

XCVI.—*The Colour Changes exhibited by the Chlorides of Cobalt and some other Metals, from the Stand-point of the Theory of Electroaffinity.*

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THE colour phenomena exhibited by cobalt chloride have attracted attention for a long time, with the result that a great many interesting facts have been accumulated. Without going into details, these may be briefly stated as follows. The familiar red solid is the hexa-

3 R 2

hydrate, which, on loss of water, passes into lower hydrates possessing tints varying from violet-red to blue-violet. The anhydrous salt, as obtained by sublimation in a stream of chlorine, possesses a pale sky-blue colour. Aqueous solutions of cobalt chloride may be either red, violet, or blue, the colour depending on the concentration and temperature. The higher the temperature and the greater the concentration, the bluer the solution tends to become. Red aqueous solutions may also be turned blue by the addition of the chlorides of the metals of pronounced basic function. In this respect, the very soluble chlorides of magnesium and calcium are particularly effective. Thus, if cobalt chloride be added to strong solutions of calcium or magnesium chloride at the ordinary temperature, violet to blue solutions are obtained. The chlorides of potassium and sodium appear to be not so effective, but that they act in a similar manner is clear from the fact that solutions of cobalt chloride containing them become blue when heated at lower temperatures than the pure solutions. The chlorides of zinc, mercury, antimony, tin, &c., act in the opposite manner, that is, if added in sufficient quantity they turn blue solutions of cobalt chloride red, whether these blue solutions have been obtained by the addition of the chlorides enumerated previously or by elevation of temperature.

Hydrochloric acid is still more effective than magnesium and calcium chloride in producing blue solutions at the ordinary temperature.

With respect to other solvents, it may be remarked that very dilute solutions in methyl alcohol are reddish and resemble the aqueous solutions at the ordinary temperature, whilst stronger solutions are blue. All solutions in ethyl alcohol are blue at the ordinary temperature.

Theories to Account for these Facts.

1. *Hydration Theory.*—The blue colour of the alcoholic solution and of the aqueous solution when raised to a sufficiently high temperature or when added to the solution of a dehydrating agent such as calcium chloride, taken in conjunction with the blue colour of the anhydrous salt, has led to the view that the red solutions contain the hydrated salt, whilst the blue solutions contain the anhydrous salt or, at all events, a lower hydrate. This hypothesis has been supported by von Babo (*Jahresber.*, 1857, 72), Schiff (*Jahresber.*, 1859, 52), Gladstone (this Journal, 1858, 10, 79; 1859, 11, 36), Russell (*Proc. Roy. Soc.*, 1881, 32, 258), Tichborne (*Chem. News*, 1872, 25, 133), Etard (*Compt. rend.*, 1891, 113, 699; 1895, 120, 1057), Wrewsky (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 164), Potilitzin (*Ber.*, 1884, 17, 276; *Bull. Soc. Chim.*, 1891, [iii], 6, 264), Wyrouboff (*Bull. Soc. Chim.*, 1891, [iii], 5, 460), Charpy (*Compt. rend.*, 1891, 113, 794), and Hartley (*Trans. Roy. Dub. Soc.*, 1900, [ii], 7, 253).

The spectroscopic researches of Russell led him to favour the hydration theory. He observed a great similarity in the absorption spectra of fused mixtures of cobalt chloride with alkali chlorides, of the blue hydrochloric acid solutions, and of the concentrated solutions of cobalt chloride in methyl, ethyl, and amyl alcohols, glycerol, and various esters, ascribing this similarity to the presence of the uncombined anhydrous chloride. The spectrum of the aqueous solution varied with the concentration. Saturated solutions showed the bands at λ 610 and 625 which are characteristic of the above, whilst dilute solutions showed a faint, wide absorption band between λ 550 and 485. The absorption spectra have also been studied by Etard, Vogel (*Ber.*, 1878, 11, 913), and very fully by Hartley. The latter gives photographs of the absorption spectra which show their inter-relationships very clearly. The increase of absorption at the red end of the spectrum on rise of temperature, is very clearly shown in the case of saturated solutions of cobalt chloride, either pure or mixed with a saturated solution of calcium chloride. It is evident from the spectra that solutions of cobalt chloride in hydrochloric acid and in saturated calcium chloride solution contain something which is also produced in the strong aqueous solution on rise of temperature. This is regarded by Hartley as the anhydrous chloride and adduced as evidence in support of the hydration theory, but the facts admit of another interpretation, as will be shown in the course of this paper.

