270. *The Absorption Spectrum of Cobalt Chloride in Presence of Magnesium Chloride in Aqueous Solution.*

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THE absorption spectra of a number of cobaltous compounds, both solid and in solution, have been measured (Hill and Howell, *Phil. Mag.*, 1924, **48**, 833), and, from the known crystal structure of several of these, it was suggested that the colour both of the crystal and of the solution is determined by the number of atoms or groups surrounding the cobalt atom : with four, the colour is blue ; with six, it is red. The crystal structures of a number of compounds then examined have since been determined and have confirmed the hypothesis (see *Ann. Reports*, 1927, **24**, 288).

The change in colour from red to blue of aqueous cobalt chloride solution with increasing concentration of hydrochloric acid has been examined by measuring the change of density and viscosity (Howell, J., 1927, 158), refractive index and surface tension (*idem*, p. 2039), and electrical conductivity (*idem*, p. 2843). The discontinuities in the change of these physical properties showed that a radical change in the solution occurred at a concentration of 5*N*-acid and that this change was almost complete at 9*N*.

The same transition from red to blue has recently been followed by measuring the absorption spectra of a series of solutions containing the same amount of cobalt with increasing concentration of hydrochloric acid (Howell and Jackson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 587). For each of the four bands 6950, 6660, 6260, and 6100 A., the extinction coefficient remains practically zero until the concentration of acid reaches 5·0*N*. No blue constituent, therefore, is formed over this wide range. The extinction coefficient then increases rapidly with increasing concentration of acid and the relation becomes linear at 7·1*N*. For the two principal bands, 6950 and 6660 A., the linear relation ceases abruptly at 9·0*N*, and thereafter the extinction coefficient remains unchanged. The ratio of the number of chlorine ions to water molecules in the solution at these three critical concentrations of acid is 2 : 3 : 4, and the transition from red to blue is therefore represented as follows :

$$[Co(H_2O)_6]^{\cdot\cdot} \longrightarrow \underset{\text{Stage I.}}{[CoCl_2(H_2O)_4]} \longrightarrow \underset{\text{Stage II.}}{[CoCl_3(H_2O)]'} \longrightarrow \underset{\text{Stage III.}}{[CoCl_4]''}$$

For the two subsidiary bands, 6260 and 6100 A., the linear relation between the extinction coefficient and the concentration of acid also ceases at 9·0*N*, but the extinction coefficient continues to increase ; it reaches a constant value for the 6260 A. band and, at still higher concentration of acid, approaches a constant value for the 6100 A. band. This is attributed to depression of ionisation of the complex by increasing concentration of hydrogen ion, only the two auxiliary valencies being thus affected.

From measurements of the absorption spectra with various amounts of cobalt in the same concentration of acid, it was shown that the molecular association of the cobalt atom is determined only by its environment and is independent of its concentration relative to that of the other constituents.

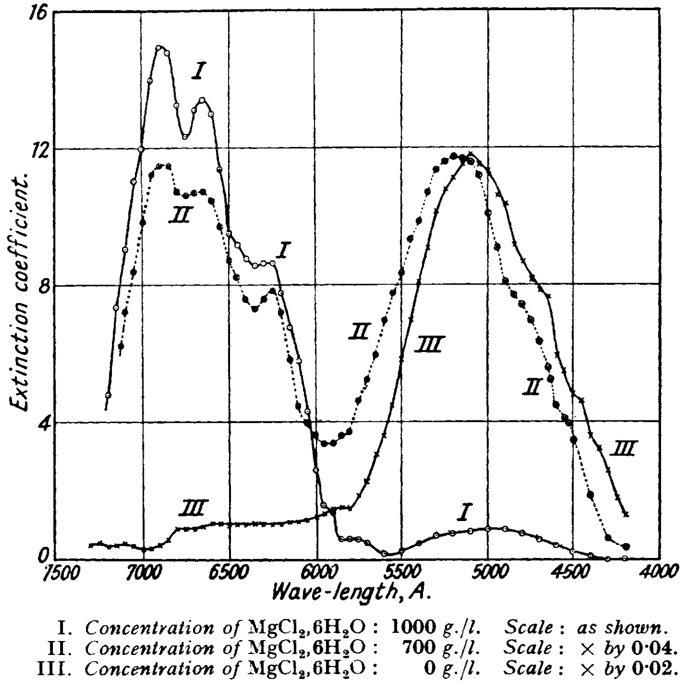
Further, it has been shown (Howell and Jackson, *Proc. Roy. Soc.*, 1936, *A*, **155**, 33) that, for any given concentration of acid, the extent of the transformation is small even over a wide range of temperature. There may appear to the eye a complete change from red to blue, but this is due to the fact that the absorption of the blue form is over 90 times as great as that of the red. By using a series of solutions with different concentrations of acid, the complete change was examined and found to follow the same course as with increasing concentration of acid at constant temperature. The fact that over the final stage the extinction coefficient is a linear function of the temperature again shows that the molecular association is not the result of simple mass action; at constant temperature it is determined by the relative numbers of chlorine ions and water molecules in solution, and the effect of temperature is probably due to the change in their relative kinetic energies.

