precipitated as sulphide, and after concentrating the filtrate, the small amount of magnesium present was precipitated as magnesium ammonium phosphate. The weight of cobalt sulphate was corrected for the small amount of cobalt present as Co_3O_4 and for the small amount of magnesium assumed to be present as sulphate.

The filtrate from the original cobalt sulphide precipitate containing the bulk of the magnesium was boiled to remove all hydrogen sulphide. A small precipitate consisting of a mixture of sulphur and cobalt sulphide always separated and was filtered off and weighed as Co_3O_4, giving another correction to be applied to the cobalt estimation. The magnesium was then precipitated as usual and weighed as pyrophosphate.

The results so obtained agree very satisfactorily amongst themselves, and the tie lines on the triangular diagrams indicate the nature of the solid phases quite clearly.

It is to be noted that, although both $MgCl_2,6H_2O$ and $CoCl_2,6H_2O$ crystallise in the monoclinic system, they are not isomorphous

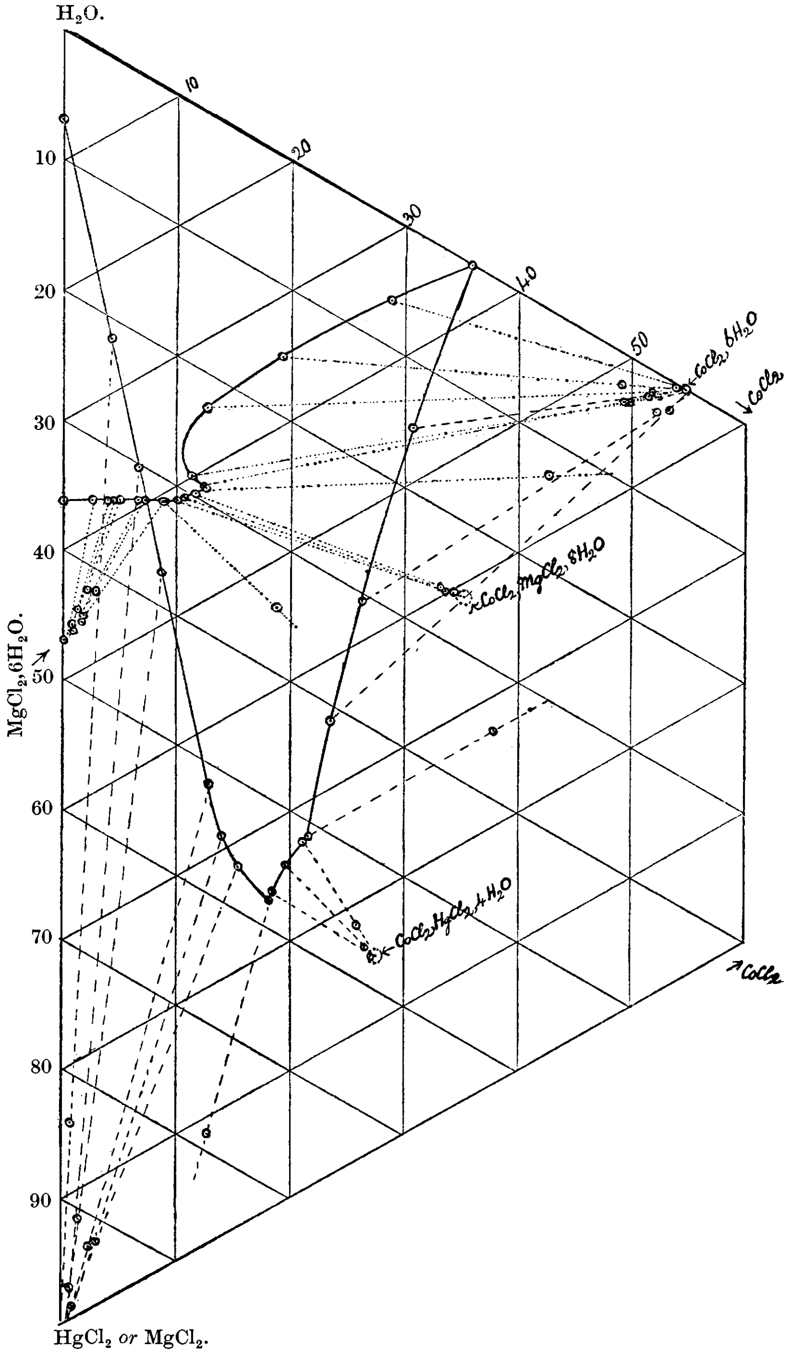

H_2O.
10
20
30
40
50
60
70
80
90
10
20
30
40
50
$\leftarrow CoCl_2,6H_2O$
$\downarrow CoCl_2$
$\times CoCl_2,MgCl_2,8H_2O$
$\leftarrow CoCl_2,HgCl_2,4H_2O$
$\nearrow CoCl_2$
$MgCl_2,6H_2O$. $\nearrow$
$HgCl_2$ *or* $MgCl_2$.

FIG. 2.

(Groth, "Chemische Krystallographie," 1906, Vol. I, p. 235). There was, however, just a possibility that a form of $CoCl_2,6H_2O$, isomorphous with $MgCl_2,6H_2O$, might be able to exist in solid solution in the latter and *vice versa*, just as $CoCl_2,4H_2O$, which cannot exist by itself, can exist in solid solution in $MnCl_2,4H_2O$ or $FeCl_2,4H_2O$ (see p. 1796). In view of the fact that a stable blue compound, $CoCl_2,MgCl_2,8H_2O$, is formed by the two chlorides under consideration, this seemed very unlikely, but we examined the possibility with some care. We consider that the tie lines run so closely to the points corresponding to pure $MgCl_2,6H_2O$ and pure $CoCl_2,6H_2O$ as to leave no doubt, when one bears in mind the possible analytical and other errors, that two of the solid phases in this system are pure $CoCl_2,6H_2O$ and pure $MgCl_2,6H_2O$.

The precise nature of the intermediate blue compound requires consideration. Taking our stand on the electrical results of Donnan and Bassett, it is clear that the compound is a magnesium salt with a complex anion containing cobalt. The eight molecules of water create a difficulty, however. Magnesium compounds at ordinary temperatures usually have 6 molecules of water co-ordinated with each magnesium atom, though at low temperatures they may have 8 or even 12, the water being present in such cases as $(H_2O)_2$ molecules (Sidgwick, *op. cit.*, p. 198). There would seem to be several possible structures for the blue compound.

If the co-ordination number of magnesium is never greater than six (Sidgwick, *op. cit.*, p. 152), the simple $[Mg(H_2O)_8]^{\cdot\cdot}[CoCl_4]''$ is out of the question and, if all the water is associated with the magnesium, the structure is more likely to be $[Mg\{(H_2O)_2\}_4]^{\cdot\cdot}[CoCl_4]''$. Another alternative is $[Mg(H_2O_6)]^{\cdot\cdot}\left[Co^{Cl_4}_{(H_2O)_2}\right]''$ with a double octahedral structure, but such a compound should be capable of existing as *cis*- and *trans*-isomerides; we have seen no indications of more than one form, however, although this might be because the other form is much less stable. On the whole, the most likely structure for the blue compound would appear to be $[Mg\{(H_2O)_2\}_4]^{\cdot\cdot}$ $[CoCl_4]''$. It crystallises in deep blue rhombohedra : small crystals have a reddish tinge when seen by transmitted light. We consider that the presence of the blue anion $CoCl_4''$ in the blue solutions is thus established.

Both Benrath (*loc. cit.*) and Foote (*Amer. J. Sci.*, 1927, **13**, 158) have examined the systems $CoCl_2$–$RbCl$–H_2O and $CoCl_2$–$CsCl$–H_2O and described double salts in each case, but their results do not agree and require checking. They seem to indicate the probability of a blue ion $CoCl_4''$. This is also suggested by work of Ferrari (*Atti R. Accad. Lincei*, 1928, **7**, 848) on the two-component system $CoCl_2$–

LiCl, for the freezing-point curve showed a maximum corresponding to the compound Li_2CoCl_4.

Since the present work was finished, Percival and Wardlaw (J., 1929, 1505) have published an important paper in which they describe the preparation of a series of salts of organic bases of the type $R^{\bullet}_2[CoCl_4]''$ (R = pyridinium, quinolinium, or quinaldinium). These are all blue and were shown to have properties consistent with the above formulation involving a negative ion $CoCl_4''$. Similar bromides and iodides were also prepared.

The System $CoCl_2$–$HgCl_2$–H_2O.

Von Bonsdorff (*Pogg. Ann.*, 1829, **17**, 249) obtained the double salt $CoCl_2,HgCl_2,4H_2O$, described it accurately, and gave it the correct formula. He does not appear to have analysed it, but noted its isomorphism with $MnCl_2,HgCl_2,4H_2O$, which he did analyse, and so deduced its formula. Benrath (*loc. cit.*) examined the same system at 25° but failed to find any double salt.

This system presented no analytical difficulties. The mercury was separated as sulphide and weighed as such; a trace of cobalt was sometimes found in the precipitate by volatilising the mercuric sulphide after weighing, but usually its amount was inappreciable. Cobalt was precipitated as cobalt ammonium phosphate in the filtrate after concentration and removal of hydrogen sulphide, and weighed as pyrophosphate.

The results obtained for this system are given in Table III and Fig. 2. The isotherm consists of three branches, corresponding to solid phases $CoCl_2,6H_2O$, $HgCl_2$, and a double compound $CoCl_2,HgCl_2,4H_2O$. The effect of cobalt chloride in increasing the solubility of mercuric chloride is remarkable and strikingly shows the great tendency of the latter compound to form negative complex ions. It will be noted that the solubility curve of the mercuric chloride is concave to the water apex of the triangle. This is unusual, for in three-component systems containing water and two electrolytes the solubility curves are nearly always convex to this point. This convexity is due to the opposition of two effects, one causing a diminution of solubility and the other an increase. In the present instance, since mercuric chloride is very slightly ionised, the depressing effect of the chlorine ions from the cobalt chloride is very slight but their effect in producing $HgCl_4''$ complexes is very great indeed. From the first additions of cobalt chloride there is, therefore, an increase in solubility of the mercuric chloride, but the proportionate effect diminishes with increasing additions and so a concave curve results. We have found that many systems of the type MCl_2–$HgCl_2$–H_2O give, in this way, a concave solubility curve for mercuric chloride.