2. *Engel's Theory*.—Engel (*Bull. Soc. Chim.*, 1891, [iii], 6, 239) has brought forward many arguments to show that the observed phenomena cannot be explained by the hydration or dehydration of the cobalt chloride molecule in solution. Thus zinc chloride, although a dehydrating agent, produces the opposite effect to calcium chloride. According to Engel, the changes of colour of the solutions from red to blue or *vice versa* are due to the formation of double haloid salts. In the case of cobalt chloride alone, he supposes that rise of temperature produces hydrochloric acid owing to increased hydrolysis of the salt, and that this then combines with the cobalt chloride to form a blue double compound. Double salts containing cobalt chloride and another chloride have in fact been isolated by Engel, Le Chassevent (*Bull. Soc. Chim.*, 1891, [iii], 6, 3), Hautz (*Ann. Phys. Chem.*, 1848, [ii], 66, 284), and Russell.

Although the explanation given by Engel of the colour-change produced by rise of temperature in solutions of cobalt chloride is almost certainly incorrect, as has been pointed out by Le Chatelier (*Bull. Soc. Chim.*, 1891, [iii], 6, 3, 84, 209), nevertheless his views concerning the effects produced by the addition of other chlorides indicate an undoubted advance in the subject.

3. *Bersch's Theory*.—Bersch (*Wien Akad. Sitzungsber.*, 1867, [ii],

56, 724) thought he observed a change of the red hexahydrate to blue at a temperature of $30-35^{\circ}$ without decomposition, and on this based the view that cobalt salts could exist in two isomeric modifications possessing different colours. This has, however, been disproved by Potilitzin (*loc. cit.*), who showed that no change occurs below 54° (Etard's solubility curves would make this temperature about 50°). At this temperature a transition point is reached, the hexahydrate changing into the lower hydrate, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. These results have been confirmed by Lescoeur's (*Ann. chim. phys.*, 1890, [vi], 19, 551) investigations on the hydrates of cobalt chloride. When the transition point is attained, the hexahydrate "melts in its water of crystallisation" and a small amount of blue saturated solution is produced. It was probably this which led to the mistake on Bersch's part.

4. *Ostwald's Theory*.—According to Ostwald (see the *Lehrbuch der allgem. Chemie*, and also *Grundlinien der anorg. Chem.*, p. 620), the blue colour is due to the non-ionised salt, the red colour to the cobalt cation. The production of blue solutions on rise of temperature may then be explained as due to a decrease of ionisation, whilst the addition of other chlorides would tend to make the solutions blue by diminishing the ionisation of the cobalt chloride. According to Salvadori (*Gazzetta*, 1896, [i], 26, 237), cobalt chloride is in fact more dissociated in aqueous solution at 0° than at 100° . His experimental numbers appear, however, to point to an opposite conclusion. Moreover, the values of van't Hoff's factor, as found by Tarugi and Bombardini (*Gazzetta*, 1900, [ii], 30, 405), for cobalt chloride solutions at the boiling point, agree very well with the values found by us at the freezing point.

Preliminary Experiments. In conjunction with C. J. J. Fox.

The following experiments show that there is a more or less complete parallelism between the colour changes as shown by aqueous and alcoholic solutions, so that these changes can scarcely be ascribed to varying degrees of hydration.

The effect of temperature on the colour of the aqueous solutions is shown also by the solution of the anhydrous salt in anhydrous alcohol, the only difference being that the change from red to blue occurs in the latter case at a very much lower temperature.

The alcohol used in all these experiments had been carefully dried by long-continued boiling in presence of excess of fresh calcium oxide. The cobalt chloride was obtained by reducing the oxalate in a current of hydrogen and then subliming the chloride in a current of dry chlorine.

On cooling the blue alcoholic solution down to -79° in a mixture of ether and solid carbon dioxide, it becomes perfectly red, resembling the dilute aqueous solution at the ordinary temperature. Moreover, the

pale blue, solid anhydrous chloride, if cooled down to the temperature of boiling liquid air, becomes reddish-violet in colour. It is known that the red anhydrous cobalt sulphate becomes violet when heated. If a solution of the sulphate in concentrated sulphuric acid be heated to the boiling point of the acid, it becomes bluish-purple in colour. All these results leave no doubt that the presence or absence of water plays no essential part in the colour changes shown by cobaltous salts.

The parallelism between the aqueous and alcoholic solutions extends even to the effects produced by zinc and mercuric chlorides, for these salts, if added in sufficient quantity to the blue solutions of cobalt chloride in alcohol, turn them red just as they redden the hot, blue aqueous solution. Experiments made by Beckmann's boiling point method in alcoholic solution show that combination occurs between cobalt and mercury chlorides, as the following results show :

*Mercuric Chloride.** $\text{HgCl}_2 = 270$.