The change in colour of cobalt solutions on addition of salts has long been known, but most of the observations have been qualitative and the mechanism of the change has not been satisfactorily elucidated. It was therefore deemed of interest to examine the change in colour of cobalt chloride solution on addition of magnesium chloride in the same manner as already described for the addition of hydrochloric acid.

EXPERIMENTAL.

Solutions.—As in the investigation with hydrochloric acid, a concentration of 12 g./l. of $CoCl_2,6H_2O$ was employed. Kahlbaum's pure salt, free from iron and nickel, was used. Two solutions were prepared, one in pure water and one in magnesium chloride solution containing 1000 g. of $MgCl_2,6H_2O$ per l. A series of intermediate solutions, all containing the same concentration of cobalt but varying amounts of magnesium chloride, were prepared by taking x c.c. of one of these and $100 - x$ c.c. of the other, both at 18°, mixing and making up to 100 c.c. with water.

FIG. 1.



I. *Concentration of* $MgCl_2,6H_2O$: 1000 *g./l.* *Scale : as shown.*
II. *Concentration of* $MgCl_2,6H_2O$: 700 *g./l.* *Scale :* × *by* 0·04.
III. *Concentration of* $MgCl_2,6H_2O$: 0 *g./l.* *Scale :* × *by* 0·02.

An exactly similar series of solutions was prepared from water and a solution of 1000 g./l. of $MgCl_2,6H_2O$ only, for use as compensating blanks in the other beam.

Concentrations were checked by titration against standard silver nitrate solution.

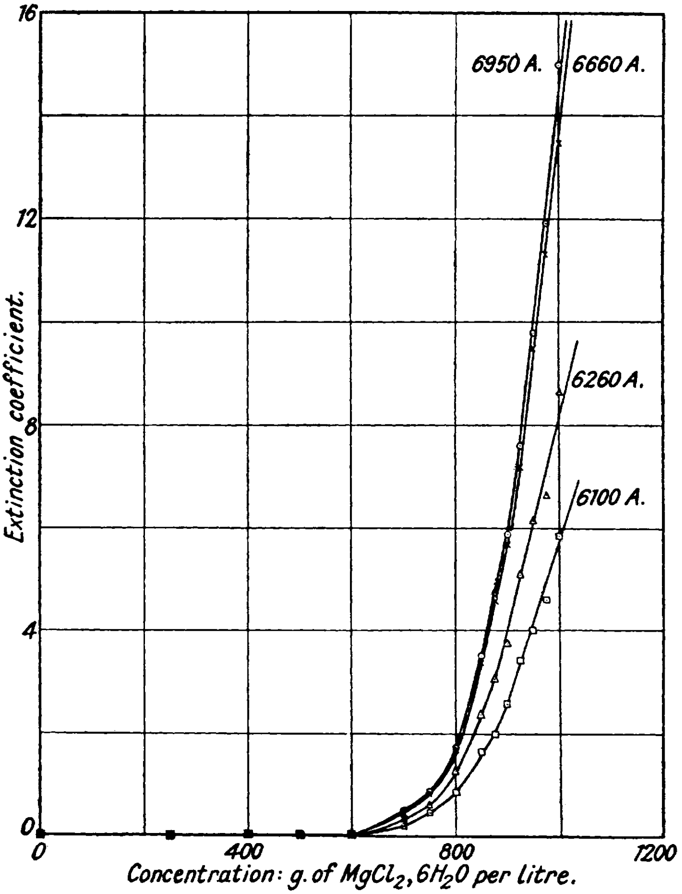
Apparatus.—All measurements were made with the latest model of the Hilger–Nutting spectrophotometer. Readings were taken every 50 A. from 7200 to 4200 A. The accurately ground cells used for the previous investigations were again employed, and were immersed in the special thermostat already described. The working temperature was 20° ± 0·01°.

Results.—The values of the Bunsen extinction coefficient were plotted against the wave-length for each solution. Typical curves for the wholly red, a partly blue, and the bluest solution obtained are shown in Fig. 1.

There are four pronounced band maxima for the blue form. The exact positions depend slightly on the composition of the solution as well as on the interval reading. For the wholly blue solution in concentrated hydrochloric acid, they are at 6950, 6660, 6260, and 6100 A. (compare Brode, *Proc. Roy. Soc.*, 1928, *A*, **118**, 286) and are so designated throughout.