The red double salt forms square-ended prisms, with all the edges bevelled, of the same colour and of practically the same form as cobalt chloride hexahydrate crystals, and since the red colour of the solutions is due to a red kation (Donnan and Bassett, *loc. cit.*), it is reasonable to conclude that the red compound has the structure $[Co(H_2O)_4]^{\cdot\cdot}[HgCl_4]''$.

Although incapable of existing in the pure state, cobalt chloride tetrahydrate can exist in solid solution in the tetrahydrates of ferrous chloride or manganous chloride, as has been shown by Stortenbecker (*Z. physikal. Chem.*, 1895, **16**, 250). Two series of such solid solutions exist corresponding to the α- and β-crystalline forms of the tetrahydrates of these two chlorides. The tetrahydrate of cobalt chloride no doubt has the structure $[Co(H_2O)_4]^{\cdot\cdot}Cl_2'$ and contains the same red ion as the above-described cobalt mercuric chloride. The existence of a red 4-co-ordinated cobalt kation is of great importance and is, by itself, sufficient to invalidate the theory of Hill and Howell (*loc. cit.*).

The instability of $[Co(H_2O)_4]^{\cdot\cdot}Cl_2'$ in the pure state is shown by its non-appearance in the solid form as an intermediate stage between the hexa- and the di-hydrate in any of systems, $CoCl_2$–H_2O (Étard, *Compt. rend.*, 1891, **113**, 699; *Ann. Chim. Phys.*, 1894, **2**, 537), $CoCl_2$–HCl–H_2O (Foote, *loc. cit.*—confirmed by the present authors' work), or $CoCl_2$–$ZnCl_2$–H_2O (see p. 1797). The statement of de Coninck (*Bull. Acad. roy. Belg.*, 1904, 1170) that the tetrahydrate is formed as an intermediate stage in the hydration of anhydrous cobalt chloride by moist air is based on observations which are valueless.

The System $CoCl_2$–$ZnCl_2$–H_2O.

This system is the most complex and at the same time the most interesting of those dealt with in this paper. Owing to the ease of hydrolysis of zinc chloride, complications arise, which are not met with in the other systems examined. After trying other methods, it was found that the most suitable way to make up the various mixtures was to use a carefully analysed stock of pure zinc chloride sticks and to add the amount of concentrated hydrochloric acid calculated to be needed by the amount of zinc oxide present in the weight of zinc chloride used : this was of necessity rather a rough method, but good results could be obtained. The sticks contained $ZnCl_2$, 93·5; ZnO, 3·3; H_2O (by diff.), 3·2%, but the amount of water present slowly increased every time the bottle was opened. It is very important to ensure that the zinc chloride does not contain ammonium chloride : one sample, from the same source as the above satisfactory one, contained over 1% of this impurity.

The method of analysis used was the following. The weighed amount of solution or moist solid was made up to a known volume. Cobalt was precipitated in a portion of the diluted solution by α-nitroso-β-naphthol, the total chlorine in another portion was determined gravimetrically as silver chloride, and in a third portion (generally only in the case of the equilibrium-solution analyses) both cobalt and zinc were precipitated together with ammonium phosphate and weighed as mixed pyrophosphates. The data so obtained enabled the percentage of zinc chloride to be calculated either from the estimations of cobalt and of total chlorine or from the data for cobalt and for mixed phosphates.

The results obtained by these two methods seldom differed greatly, and in preparing the mixtures the aim was always to have a slight excess of base rather than of acid. In such cases, the correct value for the zinc chloride content was taken to be that calculated from the total chlorine determination: the justification for this lies in the fact that the results so obtained are remarkably concordant even with considerable variation in the amount of free base present. The presence of a small excess of hydrochloric acid was liable to lead to erratic results [as illustrated by Expts. (*a*) and (*g*) in Table IV] although, if it was only very small in amount, the value for zinc chloride, calculated from the mixed phosphates, gave a composition for the equilibrium solution which fell on the curves passing through the points corresponding to slightly basic solutions. The cobalt α-nitroso-β-naphthol precipitate was always ignited over a good Bunsen burner in an uncovered porcelain crucible, and weighed as Co_3O_4. The results so obtained were shown to be absolutely trustworthy.

The numerical results of our examination of this system are given in Table IV and are plotted in Figs. 3 and 4, the latter giving the left-hand portion of the former on twice the scale. The isotherm of the system consists of eight well-marked portions. The solutions richest in cobalt chloride are in equilibrium with the hexahydrate. Addition of zinc chloride causes, first, a fall in the amount of cobalt chloride present in the solution (reckoned as a percentage of the total weight of solution), followed by a slight rise until, when the solution contains 31·20% of cobalt chloride and 27·91% of zinc chloride, the dihydrate $CoCl_2,2H_2O$ becomes the stable solid phase. Its range of existence is comparatively short, and at 29·48% $CoCl_2$ and 33·31% $ZnCl_2$ the compound $CoCl_2,ZnCl_2,6H_2O$ appears. From this point to 13·60% $CoCl_2$ and 60·09% $ZnCl_2$, the triangular diagram shows quite clearly that one is dealing with a solid phase which can

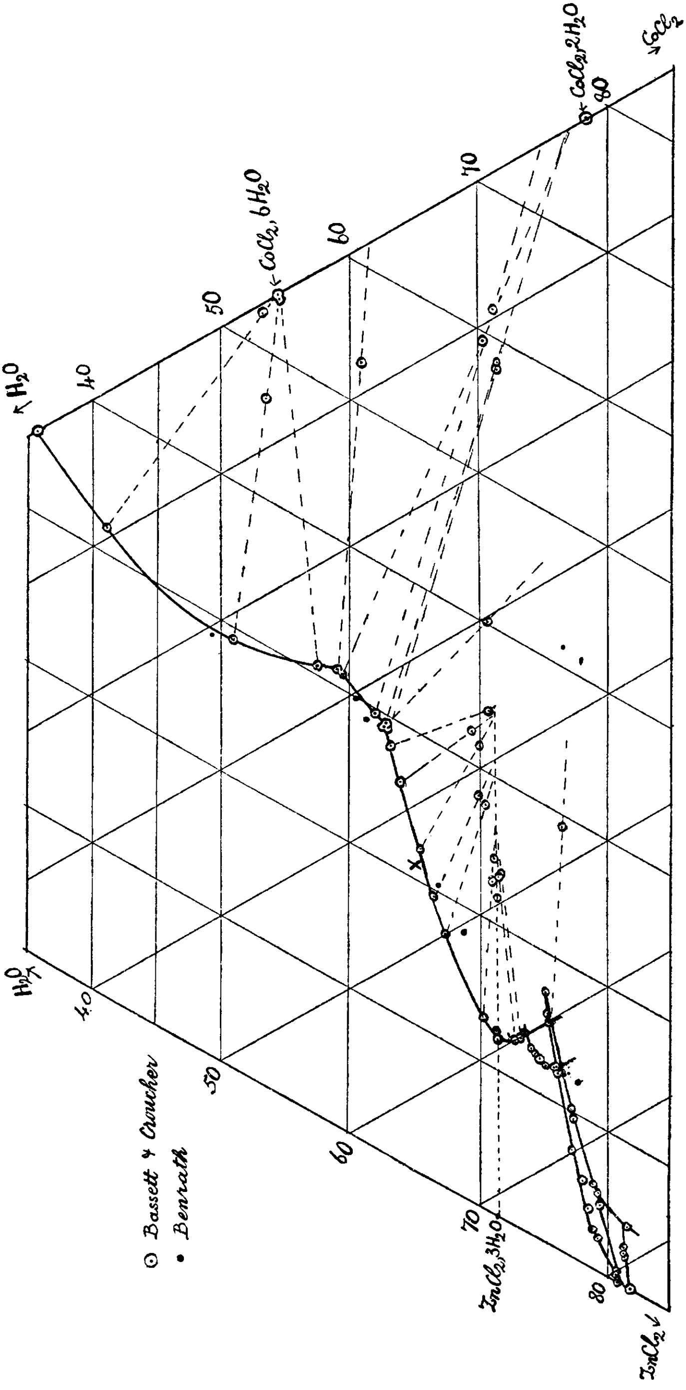
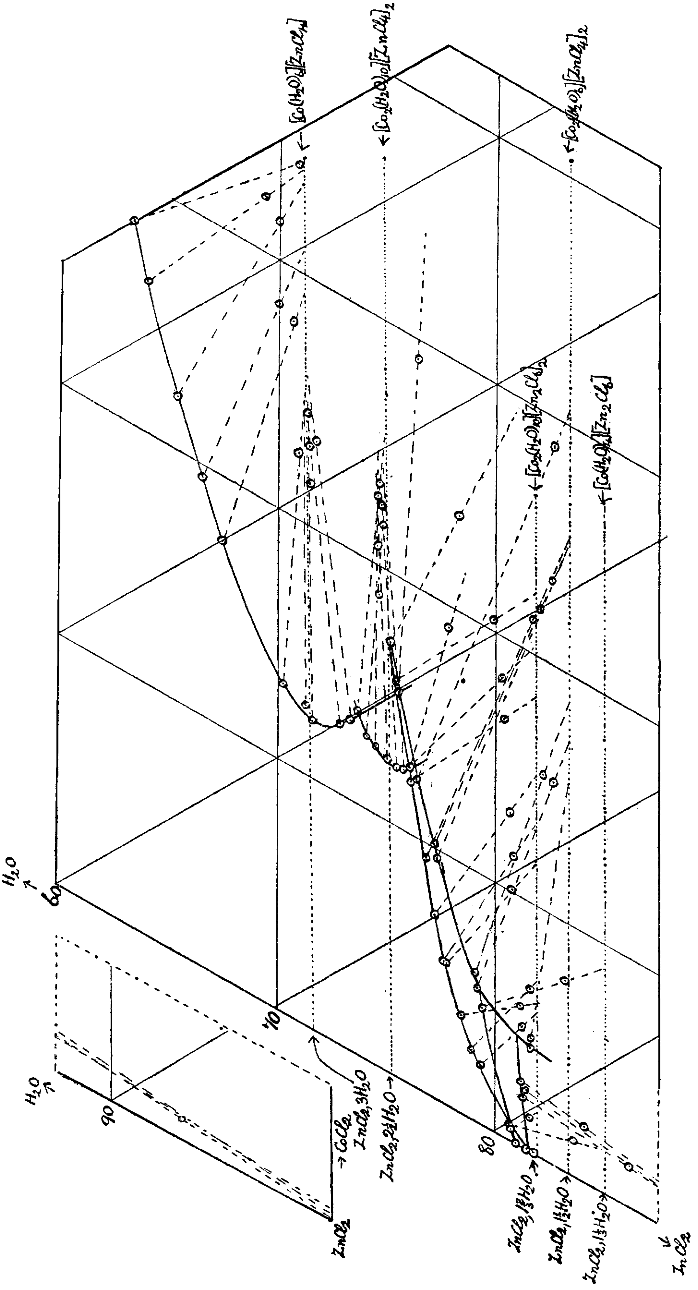