Wt. of alcohol employed = 12.77 grams.

Weight of HgCl_2 added.	Elevation of boiling point.	Mol. wt. calculated.
0.1409 gram	0.044°	288
0.2007 „	0.067	270

A series of experiments was now made in which cobalt chloride was first added to the alcohol and the rise of boiling point determined, mercuric chloride and cobalt chloride being then added to the same solution :

Wt. of alcohol = 10.07 grams.

Weight of cobalt chloride.	Elevation of boiling point.	Calculated molecular wt.
0.0139 gram	0.026°	140
0.0463 „	0.037	143
Weight of mercuric chloride added :		
0.1760 gram	0.054	373
0.2346 „	0.075	363
0.2791 „	0.090	354
0.5337 „	0.177	344
Weight of cobalt chloride added :		
0.0410 gram	0.024	195
0.0600 „	0.035	196
0.0982 „	0.058	193

* The mol. wt. of mercuric chloride in alcoholic solution has been already determined by Beckmann (*Zeit. physikal. Chem.*, 1890, **6**, 453).

The high values obtained for the "calculated molecular weights" of the mercuric chloride show clearly that the cobalt chloride already present in the solution enters into combination with it to a considerable extent. The amount of combination can be readily calculated in any particular case. Thus, the addition of 0.5337 gram of mercuric chloride would, if unaffected by the cobalt chloride, have produced an elevation of 0.218° as follows from the results given in the first table. Instead of that the elevation was only 0.177° , the deficit being 0.041° .

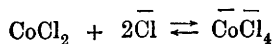
This deficit is proportional to the number of "active units" which have disappeared owing to combination in solution. The percentage disappearance of active units is accordingly equal to $\frac{0.041 \times 100}{0.218 + 0.037} =$

$\frac{0.041 \times 100}{0.255} = 16$ per cent. The results obtained on further addition

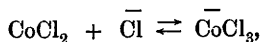
of cobalt chloride to the same solution confirm the above conclusion. The reddening effect produced by mercuric chloride is thus independent of the solvent, and is connected with a simultaneous disappearance of active units from the solution. We shall defer the discussion of this until later.

Existence of Complex Cobalt Anions.

None of the theories hitherto put forward being capable of giving a satisfactory account of the observed phenomena, it occurred to us that the colour of the blue solutions might be very largely due to the presence of complex anions containing cobalt. The formation of such complex ions has been shown by Abegg and Bodländer (*Zeit. anorg. Chem.*, 1899, 20, 453) to play a very important part in inorganic chemistry. These complex ions are regarded by Abegg and Bodländer as being formed by the union of simple ions with undissociated molecules. Thus, in the case of cobalt chloride we should have:

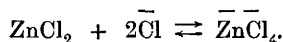
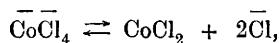


or



or perhaps both. Cobalt is already known to have a strong tendency to form complex negative ions. Thus it is distinguished from nickel by its power of forming a stable complex anion with the cyanogen ion. In the present case, the complex anions exist in a state of dissociation-equilibrium with the undissociated salt and the chlorine ions. Their formation will be evidently favoured by increase of concentration. It follows also from the above equations that an increase in the concentration of the chlorine ions will produce an increase in the amount of the complex ions. This can be effected by the addition of other

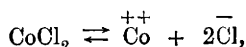
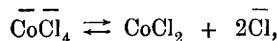
chlorides, particularly if they are very soluble, so that a large amount of chlorine ions can be introduced into the solution. It is necessary, however, that the metallic ions, simultaneously introduced with the chlorine ions should possess a smaller tendency than cobalt to form negative complexes. This condition is fulfilled by metals of relatively strong basic function, such as the metals of the alkalis and alkaline earths, as also by hydrogen. On the other hand, metals such as zinc, mercury, cadmium, antimony, tin, &c., possess a greater tendency to form negative complex ions than cobalt, and so their effect is to break up the cobalt complexes, with the formation of new complexes in which they take the place of cobalt. This may be represented as follows:



This view of the matter affords a simple explanation of the different effect produced by the two classes of chlorides enumerated above.

Although the particular form of the equations of equilibrium in the case of highly dissociated electrolytes is a matter of considerable uncertainty at the present time, nevertheless, the simple thermodynamic law of mass-action may be utilised to illustrate the conditions of equilibrium in such a case as the present.