The values of the extinction coefficient at each of these maxima were read from the curves and are given for each concentration of magnesium chloride in Table I. They are plotted against the concentration of magnesium chloride in Fig. 2.

FIG. 2.



Since the intensity of the blue form is so great compared with that of the red, its absorption in the neighbourhood of the maximum of the red form, although only a very small fraction of the absorption at its own maxima, is very great compared with the maximum absorption of the red form. To allow for it would involve an excessively great correction. The change in the absorption of the red form cannot therefore be followed with accuracy, and attention is confined to that of the blue.

TABLE I.

Thickness of layer, cm.	$MgCl_2,6H_2O$, g./l.	Bunsen extinction coefficient.			
		6950 A.	6660 A.	6260 A.	6100 A.
10·0	0	0·01	0·02	0·02	0·02
	250·0	0·01	0·01	0·01	0·01
5·0	400·0	0·02	0·03	0·03	0·03
	500·0	0·06	0·07	0·06	0·06
	600·0	0·07	0·09	0·10	0·10
2·5	700·0	0·46	0·45	0·32	0·18
	750·0	0·85	0·84	0·60	0·44
1·0	800·0	1·72	1·72	1·27	0·85
0·50	850·0	3·52	3·39	2·37	1·63
	875·0	4·74	4·59	3·06	1·96
0·25	900·0	5·90	5·69	3·74	2·58
	925·0	7·60	7·20	5·10	3·42
0·10	950·0	9·8	9·5	6·15	4·00
	975·0	11·9	11·3	6·65	4·60
	1000	15·0	13·5	8·65	5·85

DISCUSSION.

The curves of the extinction coefficient against the concentration of magnesium chloride are exactly similar to those obtained with increasing concentration of hydrochloric acid except that, owing to the limited solubility of magnesium chloride, the transformation cannot be taken to completion.

Until a very considerable concentration of magnesium chloride is reached (575 g. $MgCl_2,6H_2O$/l.), no blue constituent is formed. As in the case of increasing concentration of hydrochloric acid over this initial range, however, it is evident, from the appearance of the solution and the greater ease with which it changes colour on warming, that some change in the association of the cobalt atom has occurred. Since this is not accompanied by change of colour, the cobalt atom retains its six-grouping and the change consists in the replacement of two of the six water molecules by two chlorine atoms as in stage I.

With further increasing concentration of magnesium chloride, the curves begin to rise sharply and soon become linear. The linear portion on projection strikes the axis of concentration at 835 g. $MgCl_2,6H_2O$/l. Over this range, therefore, the six-grouping is replaced by a four-grouping, and it will be seen that, as with increasing concentration of hydrochloric acid, the change consists in the introduction of a third atom of chlorine (stage II).

As already stated, the end of the third range is not reached because a sufficient concentration of chloride ions could not be attained. Thus for the 6950 A. band the extinction coefficient with 1000 g. $MgCl_2,6H_2O$/l. is only about 15, whereas the value for the completed change with hydrochloric acid is 22·0. Even with this great concentration of magnesium chloride, therefore, the change to the blue form is only about 68% complete. It is hoped later to examine the change at higher temperatures; it will doubtless then be possible to reach the constant limiting value for the extinction coefficient as with increasing concentration of hydrochloric acid.

The ratios of the number of chlorine atoms to water molecules are worked out in Table II for the two critical solutions; these ratios, *viz.*, 0·110 and 0·166, are very similar to those for the corresponding critical concentrations with hydrochloric acid, *viz.*, 0·100 and 0·149.

TABLE II.

Conc. of $MgCl_2,6H_2O$, g./l.	575·0.	835·0.
Normality of Cl :		
(a) From $MgCl_2$	5·66	8·22
(b) From $CoCl_2$	0·01	0·01
Total, g.-atoms/l.	5·67	8·23
Concn. of H_2O :		
Wt. of 100 c.c. of solution, g.	120·5	128·8
,, $MgCl_2$ present, g.	26·9	39·07
,, $CoCl_2$ present, g.	0·65	0·65
,, H_2O present, g.	92·9	89·1
Concn. of H_2O, g.-mols./l.	51·6	49·5
$[Cl]/[H_2O]$	0·110	0·166
Ratios	1	1·5
Ratios of Cl atoms in the complexes	1	1·5

The relative concentration of chlorine atoms, *viz.*, 2 : 3, is the same in both instances, and it is also the ratio of the number of chlorine atoms in the postulated complexes. It is clear therefore that the change of colour caused by the addition of magnesium chloride follows precisely the same course and is due to the same cause as that resulting from addition of hydrochloric acid.