H₂O
40
50
60
70
80
CoCl₂, 6H₂O
CoCl₂, 2H₂O
CoCl₂
H₂O
40
50
60
70
80
ZnCl₂, 3H₂O
ZnCl₂
⊙ Bassett & Croucher
• Benrath

FIG. 3.

FIG. 4.


$[Co(H_2O)_6][ZnCl_4]$
$[Co_2(H_2O)_{10}][ZnCl_4]_2$
$[Co_2(H_2O)_6][ZnCl_4]_2$
$[Co_2(H_2O)_{10}][Zn_2Cl_6]_2$
$[Co(H_2O)_4][Zn_2Cl_6]$
H_2O
60
70
80
H_2O
90
$CoCl_2$
$ZnCl_2,3H_2O$
$ZnCl_2,2\frac{1}{2}H_2O$
$ZnCl_2$
$ZnCl_2,1\frac{2}{3}H_2O$
$ZnCl_2,1\frac{1}{2}H_2O$
$ZnCl_2,1\frac{1}{3}H_2O$
$ZnCl_2$

only be a series of solid solutions of $ZnCl_2,ZnCl_2,6H_2O$ (*i.e.*, $ZnCl_2,3H_2O$, see below) in $CoCl_2,ZnCl_2,6H_2O$, which can undoubtedly be regarded as being $[Zn(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''$ and

$[Co(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''$

respectively. This will be referred to as Solid Solution A.

The highest known hydrate of zinc chloride is the tetrahydrate and it is doubtless $[Zn(H_2O)_4]^{\cdot\cdot}Cl'_2$. The next lower hydrate is the trihydrate, but, from solutions containing only water and zinc chloride, it only separates below + 6·5°, its melting point. The present results show that the trihydrate really has the double formula and is $[Zn(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''$. When protected by the cobalt compound, it can separate under conditions where it is otherwise unstable. It will be noticed that the solid separating from the more concentrated solutions contains more water than does the solution from which it separates. (This is also the case with $CoCl_2,6H_2O$ but not in such a striking way.*) The liquidus consequently cuts the solidus (produced), and as one proceeds along the liquidus into regions of high zinc chloride content, the equilibrium solid solution contains more and more zinc until a maximum is reached at about 48·5% $ZnCl_2$, which is the amount required for a mixture of one molecule of $[Zn(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''$ with two of $[Co(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''$. Such a mixture simulates a compound $CoCl_2,2ZnCl_2,9H_2O$, which does not, however, exist. As the zinc chloride in solution becomes still greater, the zinc content of the equilibrium solid solution falls off again.

The solubility curves of $CoCl_2,6H_2O$ and of $[Co(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''$ should intersect at a point corresponding to about 32·7% $CoCl_2$ and 29·0% $ZnCl_2$. We have not been able to realise this point, however, owing to the readiness with which $CoCl_2,2H_2O$ separates from such solutions. Neither the hexa- nor the di-hydrate of cobalt chloride appears to contain any trace of zinc chloride in solid solution.

At a concentration of 13·60% $CoCl_2$ and 60·09% $ZnCl_2$ a new solid phase appears. The precise nature of this and of the other solid solutions mentioned below is considered later, but this is apparently a solid solution of which $ZnCl_2,2\frac{1}{2}H_2O$ is one constituent. It will be called Solid Solution B. The tie lines for this solid solution are almost parallel to the $ZnCl_2$–$CoCl_2$ side of the triangular diagram. Their direction is consequently extremely sensitive to any slight change in the moisture content of the solids previous to weighing. As the moist solid is very hygroscopic, it is almost

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* This corresponds to the state of affairs at temperatures close to the melting points of many simple hydrated salts. At temperatures just above their melting points the hydrated salts can separate from solutions containing a smaller proportion of water than is contained in the solids.

impossible to avoid some absorption of moisture during the pressing between filter paper, etc. This is undoubtedly the reason why the tie lines for this solid are tilted too much towards the water apex. The extent of this deviation indicates an absorption of about 0·5% of moisture from the air by the moist solids during the separation and handling prior to weighing.

At 13·00% $CoCl_2$ and 63·00% $ZnCl_2$, Solid Solution B gives way to Solid Solution C, of which one constituent is $ZnCl_2,1\frac{2}{3}H_2O$, and this in turn is replaced by Solid Solution E at a concentration of 0·61% $CoCl_2$ and 80·02% $ZnCl_2$. One constituent of Solid Solution E is $ZnCl_2,1\frac{1}{3}H_2O$, which is the hydrate of zinc chloride in stable equilibrium with a saturated aqueous solution of pure zinc chloride at 25°. The solubility curves of Solid Solutions C and E can be followed some distance into the metastable region, while there is still another solid solution (D)—based on $ZnCl_2,1\frac{1}{2}H_2O$ as one constituent—which is metastable over its whole, moderately extensive, range. Lastly, anhydrous zinc chloride may be obtained at 25° in metastable equilibrium with a limited range of $CoCl_2$–$ZnCl_2$ solutions. The curve for anhydrous zinc chloride is difficult to determine owing to the readiness with which Solid Solution C tends to separate. In experiment (*j*), Table IV, the hot mixture was cooled slowly from 80° to 25°, solid separating all the time, and only kept at 25° for 15 minutes before filtration which gave a moist solid that was relatively dry. The solution was probably still slightly supersaturated with respect to zinc chloride. In experiments (*i*) and (*k*) the mixtures were kept at 25° for 15 hours and 3 days, respectively, with only occasional shaking. The solutions analysed were filtered, but the amount of solid phase was small and had to be obtained by inverting the bottle and draining the solid in the thermostat so that the moist solid analysed contained a very large proportion of water in these two experiments. The tie lines of experiments (*i*), (*j*), and (*k*) show that all the solids consisted of anhydrous zinc chloride with no cobalt chloride in solid solution. The solid phases in experiments (*i*), (*j*), and (*k*) were, respectively, the hexagonal plate form, the octahedral form, and the long double pyramid form of anhydrous zinc chloride. The fact that the solubilities fall on the same curve indicates that the three kinds of crystal are, probably, mere varieties of the same crystallographic form (see p. 1807).

Since Solid Solutions A, B, C, D, and E all have a reddish colour, and red $CoCl_2$–$ZnCl_2$ solutions were shown by Donnan and Bassett (*loc. cit.*) to contain red kations, we assume, in considering the probable nature of these several solid solutions, that kationic cobalt is present. It is not so easy to deduce structures for the last four solid solutions as for Solid Solution A. When attempting to do this it is necessary to consider the nature of the hydrates formed by pure zinc chloride, for it is evident that each of the five solid solutions contains one of these hydrates as one constituent.

The system $ZnCl_2$–H_2O has been examined in detail by Mylius and Dietz (*Z. anorg. Chem.*, 1905, **44**, 209), according to whom hydrates containing 4, 3, 2·5, 1·5, and 1 molecules of water are capable of existence. With the tetrahydrate we are not now concerned, for it can only exist at temperatures below about $-30°$ and no solid solution corresponding to it appears under the conditions of our experiments at 25°.

Our *Solid Solution A*, as already mentioned, corresponds to the trihydrate which is really $[Zn(H_2O)_6]^{\cdot\cdot}\,[ZnCl_4]''$.