Thus, corresponding to the equilibria:



we have the equations:

$$k' C_{\overline{\text{CoCl}}_4} = C_{\text{CoCl}_2} \cdot C_{\overline{\text{Cl}}}^2,$$

$$k C_{\text{CoCl}_2} = C_{\text{Co}} \cdot C_{\overline{\text{Cl}}}^2,$$

whence

$$kk' C_{\overline{\text{CoCl}}_4} = C_{\text{Co}} \cdot C_{\overline{\text{Cl}}}^4.$$

From these equations, we have also

$$\frac{C_{\overline{\text{CoCl}}_4}}{C_{\text{Co}} + C_{\text{CoCl}_2}} = \frac{1}{k'} \frac{C_{\overline{\text{Cl}}}^4}{k + C_{\overline{\text{Cl}}}^2}.$$

This ratio may be termed the "complexity-ratio" of the cobalt. It expresses the ratio of the cobalt present in the solution as complex anion to that present as cation + undissociated salt. If, now, another metal is present in the solution, which can also form complex anions of similar type, say zinc, we shall have a similar equation for it. If

we suppose, for simplicity, that the value of k is the same in both cases, then we obtain the simple result :

$$\frac{r_{\text{Co}}}{r_{\text{Zn}}} = \frac{k''}{k},$$

denoting by r the ratio above referred to.

Electrolytic Experiments.

(a) *Aqueous Solutions.*—The simplest way of ascertaining the presence of complex anions in the blue solutions was to employ the method used by Orme Masson (*Phil. Trans.*, 1899, 192 A, 331). We found it impossible, however, to get the gelatin to set in the strong salt solutions required. Many experiments were tried with a modified apparatus in which no gelatin was employed, the ends of the glass connecting tube being closed by plugs of plaster of Paris. The results obtained by this method agreed in every case with those to be described presently. Thus, when the two end vessels were filled with the blue calcium chloride solution and the connecting tube contained pure calcium chloride, a blue layer entered the tube from the cathode vessel on passing the current, and travelled towards the anode, whilst no colour appeared on the anode side. If, on the other hand, the end vessels contained red cobalt chloride solution, whilst the connecting tube was filled with potassium chloride solution, a pink layer entered the tube from the anode vessel and travelled towards the cathode, and no colour appeared on the cathode side. Many control experiments were tried with copper sulphate solution, Fehling's solution, &c., and the results appeared to show that the influence of electric endosmose was negligible. Direct measurement showed, in fact, that no easily measurable amount of electric endosmose occurred. As, however, the possibility was always present that our results might be due to a small amount of endosmose, we tried many other forms of apparatus, in which no porous plugs were present, but in which bodily streaming of the liquid was prevented by the use of a closed mercury electrode.

The results were, however, almost invariably disturbed by the occurrence of uncertain volume-changes, owing to separation of substances at the closed electrode, so that we finally adopted a simple U-tube, similar to that recommended by Nernst (*Zeit. Elektrochem.*, 1897, 3, 308). This was first filled with the lighter, colourless liquid, the heavier coloured layer being subsequently introduced from underneath by means of a capillary tube, one end of which was sealed to the bottom of the U-tube, the other end being attached to a tap and funnel. Platinum wires were employed as electrodes. The 110-volt lighting circuit was connected to the electrodes through a single

200-ohm lamp. The U-tubes employed were about 20 cm. in height and 6 mm. in internal diameter. During the passage of the current, the tubes were cooled by being immersed in beakers, through which water from the main constantly flowed. In this way, a fairly constant temperature was obtained. The following solutions were electrolysed in this way :

<i>Lower Coloured Layer.</i>	<i>Upper Colourless Layer.</i>
1. Cobalt chloride in concentrated hydrochloric acid (blue).	Concentrated hydrochloric acid.
2. Cobalt chloride in concentrated magnesium chloride solution (blue).	Concentrated magnesium chloride solution
3. Cobalt chloride in concentrated calcium chloride solution (blue).	Concentrated calcium chloride solution.
4. Cobalt chloride solution (fairly dilute).	Potassium chloride solution.
5. Cobalt chloride + concentrated calcium chloride + zinc chloride (red).	Concentrated calcium chloride solution + zinc chloride.

In experiments 1, 2, and 3, the blue lower layer moves towards the anode, going down on the cathode side and up on the anode side, whereas in experiments 4 and 5 the lower red layer behaves in exactly the opposite manner. These results are not due to changes of level, resulting from differences of density produced by decomposition at the electrodes, or from unequal evaporation, as the upper levels of the colourless liquid were always marked, and were not found to change to any appreciable extent during the course of an experiment.