The presence of a complex anion, either $[CoCl_3]'$ or $[CoCl_4]''$, in aqueous solutions of cobalt chloride with hydrochloric acid was demonstrated by Donnan and Bassett (J., 1902, **81**, 939). The course of the colour change as elucidated by the spectroscopic and other physical measurements of Howell (see above) shows that in the blue solutions the cobalt is surrounded by four groups. Other spectroscopic measurements (Job, *Compt. rend.*, 1933, **196**, 181), the diffusion constant of cobalt chloride in hydrochloric acid solution (Rona, *Z. physikal. Chem.*, 1920, **95**, 62), and the density and viscosity of acid cobalt chloride solutions (Yajnik and Uberoy, *J. Amer. Chem. Soc.*, 1924, **46**, 802) confirm this view.

The final state of the cobalt atom on addition of magnesium chloride to cobalt chloride solution is doubtless also $[CoCl_4]''$, but the explanation of the colour change suggested by previous workers is either incomplete or incorrect. Benrath (*Z. anorg. Chem.*, 1907, **54**, 328), from observations of the elevation of the boiling point, concluded that it is due to dehydration. Hantzsch and Schlegel (*ibid.*, 1927, **159**, 273) failed to observe the complexity of the change, and account for the transformation on addition either of magnesium chloride or of hydrochloric acid by the conversion of the hexahydrate into dihydrate through the water-extracting action of the added substance. Denham and Pennycuick (*J. Amer. Chem. Soc.*, 1923, **45**, 1353) explain the results of their potential measurements on solutions of cobalt chloride in presence of various metallic chlorides in terms of the depression of the concentration of cobalt ions. Bassett and Croucher (J., 1930, 1784), from a phase-rule study of the system cobalt chloride–magnesium chloride–water, showed the existence of the compound $CoCl_2,MgCl_2,8H_2O$. After discussing various possible constitutions for this compound, they select $[Mg\{(H_2O)_2\}_4]^{\cdot\cdot}[CoCl_4]''$ in conformity with the views of Sidgwick ("The Electronic Theory of Valency," 1927, 198) on the hydration of magnesium. Since the compound is blue and the cobalt atom is in association with four chlorine atoms, this structure is in accord with our theory, as also is that of the blue salts of organic bases $R_2[CoCl_4]$ (R = pyridinium, quinolinium, or quinaldinium) prepared by Percival and Wardlaw (J., 1929, 1505) and quoted by Bassett in support of the suggested constitution.

It is evident, however, from the present investigation that the blue colour of the solution cannot be attributed to the presence of this compound. The curves show no discontinuity at the composition corresponding to the compound; indeed, no blue compound is formed until the concentration of magnesium is about 56 times as great. That molecular association in solution may be different from that in the solid separating from it has been shown by a study of the systems of phenol with water, *m*-cresol, aniline, or *p*-toluidine (Howell, *Proc. Roy. Soc.*, 1932, *A*, **137**, 418; *Trans. Faraday Soc.*, 1932, **28**, 912; Howell and Handford, *ibid.*, 1933, **29**, 640; Howell and Willis Jackson, *Proc. Roy. Soc.*, 1934, *A*, **145**, 539).

Bassett's claim that it is "extremely difficult to interpret any physical measurements, whether spectroscopic or otherwise, made on the actual solutions" but that "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" is therefore hardly justified. In opposition to our general theory, Bassett gives suggested constitutions for blue ions with six co-ordinated groups and for red ions with four co-ordinated groups, but there is a complete absence of any evidence for their existence.

SUMMARY.

1. The absorption spectra of a series of solutions containing a fixed amount of cobalt chloride (12 g. $CoCl_2,6H_2O$/l.) with increasing concentration of magnesium chloride have been measured at 20° and plotted.

2. The extinction coefficients at the maxima of the four chief bands, 6950, 6660, 6260, and 6100 A., have been plotted against the concentration of magnesium chloride.

3. These curves show that no blue constituent is formed until a critical concentration of magnesium chloride (575 g. $MgCl_2,6H_2O$/l.) is reached.

4. The amount of the blue constituent then increases rapidly with increasing concentration of magnesium chloride, and the relation becomes linear at a concentration of **835** g. $MgCl_2,6H_2O$/l.

5. The ratio of the relative number of chlorine atoms to water molecules in solution at these critical concentrations of magnesium chloride is 2 : 3.

6. The mechanism of the change is therefore precisely similar to that caused by addition of hydrochloric acid to cobalt chloride solution :

$$[Co(H_2O)_6]^{\cdot\cdot} \longrightarrow [Co(H_2O)_4Cl_2] \longrightarrow [Co(H_2O)Cl_3]'.$$

7. The completion of the last stage, yielding $[CoCl_4]''$, is not reached because the ratio of chlorine atoms to water molecules is insufficient even in the most concentrated magnesium chloride solution.

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