Solid Solution B, just as clearly corresponds to $ZnCl_2,2{\cdot}5H_2O$, and the evidence seems to point strongly to the two constituents of the solid solution being $[Zn_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}[ZnCl_4]''_2$ and

$$[Co_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2'',$$

but it is not so convincing as in the case of the preceding solid solution owing to the very short range of solutions with which Solid Solution B can be in stable equilibrium. At first sight, the triangular diagram would appear to indicate that this solid solution is in reality a compound $CoCl_2,2ZnCl_2,7{\cdot}5H_2O$, which would contain 24·18% $CoCl_2$ and 50·74% $ZnCl_2$. This is very unlikely, however, in view of the fact that the other four solids are undoubtedly solid solutions, while there is actually a hydrate $ZnCl_2,2{\cdot}5H_2O$ which can quite naturally form one constituent of a solid solution in the position of our solid B. When the small portion of the solubility curve of B which is realisable is contrasted with the corresponding portion of the solubility curve of A, it can be deduced that the composition of the limiting solid on the cobalt chloride side would be, not $CoCl_2,2ZnCl_2,7{\cdot}5H_2O$, but $2CoCl_2,2ZnCl_2,10H_2O$ (or

$$CoCl_2,ZnCl_2,5H_2O).$$

We hoped to get confirmation of this by obtaining solubility determinations of B well into the unstable region, but did not succeed owing to the great readiness with which $[Co(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''$ separated from such solutions. The fact that the *moist* solid phase of Expt. (*b*) has almost the exact composition of $CoCl_2,2ZnCl_2,7{\cdot}5H_2O$, is convincing evidence that the *dry* solid could not have such a composition, for the moist solid, though well dried between filter paper, probably contained about 20% of the very viscous equilibrium solution. This limiting solid might conceivably have the constitution $[Co(H_2O)_5]^{\cdot\cdot}[ZnCl_4]''$ with 5-co-ordinated cobalt, but we consider such a structure most improbable, and we believe the constitution to be rather $[Co_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2''$, in which the kation has the double octahedral structure $[(H_2O)_4Co(H_2O)_2Co(H_2O)_4]^{\cdot\cdot\cdot\cdot}$ which can be regarded as being formed by the linking together of a $Co(H_2O)_6^{\cdot\cdot}$ ion with a $Co(H_2O)_4^{\cdot\cdot}$ ion. We can see no reason why such linkage through water molecules should not occur. The only objection to it appears to be that it was not postulated by Werner, who did, however, assume linkage through hydroxyl. We consider that such structures must be assumed to account for a number of peculiar hydrates.* On this basis $ZnCl_2,2{\cdot}5H_2O$ would become $[Zn_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2^{\prime\prime}$.

It is noteworthy that zinc chloride does not form a dihydrate and, moreover, that there is neither any compound nor solid solution of cobalt and zinc chlorides which could in any way correspond to such a dihydrate. Engel (*Compt. rend.*, 1886, **102**, 1111) stated that a dihydrate existed but his evidence for it is practically valueless. Dietz, in earlier papers (*Ber.*, 1899, **32**, 90; *Z. anorg. Chem.*, 1899, **20**, 240), also thought he had obtained such a hydrate, but in his later and more careful work (Mylius and Dietz, *loc. cit.*) he concluded that no dihydrate exists: we consider that the non-existence of any corresponding series of solid solutions in our system is very strong confirmatory evidence of the correctness of this conclusion.

Our *Solid Solution C* raises some interesting problems. At first we thought it corresponded to Mylius and Dietz's $ZnCl_2,1{\cdot}5H_2O$, and we still believe that it corresponds to the hydrate of zinc chloride which they considered to be $ZnCl_2,1{\cdot}5H_2O$. Their description of the latter as "forming crystals like potassium nitrate" applies to Solid Solution C and the corresponding zinc chloride hydrate quite well. There can be no doubt, however, that this hydrate is, in reality, $ZnCl_2,1\frac{2}{3}H_2O$. There is a hydrate $ZnCl_2,1{\cdot}5H_2O$, however, which is probably always metastable, and is one constituent of Solid Solution D, but it crystallises in diamond-shaped rhombs which are not at all like crystals of potassium nitrate. It can be seen at once from the position of the solubility curve of Solid Solution C that at 25° our $ZnCl_2,1\frac{2}{3}H_2O$ is obviously very close to its melting point, which agrees well with Dietz's statement (*Z. anorg. Chem.*, 1899, **20**, 240) about his $ZnCl_2,1{\cdot}5H_2O$, *viz.*, that it forms large well-formed prisms melting at 26°.

The triangular diagram indicates that the limiting composition of Solid Solution C on the cobalt chloride side would probably correspond to $(CoCl_2,2ZnCl_2,5H_2O)_x$. We consider that, in this case also, 5-co-ordinated cobalt is unlikely, and so reject the structure $[Co(H_2O)_5]^{\cdot\cdot}$ $[(ZnCl_2)_2Cl_2]^{\prime\prime}$ for this compound in favour of $[Co_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}$ $[(ZnCl_2)_2Cl_2]_2^{\prime\prime}$. The kation of Solid Solution C is

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* For instance, $Co_3(PO_4)_2,8H_2O$, which is pink and which we should formulate $[(H_2O)_2Co(H_2O)_2Co(H_2O)_2Co(H_2O)_2][PO_4]_2$.

thus the same as that found in Solid Solution B, but the anion is more complex and probably consists of two tetrahedra united by an edge, $\left[{}^{Cl}_{Cl}Zn^{Cl}_{Cl}Zn^{Cl}_{Cl}\right]''$, although the zinc atoms may be at the centre of a square with the chlorine atoms at the corners. $ZnCl_2,1\frac{2}{3}H_2O$ on this basis becomes $[Zn_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}$ $[Zn_2Cl_6]_2''$.

It is not so easy to decide between two compounds, $ZnCl_2,1\frac{2}{3}H_2O$ and $ZnCl_2,1{\cdot}5H_2O$, and solid solutions based upon them when it is almost impossible to obtain the solids in an absolutely dry state for analysis. This was fully appreciated and, except in some of the earlier determinations, efforts were made to get the moist solid phases, which were analysed, as free as possible from adhering solution. The general appearance of the moist solids, *i.e.*, the amount of solution which appeared to be present, was in good agreement with the position of the moist solid points with reference to a solidus based on $ZnCl_2,1\frac{2}{3}H_2O$, whereas, had the solidus been based on $ZnCl_2,1{\cdot}5H_2O$, far more solution than appearances suggested would have had to be contained in the moist solids analysed. The massive crystals of the pure $ZnCl_2,1\frac{2}{3}H_2O$ which were analysed gave figures in almost perfect agreement with this formula.

It is well known that the precise composition of the solid solution in equilibrium with any given liquid solution is difficult to determine because the composition of the former depends on that of the solution from which it separates, and unless the amount separating is negligibly small, the concentration is altering all the time that the solid solution is crystallising out. Small irregularities in the slope of some of the tie lines arise in this way. Comparatively large variations in the proportion of solid solution separating only seem to cause a relatively small effect on the slope of the tie lines, and as we kept the proportions of solid phase fairly constant (see p. 1787), the slope of the tie lines varies in a regular way as one passes along any given solubility curve.

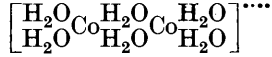
The experiments marked (*c*), (*d*), and (*e*) in Table IV show the effect of various proportions of solid phase on the tie lines of Solid Solution C : in the first two the proportion of solid to liquid was approximately 1 : 6, while in the third it was about 1 : 17. The tie lines of Expts. (*c*) and (*d*) are much steeper than that of (*e*), indicating that they contain a smaller proportion of cobalt chloride, in spite of the fact that when crystallisation began in (*c*) and (*d*) the ratio $CoCl_2/ZnCl_2$ was higher than in (*e*). The water content of solutions (*c*) and (*d*) at the commencement of crystallisation would be smaller than in (*e*), however, and that has actually a greater effect on the composition of the Solid Solution C which separates than does the $CoCl_2/ZnCl_2$ ratio. Expts. (*c*), (*d*), and (*e*) were carried out on one initial mixture. A portion was filtered off for (*c*); the rest was warmed gently to dissolve all the solid, inoculated with Solid Solution C, and again shaken for another 40 hours before another portion was separated for Expt. (*d*). It will be seen that the analytical figures for (*d*) are practically identical with those for (*c*), even for the moist solid pressed between filter paper (which was quite unexpected); both these are given to show how reproducible are our results. In Expt. (*e*) all but a small proportion of the solid phase remaining from (*d*) was separated, and a weighed mixture of equilibrium solution and moist solid warmed to dissolve the solid. The mixture was inoculated with Solid Solution C, shaken for 4 days, and then separated for analysis as usual.

Another way in which an unusually steep tie line can originate is illustrated by Expt. (*f*). Far too much solid phase separated from this mixture (which weighed 10 g.), so 0·3 g. of water was added to reduce the solid to a suitable amount. The mixture was then shaken at 25° for 40 hours, but the solid was not dissolved by warming first of all. Consequently, the solid phase really corresponds, in the main, to a solution containing very much less water than the solution in equilibrium with the outside layer of the crystals, which was actually analysed at the end of the experiment.

Solid Solution D is undoubtedly based on the hydrate $ZnCl_2,1{\cdot}5H_2O$, though, as explained above, we are satisfied that Mylius and Dietz (*loc. cit.*) never actually obtained this hydrate. From the position of the solubility curve it is clear that the pure hydrate cannot exist at 25°; it could only be formed at some considerably lower temperature, and it seems probable that it would be still more unstable with reference to some higher hydrate at these temperatures than it is at 25°.

The tie lines for Solid Solution D slope far more towards the cobalt chloride side of the diagram than do those for Solid Solution C, and the limiting compound on that side appears to be

$$(CoCl_2,ZnCl_2,3H_2O)_x.$$

A structure $[Co(H_2O)_3]^{\cdot\cdot}$ $[ZnCl_4]''$ with 3-co-ordinated cobalt seems very improbable, and we believe that in this case also we are dealing with a complex kation with two cobalt atoms linked through two water molecules,  $\left[\begin{matrix}H_2O\\H_2O\end{matrix}Co\begin{matrix}H_2O\\H_2O\end{matrix}Co\begin{matrix}H_2O\\H_2O\end{matrix}\right]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2''$; $ZnCl_2,1{\cdot}5H_2O$ thus becomes $[Zn_2(H_2O)_6]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2''$.

Solid Solution E is certainly based on $ZnCl_2,1\frac{1}{3}H_2O$. We believe that this is the hydrate which Mylius and Dietz (*loc. cit.*) considered to be a monohydrate for it forms large six-sided plates in agreement with their description of the monohydrate. Actually, no monohydrate appears to exist, for we have entirely failed to obtain one.