These results seem to prove without doubt the existence of complex anions in the blue solutions experimented with. The motion of the boundaries is, however, a much more complicated matter than in the simple case where each solution contains only one sort of negative ion, these ions being both perfectly stable. The blue complex anions can only exist in presence of a large excess of chlorine ions, and so the negative current is very largely carried by the latter. Moreover, as the blue anions move upwards into the colourless layer where no cobalt is present, they will dissociate to some extent, and the positive cobalt ions so produced will constantly move downwards towards the cathode. The rate of movement of the blue layer towards the anode will accordingly depend on the relative concentration of the complex cobalt anions and on their stability in the upper colourless layer into which they

advance. We should therefore expect that the rate of movement towards the anode would run parallel with the "blueness" of the solution. As a matter of fact, this rate is greater in 1 than in 2, and greater in 2 than in 3, and in agreement with this solution 1 is bluer than solution 2, and 2 bluer than 3. The motion is comparatively fast in the hydrochloric acid solution, the boundary moving under the above conditions about 2 cm. per hour, so that this case is well adapted for a lecture-experiment.

Control experiments were made in the same apparatus with the following solutions :

<i>Lower Coloured Layer.</i>	<i>Upper Colourless Layer.</i>
6. Fehling's solution.	Alkaline tartrate solution.
7. Ammoniacal copper sulphate solution.	Ammonium hydroxide + ammonium sulphate.

The colour of Fehling's solution is due to a negative ion which, as Masson has shown, moves towards the anode, whilst the deep blue colour of the ammoniacal copper solution is known to be due to a positive copper-ammonia ion. In agreement with this, the blue liquid moves towards the anode in 6, and towards the cathode in 7.

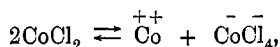
(6) *Solutions in Ethyl Alcohol.*—The solutions of anhydrous cobalt chloride, calcium chloride,* and hydrochloric acid in anhydrous ethyl alcohol conduct electricity fairly well, so analogous experiments were made in alcoholic solution with very satisfactory results. Owing to the relatively small conductivity, much smaller U-tubes were used with the same potential difference. The following solutions were electrolysed :

<i>Lower Coloured Layer.</i>	<i>Upper Colourless Layer.</i>
8. Cobalt chloride in alcohol (blue).	Calcium chloride or hydrochloric acid in alcohol.
9. Cobalt chloride + mercuric chloride in alcohol (red).	Mercuric chloride in alcohol.
10. Ditto.	Hydrochloric acid in alcohol.

In experiment 8, the anodic boundary remained sharp and moved up quite rapidly towards the anode. The cathodic boundary moved downwards away from the corresponding electrode, but on this side considerable mixing occurred. This experiment is very important as it proves the existence of blue complex anions in the solution of cobalt chloride

* The anhydrous calcium chloride was obtained by heating the ordinary "dry" calcium chloride (which contains about half a mol. of water of crystallisation) with excess of ammonium chloride, and the freedom of the product from water or basic chloride proved by titration with silver nitrate solution.

in anhydrous alcohol. The importance of this experiment is connected not so much with its bearing on the present subject as with its relation to the general theory of solutions. As we have seen, the molecular weight of cobalt chloride in alcoholic solution as determined by the boiling point method is somewhat greater than normal (140 instead of 130), and yet the solution evidently contains a considerable number of ions owing to its moderately good conductivity.* Many examples of a similar sort, for example, silver nitrate in pyridine, have been recently brought forward by Kahlenberg (*J. Physical Chem.*, 1901, 5, 339) as evidence against the electrolytic dissociation theory. The apparent contradiction disappears in the case of cobalt chloride in alcohol now that the existence of complex anions in this solution has been definitely proved. For example, if the net result of solution of cobalt chloride in alcohol correspond to the following equation,



the solution will conduct electricity and yet the calculated molecular weight will be normal. As some of the undissociated compound $\text{Co}(\text{CoCl}_4)$ may exist in the solution as well as its ions, it is not surprising that the calculated molecular weight is greater than "normal." It seems very probable that many of the anomalies to which Kahlenberg and others have recently directed attention may admit of explanation in a similar manner.

With regard to the particular problem dealt with in this paper, the proof of the existence of complex cobalt anions in the blue alcoholic solution containing only cobalt chloride is of importance because, reasoning by analogy, it is fair to assume that the blue colour exhibited by the hot concentrated aqueous solutions has a similar origin. Attempts were made to obtain a direct proof of this by the electrical method, but the conditions were too unfavourable. For one thing, it is difficult to know what solution to employ as the upper colourless layer in which the stability of the complex ions will be preserved without being increased, and secondly, the heat produced by the current if a sufficient potential-difference is used results invariably in very great mixing and even causes the solution to boil.