We obtained a single crystal of $ZnCl_2,1\frac{1}{3}H_2O$ which weighed 0·5 g., exceeded 1 cm. in diameter, and was almost quite free from adhering solution. The analysis agreed almost exactly with the above formula which we suppose to correspond to the structure

$$[Zn(H_2O)_4]^{\cdot\cdot}[Zn_2Cl_6]''.$$

No analyses of zinc chloride hydrates can be considered satisfactory unless both chlorine and zinc determinations are made. None of the analyses recorded in the literature fulfils this requirement, and most are very misleading because they give merely the percentage of water without stating whether this has been got by difference, after calculating the percentage of zinc chloride from a determination of zinc or chlorine. In Dietz's papers, since both zinc and water percentages are sometimes given, it is possible that some sort of direct determinations of water had been made, but necessarily they could not be very trustworthy.

Anhydrous zinc chloride, which can separate from $CoCl_2$–$ZnCl_2$ solutions containing over 78% of $ZnCl_2$, is actually metastable with respect to $[Zn(H_2O)_4]^{\cdot\cdot}[Zn_2Cl_6]''$ at 25° in the case of the simple system $ZnCl_2$–H_2O. It contains no anhydrous cobalt chloride in solid solution. Our value for the solubility of $ZnCl_2,1\frac{1}{3}H_2O$ is practically identical with that found by Mylius and Dietz (*loc. cit.*) and attributed to $ZnCl_2,H_2O$, but our figures for $ZnCl_2,1\frac{2}{3}H_2O$ and for the anhydrous salt are distinctly higher than those given by those authors and attributed to $ZnCl_2,1{\cdot}5H_2O$ and anhydrous zinc chloride respectively. We differ from them in finding $ZnCl_2,1\frac{1}{3}H_2O$ to be stable at 25°, and $ZnCl_2,1\frac{2}{3}H_2O$ to be metastable. They found their $ZnCl_2,1{\cdot}5H_2O$ to be the stable form at 25°, their monohydrate being slightly metastable with respect to it.

Mylius and Dietz's results were obtained by warming suspensions of the various hydrates, observing the temperatures at which the solid just vanished, and then analysing the solution. This method is likely to give low results for the solubilities owing to the high viscosities of the solutions and the comparative slowness with which equilibrium between solid and solution is established.

Our five solid solutions form very characteristic crystals which enable them to be distinguished quite readily. Solid Solution A crystallises in prisms, in which the length and breadth are generally about equal, although some fairly long prisms are often present; the angles are almost, but not quite, right angles, and the crystals usually are fairly thick. This is the only cobalt zinc chloride which has a clear red colour, and this at once marks it out from the other compounds which have a purplish tinge (see p. 1816). Mylius and Dietz (*loc. cit.*) describe $ZnCl_2,3H_2O$ as forming "rhombohedral like" crystals.

Solid Solution B crystallises in thin rectangular plates (the angles appear to be exactly right angles); these are frequently almost exactly square, but often they take the form of rectangles several times as long as they are broad. This agrees with Mylius and Dietz's description of $ZnCl_2,2·5H_2O$ as forming " rectangular, often quadratic, plates."

Solid Solution C crystallises in long, oblique-ended prisms.

Solid Solution D forms small diamond-shaped plates, and rhombs rather like those of calcite.

Solid Solution E forms large, clear, six-sided plates, though the diamond-shaped prismatic form from which these are derived is often present as well—more or less modified.

The shape of the crystals of anhydrous zinc chloride varies considerably in different experiments, but as far as we have been able to ascertain only one crystalline form is actually involved, and this probably belongs to the rhombic system. The crystals sometimes are double, square-based, acute-angled pyramids, which may be so modified as to appear almost like regular octahedra. In other cases they are hexagonal plates which appear to be complex twins built up from diamond-shaped plates that also occur sometimes in the untwinned form. On some occasions all three shapes have been found together, and there seems no tendency for one form to change into another. The solubility of the three forms at 25° appears to be the same within the limits of experimental error.

Benrath (*loc. cit.*) examined the system $CoCl_2$–$ZnCl_2$–H_2O at 25°. In view of the nature of his conclusions we have recalculated his results to our units; the points so obtained are shown on Fig. 3. It will be seen that only six points were determined apart from those

TABLE I.

$CoCl_2$–HCl–H_2O.

Solution.		Moist solid.		Solid
$CoCl_2$.	HCl.	$CoCl_2$.	HCl.	phase.
35·87	—	—	—	$[Co(H_2O)_6]Cl_2$
28·54	5·29	49·52	1·12	
22·78	9·34	51·81	0·84	
18·57	12·76	53·54	0·32	
14·05	17·66	49·54	2·15	
12·93	19·55	53·05	0·69	
12·77	20·50	48·55	2·99	
13·04	20·67	43·33	5·59	
13·10	21·09	45·04	4·77	
13·90	22·00	41·30	7·09	
15·50	22·51	44·75	5·46	
18·62	22·92	61·57	1·25	$[Co(H_2O_6)]Cl_2$ & $CoCl_2,2H_2O$
18·50	22·85	54·54	3·21	
18·64	22·76	64·47	1·42	
18·18	23·45	64·42	5·24	$CoCl_2,2H_2O = [Co(H_2O)_4]CoCl_4$
18·04	23·90	65·04	5·25	
17·84	24·50	56·50	8·36	
17·57	25·63	63·91	5·89	
17·55	26·72	58·38	8·58	
17·90	28·08	64·54	6·18	
18·09	29·10	58·97	8·94	
18·37	29·95	49·50	13·82	
17·93	30·35	60·70	7·87	
17·62	30·94	63·96	7·04	
18·32	31·57	43·34	17·48	
18·52	31·76	58·12	10·38	
19·48	29·57	66·40	5·60	
20·14	31·06	71·15	2·50	
21·00	31·10	61·68	8·19	

TABLE II.

$CoCl_2$–$MgCl_2$–H_2O.

Solution.		Moist solid.		
$CoCl_2$.	$MgCl_2$.	$CoCl_2$.	$MgCl_2$.	Solid phase.
35·87	—	—	—	$[Co(H_2O)_6]Cl_2$
28·78	6·20	53·96	0·20	,,
19·16	15·40	49·19	2·60	,,
12·56	22·70	51·80	1·76	,,
11·09	28·78	49·35	3·76	,,
12·08	29·04	49·87	3·50	,,
12·43	28·89	42·76	12·78	$[Co(H_2O)_6]Cl_2$ and $[Mg\{(H_2O)_2\}_4]CoCl_4$
11·61	29·72	33·02	26·00	$[Mg\{(H_2O)_2\}_4]CoCl_4$
10·54	30·54	33·66	25·90	,,
10·00	31·00	34·28	25·80	,,
8·95	31·66	18·70	34·80	$[Mg\{(H_2O)_2\}_4]CoCl_4$ and $[Mg(H_2O)_6]Cl_2$
8·64	31·95	1·56	44·73	$[Mg(H_2O)_6]Cl_2$
7·10	32·52	1·71	44·13	,,
6·65	32·80	2·73	41·70	,,
4·97	33·55	2·05	41·96	,,
4·44	34·00	1·34	43·90	,,
3·93	34·30	0·84	45·80	,,
2·57	34·83	0·74	45·20	,,
—	36·20	—	—	,,

$[Mg\{(H_2O)_2\}_4]CoCl_4$ contains $CoCl_2$, 35·20; $MgCl_2$, 25·80; H_2O, 39·00%.

TABLE III.

$CoCl_2$–$HgCl_2$–H_2O.

Solution.		Moist solid.		
$CoCl_2$.	$HgCl_2$.	$CoCl_2$.	$HgCl_2$.	Solid phase.
35·87	—	—	—	$[Co(H_2O)_6]Cl_2$
30·69	15·14	51·28	2·21	,,
26·04	30·68	52·00	3·08	,,
23·38	41·25	53·17	2·42	,,
21·54	51·00	37·70	34·86	$[Co(H_2O)_6]Cl_2$ and $[Co(H_2O)_4]HgCl_4$
20·96	51·76	26·02	55·55	$[Co(H_2O)_4]HgCl_4$
19·50	54·34	26·52	57·02	,,
18·34	56·95	27·07	57·45	,,
18·02	57·81	12·62	78·64	$[Co(H_2O)_4]HgCl_4$ and $HgCl_2$
15·14	56·54	2·80	91·75	$HgCl_2$
13·95	54·92	0·97	98·02	,,
12·95	51·43	2·21	92·71	,,
8·59	37·39	1·42	90·97	,,
6·70	30·26	0·71	96·65	,,
4·33	21·56	0·68	83·76	,,
—	6·90	—	—	,,

$[Co(H_2O)_4]HgCl_4$ contains $CoCl_2$, 27·45; $HgCl_2$, 57·34; H_2O, 15·21%.

for the solubilities of cobalt chloride and zinc chloride in pure water. No analyses of the solid phases were made. The eight points were supposed to give three curves—one corresponding to $CoCl_2,6H_2O$, one to zinc chloride, and one to a compound of the two. This compound was supposed to melt congruently at the point X, which corresponds to a formula $2ZnCl_2,CoCl_2,12H_2O$. This, therefore, was stated to be the double salt which was formed. A similar

TABLE IV.

$CoCl_2$–$ZnCl_2$–H_2O.

	Solution.			Moist solid.		
	$CoCl_2$.	$ZnCl_2$ from Cl.	$ZnCl_2$ from mixed phosphates.	$CoCl_2$.	$ZnCl_2$.	Solid phase.
	35·87	—	—	—	—	$CoCl_2,6H_2O$
	32·03	9·26	—	52·63	0·63	,,
	29·35	21·75	—	46·95	6·63	,,
	30·86	26·74	(27·07)	54·34	0·27	,,
	31·20	27·91	—	53·04	7·95	$CoCl_2,6H_2O$ & $CoCl_2,2H_2O$
	31·08	28·43	—	59·20	11·12	$CoCl_2,2H_2O$
	29·77	32·16	(32·40)	61·76	9·38	,,
	29·64	33·21	(33·26)	58·27	13·16	,,
	29·40	33·62	(34·01)	57·95	13·55	,,
	29·48	33·31	(33·72)	40·14	30·47	$CoCl_2,2H_2O$ & Solid Soltn. A
	28·22	34·99	(35·00)	34·38	36·50	Solid Soltn. A
	26·09	37·86	(38·34)	32·25	37·05	,,
	22·20	(43·19)	43·09	31·52	38·47	,,
	19·56	47·00	(47·17)	28·12	41·86	,,
	17·45	50·00	(50·81)	27·84	42·79	,,
	13·10	(57·15)	57·08	22·76	48·25	,,
(*a*)	[12·82	(59·29)	58·52	24·58	46·75]	,,
	12·34	59·29	(59·75)	21·79	49·77	,,
	12·78	(60·29)	60·03	23·32	48·16	,,
	13·19	60·10	(61·26)	23·59	48·12	,,
	13·51	60·09	—	—	—	Solid Soltns. A & B *
(*b*)	13·77	59·92	(60·67)	23·36	51·28	Solid Soltn. B
	12·91	61·15	—	18·87	55·69	,,
	12·72	61·82	(62·30)	22·83	51·76	,,
	12·50	62·59	(62·62)	20·80	53·79	,,
	12·28	63·08	(63·08)	21·83	52·99	,,
	12·40	63·38	(63·39)	22·50	52·20	,,
	12·61	63·40	(64·10)	19·15	58·63	Solid Soltns. B & C
	15·78	59·54	(59·80)	20·49	59·37	Solid Soltn. C
	12·63	63·40	(63·86)	18·34	61·95	,,
	12·16	64·00	(64·56)	16·81	63·56	,,
	7·35	(69·98)	69·88	13·18	67·50	,,
(*c*)	5·69	(72·35)	72·07	10·13	70·58	,,
(*d*)	5·66	(72·32)	72·07	10·10	70·58	,,
(*e*)	5·64	(72·45)	71·95	11·51	69·32	,,
(*f*)	3·97	74·50	(75·19)	5·64	75·46	,,
	2·76	(76·36)	76·09	6·53	75·00	,,
	2·34	—	76·98	4·86	76·35	,,
	0·43	80·19	(80·34)	1·41	80·19	,,
	—	81·78	(82·06)	—	$\left\{\begin{matrix} 82·00 \\ (82·08) \end{matrix}\right\}$	$[Zn_2(H_2O)_{10}][Zn_2Cl_6]_2$ $= ZnCl_2,1\frac{2}{3}H_2O$
	17·23	57·95	(58·68)	23·93	54·44	Solid Soltns. C & D
	15·36	60·09	(60·52)	29·19	47·24	,, A & D
	12·32	64·03	(65·03)	28·83	53·85	Solid Soltn. D
	10·18	66·98	(67·16)	21·99	60·03	,,
	9·59	67·72	(68·19)	23·40	59·10	,,
(*g*)	[9·48	(68·00)	67·46	21·42	60·33]	,,
	5·96	(73·09)	73·07	15·44	66·72	,,
	5·37	73·82	(73·99)	15·28	67·33	,,

* Composition of solution deduced from curves—not experimentally determined.

TABLE IV (*contd.*).

$CoCl_2$–$ZnCl_2$–H_2O.

	Solution.			Moist solid.		
	$CoCl_2$.	$ZnCl_2$ from Cl.	$ZnCl_2$ from mixed phosphates.	$CoCl_2$.	$ZnCl_2$.	Solid phase.
	*4·19	77·38	(77·48)	4·58	77·02	Solid Soltn. D.
	4·70	74·67	(74·97)	7·69	75·47 (75·97)	Solid Soltn. E
	0·61	80·02	(80·69)	1·41	82·14 (84·24)	Solid Soltns. C & E
	—	(81·28)	80·88	—	(84·34) 84·24 †84·49	$[Zn(H_2O)_4][Zn_2Cl_6]$ $= ZnCl_2,1\frac{1}{3}H_2O$
	—	80·90	(81·08)	—	‡84·72 ‡(84·86)	,, ,,
(*i*)	2·60	78·58	—	2·24	81·82	$ZnCl_2$ (hexagonal plates)§
	—	(81·84)	81·50	—	93·75 (93·77)	,, ,,
(*j*)	2·45	79·02	(80·78)	0·89	92·35	$ZnCl_2$ (octahedra)
	—	81·44	(82·07)	—	95·30	,, ,,
(*k*)	2·06	79·20	(80·69)	1·64	84·48	$ZnCl_2$ (long double pyramids)
	—	(81·52)	81·41	—	(97·05) 97·00	,, ,,

* Owing to the small amount of solid phase, it had to be drained in the bottle in the thermostat. Hence the very high proportion of solution present in the moist solid.

† Extra large crystals. ‡ One large crystal.

§ Mixture known to be slightly basic. Mixed phosphate estimation not carried out.

In the above table, those values for zinc chloride in solution which are not in parentheses are those which have been used in plotting the results. Where two values are given for the zinc chloride content of the moist solids, the second was obtained from a mixed phosphate determination, the first being obtained from the total chloride.

Constituents of the several series of solid solutions in Table IV.

Solid Solution A.

$[Zn(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''(= ZnCl_2,3H_2O)$ and $[Co(H_2O)_6]^{\cdot\cdot}[ZnCl_4]''$.

Solid Solution B.

$[Zn_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2''(= ZnCl_2,2{\cdot}5H_2O)$ and $[Co_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2''$.

Solid Solution C.

$[Zn_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}[Zn_2Cl_6]_2''(= ZnCl_2,1\frac{2}{3}H_2O)$ and $[Co_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}[Zn_2Cl_6]_2''$.

Solid Solution D.

$[Zn_2(H_2O)_6]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2''(= ZnCl_2,1\frac{1}{2}H_2O)$ and $[Co_2(H_2O)_6]^{\cdot\cdot\cdot\cdot}[ZnCl_4]_2''$.

Solid Solution E.

$[Zn(H_2O)_4]^{\cdot\cdot}[Zn_2Cl_6]''(= ZnCl_2,1\frac{1}{3}H_2O)$ and $[Co(H_2O)_4]^{\cdot\cdot}[Zn_2Cl_6]''$.

explanation to the above will undoubtedly be found to apply to the system $CoCl_2$–$CdCl_2$–H_2O, where, according to Benrath (*loc. cit.*), a compound $2CdCl_2,CoCl_2,12H_2O$ is formed.

Discussion.

We consider that the above-described results justify us in concluding (1) that *red* aqueous cobalt chloride solutions may contain, according to the conditions of concentration, temperature, etc., either of the red kations $Co(H_2O)_6^{\cdot\cdot}$, $Co(H_2O)_4^{\cdot\cdot}$, $Co_2(H_2O)_{10}^{\cdot\cdot\cdot\cdot}$, or $Co_2(H_2O)_6^{\cdot\cdot\cdot\cdot}$; the unco-ordinated ion $[Co^{\cdot\cdot}]$ is also red but is unlikely to exist in aqueous solutions; (2) that *blue* aqueous cobalt chloride solutions may similarly contain the blue ions $CoCl_4''$ or $\left[Co\overset{Cl_3}{\underset{H_2O}{}}\right]'$.

In addition to these six ions we should expect that a seventh, the kation $\left[Co\overset{Cl}{\underset{(H_2O)_3}{}}\right]^{\cdot}$, would be capable of existence, and that it would probably be red, but at present we have no direct evidence of this ion. Still other ions seem theoretically possible. The results obtained with the $CoCl_2$–$ZnCl_2$–H_2O system indicate clearly that when the chlorides of zinc, and probably of other bivalent metals, are dehydrated beyond the stage $MCl_2,4H_2O$ they become complex, the complexity increasing with increasing dehydration. Partly for this reason, it seems likely that cobalt chloride dihydrate is not $CoCl_2,2H_2O$, but rather $[CoCl_2,2H_2O]_2$. Two alternative structures are possible for such a compound, *viz.*, $[Co(H_2O)_4]^{\cdot\cdot}[CoCl_4]''$ and $\left[Co\overset{Cl}{\underset{(H_2O)_3}{}}\right]^{\cdot}\left[Co\overset{Cl_3}{\underset{H_2O}{}}\right]'$, the former being the more probable on account of its greater symmetry. The mixed colour (purple) of solid cobalt chloride dihydrate is in perfect agreement with this view that it results from the union of a red kation with a blue anion, but the evidence available is not sufficient to decide between these two alternative structures. As already stated (p. 1791), there seems no indication that more than one solid form of the dihydrate exists.

The non-ionic, unimolecular form $\left[Co\overset{(H_2O)_2}{\underset{Cl_2}{}}\right]$ is conceivable for the dihydrate but seems improbable for the solid because there are reasons, to be explained presently, for expecting such a substance to have a clear blue colour. It is, however, possible that it may exist in aqueous solution, as was suggested by Hantzsch (*loc. cit.*). When $CoCl_2,6H_2O$ is heated to 52°, it melts partially in its water of crystallisation to a deep blue liquid together with the solid purple dihydrate. The colour of the liquid suggests that, in addition to the red ions $[Co(H_2O)_4]^{\cdot\cdot}$ and $\left[Co\overset{(H_2O)_3}{\underset{Cl}{}}\right]^{\cdot}$ and the blue ones $[CoCl_4]''$ and

$\left[\mathrm{Co}^{\mathrm{Cl}_3}_{\mathrm{H_2O}}\right]'$, a relatively large amount of some other blue substance must be present. This may be $[\mathrm{Co(H_2O)_2Cl_2}]$ or perhaps anhydrous cobalt chloride.

If cobalt chloride dihydrate is really $[\mathrm{Co(H_2O)_4}]^{\cdot\cdot}[\mathrm{CoCl_4}]''$, it would help one to understand the remarkable series of solid solutions which ammonium chloride forms with the dihydrates—and only the dihydrates—of ferrous, cobalt, and nickel chlorides. Foote (*J. Amer. Chem. Soc.*, 1912, **34**, 880) was the first to notice these in the case of cobalt chloride dihydrate. They were later studied in detail by Clendinnen (J., 1922, **121**, 801).