In experiment (9), the conductivity of the mercuric chloride in alcohol is so slight that the current had to be left on over-night in order to obtain an effect. Although the boundaries were not quite sharp the next morning, there was no doubt that the cathodic boundary had moved upwards towards the cathode, the anodic boundary having moved downwards away from the anode, showing that in this case the red colour is due to positive cobalt cations. In

* Thus the specific conductivity of a 0.9 per cent. alcoholic cobalt chloride solution was measured and found to be 0.00024 at 25°.

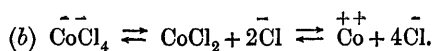
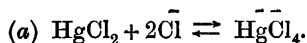
experiment (10), when the tube was filled a faint blue colour was formed at the junction of the two liquids owing to the action of the hydrochloric acid. On passing the current, the faint blue coloration at the anodic boundary moved off towards the anode, leaving a colourless layer above the lower red liquid. At the cathodic boundary, a dark blue layer soon made its appearance, its upper surface remaining coincident with the original boundary while its depth increased downwards. These results are easily explained by the motion of the mercuric chloride complexes towards the anode and of the cobalt cations towards the cathode. Both effects will conspire to favour the production of complex cobalt anions at the cathodic boundary.

An experiment was tried in which the U-tube, filled as in experiment (8), was cooled down to -79° (experiment No. 11). In this case, the cobalt chloride solution is red, as previously remarked. According to our view it must contain chiefly cobalt cations. On passing the current for several hours, a small but distinct movement of the boundaries towards the cathode was observed. The experiment is, however, difficult owing to the small conductivity of the solutions.

It may be noted here as another striking fact that the blue solution of cobalt chloride in concentrated hydrochloric acid turns to a highly viscous red liquid (glass) at the temperature of boiling liquid air. We have not attempted, however, to electrolyse this solution.

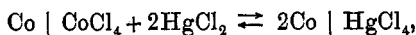
Freezing Point and Boiling Point Experiments.

The results obtained (see p. 943) by the boiling point method with cobalt and mercuric chlorides in ethyl alcohol admit now of a simple explanation. The electrolytic experiments show that the alcoholic solution contains blue complex ions and that these are broken down on the addition of mercuric chloride. The following equations illustrate the mechanism of the reaction :

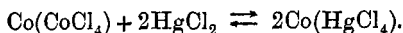


When mercuric chloride is added to the cobalt chloride solution then owing to (a) the boiling point of the solution will be raised to an abnormally small amount. This is partly counteracted by the reaction (b) in which a further dissociation of the CoCl_4 ions occurs owing to removal of the chlorine ions with which they were in equilibrium. The net effect may well be an abnormally small rise of boiling point. The matter may be also looked at from the following point of view. The reaction consists essentially in a formation of HgCl_4 complexes at the expense of the CoCl_4 complexes. If the ionisation were com-

plete, this reaction would not affect the total number of active units in solution, as the following equation shows :



whereas in the other extreme case of complete non-ionisation there would be a very considerable reduction, as shown by the equation



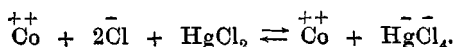
The actual state of affairs corresponds doubtless to a mean between these two extreme cases.

Experiments made by the freezing point method in aqueous solution indicate a similar state of equilibrium, as the following results show :

Substance added.	Lowering of freezing point.	Calculated molecular weight.
Wt. of water = 16.80 grams.		
0.3012 gram CoCl_2 aq.	0.388°	53.2 (for CoCl_2) *
+ 0.1947 „ HgCl_2	0.047	452.7 (for HgCl_2)
	<hr/> 0.385	
Weight of water = 16.38 grams.		
0.1898 gram HgCl_2	0.088°	243.6 (for HgCl_2)
+ 0.2937 „ CoCl_2 aq.	0.293	61.4 (for CoCl_2)
	<hr/> 0.381	

* This value agrees well with the values 50—56 found by Tarugi and Bombardini by Landsberger's boiling point method (*loc. cit.*).

In the calculation of the above results, allowance has been made for the water of crystallisation added with the cobalt chloride. The experiments were so arranged that the concentration of each salt was the same in both cases. It follows from the above that the additional lowering of freezing point produced by the second salt is much lower (and hence its calculated molecular weight much higher) than when it is added to pure water. There is therefore a disappearance of active units in the mixed solution of the two salts. The interpretation is facilitated in this case by the fact that the cobalt chloride is almost completely ionised in these dilute solutions, whilst the ionisation of the mercuric chloride is very slight. The reaction which occurs is represented most probably by the equation



The percentage disappearance of active units can be readily calculated. Thus, on the addition of mercuric chloride to the solution containing cobalt chloride, the lowering of freezing point would have been 0.088 if no interaction had occurred. The deficit = $0.088 - 0.047 = 0.041$ represents the number of units which have disappeared. The percentage disappearance is therefore $= \frac{0.041 \times 100}{0.088 + 0.338} = 9.6$. Calculating in the same way from the results given for cobalt chloride, the percentage diminution of active units is found to be 10.6. The agreement is quite as good as could be expected.