The case seems to be analogous in some ways to the isomorphism of sodium nitrate, composed of two univalent ions, with calcium carbonate, derived from two bivalent ones. It would follow that ferrous and nickelous chloride dihydrates would have similar structures to the cobalt compound, *viz.*, $[\mathrm{Fe(H_2O)_4}]^{\cdot\cdot}[\mathrm{FeCl_4}]''$ and $[\mathrm{Ni(H_2O)_4}]^{\cdot\cdot}[\mathrm{NiCl_4}]''$.

The results of the present work indicate that the behaviour of aqueous solutions of both cobalt and zinc chlorides is dependent, *inter alia*, upon the strong tendency of the metal atoms to become co-ordinated with either four or six other atoms or molecules. The 6-co-ordinated atom is relatively much more stable in the case of cobalt than of zinc (compare Mann, J., 1929, 651), and so we find that compounds of 6-co-ordinated cobalt, or solid solutions containing them, can exist at much higher temperatures than can the corresponding pure 6-co-ordinated zinc compounds (*e.g.*, $[\mathrm{Zn(H_2O)_6}]^{\cdot\cdot}\mathrm{ZnCl_4}''$ and $[\mathrm{Co(H_2O)_6}]^{\cdot\cdot}\mathrm{ZnCl_4}''$ or solid solutions of the former in the latter). By the formation of polymeric compounds, the stability of the 6-co-ordinated condition of zinc is increased so that, *e.g.*, $[\mathrm{Zn(H_2O)_6}]^{\cdot\cdot}[\mathrm{ZnCl_4}]''$ is stable at much higher temperatures than $[\mathrm{Zn(H_2O)_4}]^{\cdot\cdot}\mathrm{Cl_2}$. The increased size of the anion may be partly responsible for this. The stability of this type of structure may be greatly increased also by the formation of polynuclear ions, *e.g.*, $[\mathrm{(H_2O)_4Zn(H_2O)_2Zn(H_2O)_4}]^{\cdot\cdot\cdot\cdot}[\mathrm{ZnCl_4}]_2''$.

Pauling (*Proc. Nat. Acad. Sci.*, 1929, **15**, 709) has shown that anhydrous cobalt chloride (and similar chlorides) has a layer structure in which all the cobalt atoms are co-ordinated to six chlorine atoms. In this structure the cobalt octahedra are linked by three shared edges and the structure could result from the knitting together of a series of ${}^{\mathrm{Cl}}_{\mathrm{Cl}}\mathrm{Co}{}^{\mathrm{Cl}}_{\mathrm{Cl}}\mathrm{Co}{}^{\mathrm{Cl}}_{\mathrm{Cl}}\mathrm{Co}$ chains containing 4-co-ordinated cobalt. It is to be noted that, in discussing the structure of these anhydrous chlorides, Pauling speaks of cobalt and chlorine " ions," and the term " ion " is unfortunately used very loosely by crystallographers at the present time. We think it probable that in cobalt chloride crystals the chlorine atoms are not ionised as in a sodium chloride crystal but are attached to the cobalt atoms by covalencies, the existence of the crystals being dependent upon the maintenance of the 6-co-ordinated condition of the metal atom. As the stability of this is high in the case of cobalt, its anhydrous chloride only melts at 734°. Each layer of octahedra in the crystals of cobalt chloride can be regarded as a single very complex molecule. What is formed when the crystals melt or first dissolve can be but a matter of speculation. It is to be noted that the structure assigned by Pauling to the *blue* anhydrous cobalt chloride is quite opposed to Hill and Howell's view (*loc. cit.*) that compounds containing 6-co-ordinated cobalt are red.

All the double salts and solid solutions described in this paper are deliquescent and decomposed by water. This makes it impossible to study their structure by any of the ordinary physical methods involving the use of dilute solutions. Phase-rule methods, as here applied, alone seem to be suitable.

The anhydrous non-ionic cobalt chloride is pale blue, the negatively charged complex ions $CoCl_4''$ and $[CoCl_3,H_2O]'$ are dark blue, and the positive ions, $[Co(H_2O)_6]^{\cdot\cdot}$, $[Co(H_2O)_4]^{\cdot\cdot}$, $[Co_2(H_2O)_{10}]^{\cdot\cdot\cdot\cdot}$, $[Co_2(H_2O)_6]^{\cdot\cdot\cdot\cdot}$, and (probably) $\left[\mathrm{Co}\overset{\mathrm{Cl}}{\underset{(\mathrm{H_2O})_3}{}}\right]^{\cdot}$, as well as the simple $Co^{\cdot\cdot}$, are red. The colour of the ion does not appear to depend on its co-ordination but only on its ionic state, nor do the number of charges carried by the ions appear to affect the colour appreciably.

There seems no doubt that colour manifestation in compounds of metals like cobalt is determined by the possibility of electron transference between different quantum levels. In the case of cobaltous compounds there are three electrons which may be considered to be fairly mobile but, of these, two are on the outermost sheath and one on the next inner shell. If one or both of the two outer electrons have been lost (as in positive cobaltous ions with one or two positive charges) then the third electron can move freely between the inner and outer shells, but, the two outer positions being similar, it makes little difference to the colour whether one or both positions are empty. This state of affairs corresponds to that of the red positive ions.

Accumulation of electrons around the cobalt as in $\left[\mathrm{Co}\overset{\mathrm{Cl_3}}{\underset{\mathrm{H_2O}}{}}\right]'$ and $CoCl_4''$ tends to make one of the outer electrons move into an inner position, which is possible, since the third quantum group in the cobalt atom is not completely filled. The deep blue colour of the complex cobalt anions appears to arise in this way.

The behaviour of the non-ionic cobaltous compounds is rather more difficult to foresee. In a general way, since each valency electron of the metal is now replaced by a pair of shared electrons, the effect might be similar to that caused by the piling up of electrons in ions such as $CoCl_4''$, and in many cobaltous compounds this actually seems to be the case. Anhydrous cobalt chloride, considered by us to be non-ionic, is pale blue, and we should expect the non-ionic $[Co(H_2O)_2Cl_2]$ also to be pale blue. The two shared electrons of a co-ordination covalency, when the co-ordination is to a neutral atom or molecule, clearly do not have this effect—doubtless because they are too firmly held by the atom to which they properly belong. In the cobaltous compounds they seem to exert little effect of any kind on the colour. In general, however, some effect would be expected, for the electronic environment, in which any electron shifts occur in the outer levels of the ion, must depend to some extent on the number and nature of the atoms co-ordinated with the ion.

It is evident that any attempt to find a *general* explanation of the colour changes of cobaltous salts must not be confined to a consideration of only one cobaltous compound or even of only cobaltous compounds. The colours of cobaltous chloride and its complex chlorides are only special cases of the colours of cobaltous salts in general, and the colours of these salts are, presumably, governed by some general rule applicable to the compounds of other metals.

The case of cobaltous chloride appears to be unusually simple, since it seems clear that positive ions are red, negative dark blue, and the non-ionic compound pale blue. That such a simple rule does not hold for all cobaltous compounds is shown by the fact that potassium cobaltocyanide, $K_4Co(CN)_6$, is red (Descamps, *Compt. rend.*, 1868, **67**, 330; *Bull. Soc. chim.*, 1879, **31**, 51; *Ann. Chim. Phys.*, 1881, **24**, 193), indicating a red $Co(CN)_6''''$ ion.

Cobaltous compounds are in no way exceptional in yielding complex anions sometimes of the same colour as the kations and sometimes of a different colour. Cupric copper, to give only one other instance, yields many negative ions which have essentially the same colour as cupric kations. These are frequently derived from organic hydroxy-acids, *e.g.*, the blue negative ion of Fehling's solution. Complex cupric chloride anions have quite a different colour (yellow brown) from the kation, similar to that of anhydrous cupric chloride.

All the facts seem to us to be explicable in the following way—we consider first the case of cobalt. If the electron shift which gives rise to the colour is that of an unshared electron—passing from the third to the fourth quantum level or *vice versa*—then the compound in question has a red colour. If, however, the electron which moves between the two levels is one which is shared between the cobalt and another atom, *i.e.*, a covalency electron, then a blue colour arises.

It seems likely, however, that it is only indirectly of importance whether the moving electron is shared or unshared. The important point, in all probability, is that when an unshared electron is concerned it is a 3_3 electron of the third quantum level which moves between the third and fourth quantum levels, whereas when a shared electron is concerned it is a 1_1 electron of the fourth quantum level which makes the same jump.

Whether it is a shared or an unshared electron which moves appears to depend upon circumstances. In the case of kations it appears to be always an unshared electron, while for anions it may be either a shared or an unshared one. Non-ionic compounds appear to behave similarly to the complex anions. If a shared electron shifts, the compound is blue (*e.g.*, anhydrous cobalt chloride); if an unshared electron shifts, the compound is red (*e.g.*, cobalt*ous* nitroso-β-naphthol). Whether a shared electron can move in this way or not will obviously depend largely on the nature of the compound, and although one shared with a chlorine atom is able to penetrate into the third quantum level of cobalt, the covalency electrons holding organic complexes together appear, as a rule, to be held too firmly for this to happen. In such cases, a third-quantum electron may be able to move out into the four-quantum orbit, giving a red substance of very closely the same colour as those containing cobaltous kations.

Anhydrous cobalt sulphate and fluoride are red. This might be because they have ionic lattices and owe their colour to the $Co^{\cdot\cdot}$ ion, but this explanation is unlikely for the fluoride, at any rate, for Ruff and Ascher (*Z. anorg. Chem.*, 1929, **183**, 193) assign to it a rutile type of structure. It seems more likely that it is a case of a non-ionic cobaltous compound having a red colour for the reason stated above.