Experiments were also made by the boiling point method in alcoholic solution in order to compare the effects produced by mercuric and calcium chlorides. In two experiments, the molecular weight of anhydrous calcium chloride in alcohol was found to be 107.8 and 108.5, so that the value found is practically normal ($\text{CaCl}_2 = 111$).

Wt. of alcohol = 7.69 grams.

Substance added.	Rise of boiling point.	Calculated molecular weight.
0.0655 gram CoCl_2	0.070°	139.9 (for CoCl_2)
+ 0.1168 „ CaCl_2	0.145	120.5 (for CaCl_2)

These results also indicate a disappearance of individuals in the mixed solution of the chlorides. Thus, the rise of boiling point on the addition of 0.1168 gram CaCl_2 would have been 0.162° if no interaction had occurred (since the effective molecular weight of the calcium chloride is 108). Hence the percentage diminution of active units $= 100 \times \frac{0.162 - 0.145}{0.162 + 0.070} = 7.3$.

As the solution of calcium chloride in alcohol conducts electricity and yet gives a practically normal molecular weight for the dissolved salt, it must contain complex ions. The reactions which will occur when this solution is mixed with a solution of cobalt chloride will therefore probably be very complicated. A discussion of the above effect must therefore be deferred until more is known about these equilibria.

Other Evidence for the Existence of Complex Anions containing Cobalt.

(a) *Solubility*.—Sabatier (*Compt. rend.*, 1888, 107, 42) found that the solubility of cobalt chloride in water is at first diminished by the addition of hydrochloric acid, and then subsequently increased in the case of more concentrated solutions of the acid. Matters are some-

what complicated by the fact that as the strength of the acid increases the degree of hydration of the solid salt in equilibrium with the solution will diminish, but the existence of a minimum point with increasing solubility in stronger acid points to the formation of complex ions in the solution.

(b) *Conductivity*.—According to Trötsch's results (*Ann. Phys. Chem.*, 1890, [iii], 41, 259), the temperature coefficient of the electrical conductivity of strong solutions of cobalt chloride at first increases with the temperature and then diminishes, or, in other words, the curve connecting conductivity and temperature shows a point of inflexion at a temperature between 40° and 50° . We have verified the existence of this point of inflexion by a determination of the conductivities of a 32 per cent. solution of cobalt chloride at various temperatures between 9° and 83° .

Similar points of inflexion are shown according to Trötsch and Holland (*Ann. Phys. Chem.*, 1893, [iii], 50, 261) by solutions of cupric chloride and various sulphates, whereas solutions of salts containing two univalent ions, such as the chlorides, nitrates, chlorates, &c., of the alkali metals possess continually increasing temperature-coefficients. The point of inflexion and the subsequent falling-off of the temperature coefficient of conductivity are quite in agreement with the formation of complex negative ions, for this process would tend to diminish the conductivity both by decreasing the total number of ions in the solution and by producing ions of smaller mobility.

(c) *Transport-number*.—According to Bein's results (*Zeit. physikal. Chem.*, 1898, 27, 1) the transport-number of cobalt in solutions of cobalt chloride varies very considerably with the concentration, being 0.404 in a solution containing 0.2 per cent. of chlorine at 18° , and 0.264 in a solution containing 9.8 per cent. of chlorine at 27° . This considerable decrease in the migration-constant of cobalt in the stronger solutions indicates the formation of complex anions containing cobalt, which therefore transport cobalt towards the anode.

The case of solutions of cadmium iodide is a familiar instance of the same phenomenon in an extreme form.

(d) *Heat of Dilution*.—On diluting a concentrated solution of cobalt chloride, an evolution of heat occurs. This effect is probably due to several causes, but it is worthy of note that the dissociation of the complex ions which occurs on dilution must be accompanied by an evolution of heat, since the formation of these ions is favoured by rise of temperature, and is therefore an endothermic process. The very considerable evolution of heat which occurs on dilution of a concentrated zinc chloride solution is probably due in part to a similar cause, for, as shown above, zinc possesses a greater tendency than cobalt to enter into negative complex ions.

Colour of the Cobalt Salts.

From the foregoing results, it appears highly probable that the blue colour is largely due to complexes such as CoCl_4^- or CoCl_3^- . Taking this into consideration, together with the blue colour of the anhydrous salt, it seems reasonable to suppose that when the cobalt atom exists in close association with chlorine atoms, the system gives rise to a blue colour. The colour due to the undissociated molecule, CoCl_2 , in solution is therefore most probably also blue. On the other hand, the colour due to the cobalt atom when outside the immediate sphere of the chlorine atoms appears to be red. Thus the colour produced by the free cobalt cations in aqueous solution is red, whilst the red colour of the solid hexahydrate is doubtless due to the fact that the water molecules intervene between the cobalt and chlorine atoms. This view is in complete accordance with the theories as to the constitution of inorganic salts and salt hydrates propounded in recent years by Werner.

The colours exhibited by the double chlorides admit of a simple explanation from this point of view. Thus, owing to the greater tendency of zinc to enter into negative complex groups, the zinc double chloride will have the constitution $\text{Co}-(\text{ZnCl}_4)$, whilst the calcium double chloride will have the constitution $\text{Ca}-(\text{CoCl}_4)$, since cobalt has a greater tendency to form negative complexes than calcium. In agreement with this, the former double salt is red, whilst the latter is blue. The blue colour of the lithium double salt, $\text{CoCl}_2 \cdot \text{LiCl} \cdot 3\text{H}_2\text{O}$, may be similarly explained.

If these views be correct, it is possible that the solid anhydrous salt does not possess the simple formula CoCl_2 but may correspond to some polymeric complex form such as $\text{Co}-(\text{CoCl}_4)$, its colour being determined by the strong absorption in the red produced by the complex grouping, CoCl_4^- . It is, at all events, a curious fact that the pale blue, anhydrous chloride becomes reddish-violet at the temperature of boiling liquid air. As in the case of the solutions in alcohol and in concentrated hydrochloric acid, this change of colour may be due to the breaking up of the complex grouping on lowering of temperature, for from what has been said above this change is an exothermic one.

Other Metallic Chlorides the Solutions of which contain Complex Anions.

The well-known colour changes exhibited by solutions of cupric chloride make it very probable that these are similar in origin to those investigated in the case of cobalt chloride. Moreover, the curve connecting conductivity and temperature possesses a point of inflexion

in this case also, as shown by Holland's results. In fact, the analogy with cobalt chloride is complete if it is assumed that the colour due to the negative complex is yellow to brownish-yellow (depending on the concentration and thickness of liquid viewed), the colour due to the copper cation being of course blue. Ferric chloride solutions show similar phenomena. It is necessary, however, to add a few drops of hydrochloric acid to the ordinary brownish-red solution of ferric chloride in order to remove the colour due to the colloidal hydroxide or basic chloride. On the assumption that the colour due to the complex anion is deep yellow to yellowish-brown, whilst the colour due to the ferric ion is a very pale yellow, all the observed phenomena can be explained just as in the former cases. The following summary of results shows the analogies presented by ferric and cupric chlorides with cobalt chloride :

	Copper chloride.	Ferric chloride.	Cobalt chloride.
Colour of aqueous solution at ordinary room temperature ...	Blue (dilute)	{ Very pale yellow }	Red
Colour of aqueous solution on heating	Green (concentrated)	{ Deep brownish-yellow }	Blue
Colour of solution in concentrated calcium or magnesium chloride solution, concentrated hydrochloric acid, or alcohol	Brownish-yellow (concentrated)	{ Deep brownish-yellow }	Blue
Effect of addition of zinc* or mercury chloride to foregoing solution	Brownish-yellow.	{ Solution becomes pale yellow }	Solution becomes red

* After addition of zinc chloride, it is necessary to add a few drops of dilute hydrochloric acid to remove basic salts which may be precipitated.

On electrolysing the solution of ferric or cupric chloride in concentrated hydrochloric acid under the conditions described previously, the lower brownish-yellow layer moves towards the anode, showing that the colour is due to the existence of large amounts of complex negative ions in these solutions.

It is very probable that the formation of complex anions similar to those described in this paper is a phenomenon of very frequent occurrence in solutions of salts, especially of those containing ions of higher valency than 1. The idea of their existence dates from Hittorf's researches on ionic transport (*Ann. Phys. Chem.*, 1859, [ii], 106, 385), but attention has been drawn to them from time to time. Thus Bredig (*Zeit. physikal. Chem.*, 1894, 13, 262) and Noyes (*Zeit. physikal. Chem.*, 1901, 36, 63) have indicated the possibility of explaining certain

difficulties in this way, and during the course of our investigation papers have been published by Steele (*Phil. Trans.*, 1902, 198, A, 105) and by Biltz (*Zeit. physikal. Chem.*, 1902, 40, 185), in which the existence of such complex anions has been discussed.

In conclusion, we desire to express our best thanks to Professor Ramsay for the interest which he has taken in our work.

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