The foregoing suggestions seem to be applicable, not only to cobaltous compounds, but also to chromous, manganous, ferrous, nickel, and cupric compounds. With the compounds of the last three metals, and perhaps also with manganous compounds, there is another possibility which does not appear to exist with cobaltous or nickel compounds. The kations of all these metals are coloured, but with anionic or neutral complexes it may happen that the extra electrons in the 4-quantum shell so stabilise the system that no electron jumps can occur, and the compound is colourless. This appears to be the reason for the lack of colour in anhydrous chromous chloride, cupric sulphate, cupric pyrophosphate, and many ferrous compounds.

The colours of cobaltous compounds are thus relatively simple, involving only red, blue, and combinations of these two. With cobaltic compounds, conditions are much more complex, for the loss of the third electron has greatly increased the number of ways in which transference of an electron between the outermost shell and the next one can occur, and, as is well known, there is a great variety of colours among even comparatively simple cobaltic complex compounds.

Although the unaided eye may not be able to distinguish between doubly and singly charged positive cobaltous ions, and although the non-ionic complexes may look something like the singly or doubly charged negative complexes, there can be no doubt that, spectroscopically, each would be perfectly distinct. In this connexion, it is noteworthy that, in a spectroscopic examination of a variety of cobalt chloride solutions, Brode and Morton (*Proc. Roy. Soc.*, 1928, *A*, **120**, 21), to account for the structure of the principal bands in the several spectra, had to resolve them into six constituent bands;* from the above considerations it would appear that this result may have a real physical basis, for these six bands may correspond to six of the absorbing entities mentioned on p. 1813.

Our results with the $CoCl_2$–$ZnCl_2$–H_2O system show that even from very concentrated solutions the $Co(H_2O)_6^{\cdot\cdot}$ ion can separate, whilst, if the structure we assign to cobalt chloride dihydrate is correct, the red $Co(H_2O)_4^{\cdot\cdot}$ ion and the *blue* $CoCl_4''$ ion can separate from much less concentrated *red* solutions. It must therefore be concluded that all cobalt chloride solutions, whether dilute or concentrated, red or blue, contain all the above-mentioned ionic species and the anhydrous compound in equilibrium with one another, the position of equilibrium depending on the prevailing conditions.

There is another point of interest in the colour of the cobaltous compounds now described.

It will be found that the colours of cobalt nitrate,

$$[Co(H_2O)_6]^{\cdot\cdot}(NO_3)_2',$$

and cobalt sulphate, $[Co(H_2O)_6]^{\cdot\cdot}[SO_4,H_2O]''$, are identical and clear red, whereas cobalt chloride, $[Co(H_2O)_6]^{\cdot\cdot}Cl_2'$, though red, has, in comparison with the other compounds, a distinct purplish tinge. Now, $[Co(H_2O)_6]^{\cdot\cdot}ZnCl_4''$ and its solid solutions with

$$[Zn(H_2O)_6]^{\cdot\cdot}ZnCl_4''$$

have the clear red colour characteristic of cobalt nitrate and sulphate, and this clear red is, we feel sure, the true colour of $[Co(H_2O)_6]^{\cdot\cdot}$. On the other hand, $[Co(H_2O)_4]^{\cdot\cdot}HgCl_4''$ and the other cobalt–zinc

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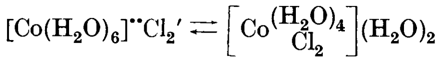
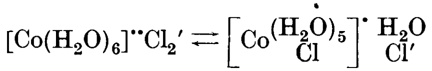
* Brode (*ibid.*, **118**, 286) made a resolution into seven constituent bands.

complexes all have a slight purplish tinge similar to that of cobalt chloride hexahydrate. This seems to suggest that the structure of even this hydrate is not quite so simple as is indicated by the formula $[Co(H_2O)_6]^{\cdot\cdot}Cl_2'$ but that it may contain a small proportion of some other form. Is it possible that the slight purplish tinge is a manifestation of that equilibrium between the un-ionised compound and its ions originally postulated by Arrhenius as occurring in dilute aqueous solutions? A slight interchange of electronic linkages may be occurring even in the solid crystals, which could be represented thus:



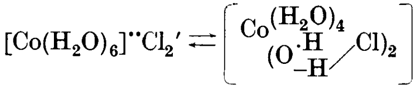
$$[Co(H_2O)_6]^{\cdot\cdot}Cl_2' \rightleftharpoons \left[Co\genfrac{}{}{0pt}{}{(H_2O)_4}{Cl_2}\right](H_2O)_2 \quad . \quad . \quad (i)$$

or



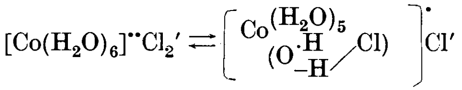
$$[Co(H_2O)_6]^{\cdot\cdot}Cl_2' \rightleftharpoons \left[Co\genfrac{}{}{0pt}{}{(H_2O)_5}{Cl}\right]^{\cdot}\genfrac{}{}{0pt}{}{H_2O}{Cl'} \quad . \quad . \quad (ii)$$

or, more probably,



$$[Co(H_2O)_6]^{\cdot\cdot}Cl_2' \rightleftharpoons \left[Co\genfrac{}{}{0pt}{}{(H_2O)_4}{\left(O\genfrac{}{}{0pt}{}{\cdot H}{-H}\diagup Cl\right)_2}\right] \quad . \quad . \quad (iii)$$

or



$$[Co(H_2O)_6]^{\cdot\cdot}Cl_2' \rightleftharpoons \left[Co\genfrac{}{}{0pt}{}{(H_2O)_5}{\left(O\genfrac{}{}{0pt}{}{\cdot H}{-H}\diagup Cl\right)}\right]^{\cdot}Cl' \quad . \quad . \quad (iv)$$

The changes represented by (i) and (ii) would mean that positions in the crystal lattice previously occupied by chlorine ions would temporarily be filled by neutral water molecules. The non-ionic complex $\left[Co\genfrac{}{}{0pt}{}{(H_2O)_4}{Cl_2}\right]$ would be pale blue and the complex $\left[Co\genfrac{}{}{0pt}{}{(H_2O)_5}{Cl}\right]^{\cdot}$ red, according to the views we have expressed. The presence of some of the pale blue complex would account for the purplish tinge of the crystals. According to the processes represented by equations (iii) and (iv), the chlorine in the non-ionic complex formed would be linked by co-ordination to the hydrogen atom of water molecules attached to cobalt. Complex (iii) would probably be blue and complex (iv) red. We consider that the changes represented by equations (iii) and (iv) are the most likely to occur, as they only involve a slight electronic shift.

If the nitrate and sulphate ions have a greater tendency to retain their charges and less tendency to become linked by covalencies than has the chlorine ion—which certainly seems to be the case—this would explain the lack of any purplish tinge in the crystals of $[Co(H_2O)_6]^{\cdot\cdot}(NO_3)_2'$ and of $[Co(H_2O)_6]^{\cdot\cdot}[SO_4,H_2O]''$. The pure red colour of $[Co(H_2O)_6]^{\cdot\cdot}ZnCl_4''$ could be similarly explained. At first sight, the purplish tinge of $[Co(H_2O)_4]^{\cdot\cdot}[HgCl_4]''$ is strange, for one would have expected the $HgCl_4''$ ion to retain its charges even more strongly than the $ZnCl_4''$ ion. The difference in colour may be due to the fact that in cobalt mercuric chloride two co-ordination positions of the cobalt atom are unfilled, resulting in a tendency to form in the crystals some $\left[\mathrm{Co}^{(H_2O)_4}_{Cl_2HgCl_2}\right]$ or even $\left[\mathrm{Co}^{(H_2O)_4}_{Cl_2}\right]HgCl_2$, both non-ionic compounds which should be blue.

In conclusion, it may be said that the results of the present investigation are in full agreement with the original theory of Donnan and Bassett (*loc. cit.*), but consideration of other compounds indicates that the connexion between colour and ionic state found to hold in the case of cobalt chloride and its complexes is largely accidental. The work has also shown that dehydration processes may be associated with the colour changes, though not themselves responsible for them. The simple dehydration theory and Hill and Howell's " varying co-ordination " theory seem definitely disproved. In regard to the former, the fact that $CoCl_2,2H_2O$ is the stable solid phase over a considerable range of solutions, not only the blue ones of the $CoCl_2$–HCl–H_2O system but also the red ones of the $CoCl_2$–$ZnCl_2$–H_2O system, is of peculiar interest, especially as, according to Hartley (*loc. cit.*), it was to the formation of $CoCl_2,2H_2O$, rather than of anhydrous cobalt chloride, that the change of colour from red to blue was chiefly due.

Summary.

The systems $CoCl_2$–HCl–H_2O, $CoCl_2$–$MgCl_2$–H_2O, $CoCl_2$–$HgCl_2$–H_2O, and $CoCl_2$–$ZnCl_2$–H_2O have been examined at 25°, a few observations at lower temperatures also having been made on the first system. No compound of cobalt chloride and hydrogen chloride could be isolated, but the blue compound, $CoCl_2,MgCl_2,8H_2O$, and the red compound, $CoCl_2,HgCl_2,4H_2O$, were obtained. In the case of cobalt chloride and zinc chloride no less than 5 series of red solid solutions were obtained, each of which contains one of the hydrates $ZnCl_2,nH_2O$ as one constituent, where $n = 3$, $2\frac{1}{2}$, $1\frac{2}{3}$, $1\frac{1}{2}$, and $1\frac{1}{3}$. The nature of all these complex compounds is discussed, and conclusions are drawn as to the ions which are present in red and blue cobalt chloride solutions.

Suggestions have also been put forward regarding the electronic shifts responsible for the red and blue colours of cobaltous salts, and in this connexion compounds of a few other metals have been incidentally considered.

In the case of cobaltous chloride, kations are red and complex anions blue, but this is largely accidental, and does not hold for

cobaltous compounds in general. Red anions and red non-ionic compounds of cobaltous cobalt can exist, although blue cobaltous kations apparently do not.

New information has been obtained with respect to the number and nature of the hydrates of zinc chloride. Some of the older statements have been shown to be erroneous.

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