XXVII.—*Molecular Structure in Solution. Part I. The Densities and Viscosities of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid.*

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THE red and blue colours of the cobaltous compounds and the change from one to the other have been the subject of many investigations. The latest work is that of Hill and Howell (*Phil. Mag.*, 1924, **48**, 833), where a fairly full account of previous work will be found.

These authors examined the absorption spectra in the visible region of a number of cobaltous solutions and solid pigments. They showed that the spectra of the red solutions were precisely similar to those of the red pigments, and the spectra of the blue solutions to those of the blue pigments. In the *red* pigments, the cobalt atom replaced the atom of another metal known from *X*-ray examination of the crystal structure to be surrounded by *six* other atoms, whilst in the *blue* pigments it replaced an atom similarly known to be surrounded by *four* other atoms. The conclusion was therefore drawn that in the red solutions the cobalt atom is surrounded by six other atoms or groups, whilst in the blue solutions it is surrounded by four. The suggestion was made that a definite association of groups or a molecular structure exists in solution, just as in solids. Thus in the dilute aqueous solution of any cobaltous salt, which is red, the cobalt atom is in association with six water molecules, whilst in the blue solution of cobalt oxide in potash it is in association with four groups, possibly hydroxylic.

Support for this view is found in the work of French and Lowry (*Proc. Roy. Soc.*, 1924, *A*, **106**, 489). These authors examined the absorption spectra of a number of cupric salts in different solvents, and showed that they all consisted essentially of one band in the infra-red or red, which was due to the cupric atom, and another in the ultra-violet, which depended on the other part of the molecule. Since the cupric atom gives only one band (which, however, varies in position with the nature of the compound), the authors concluded that the cupric atom is similarly associated in all the solutions. Since many of the salts examined were the cupric salts of organic acids, which are known to be co-ordinated compounds, the conclusion was drawn that in solution the cupric atom is always associated with four other atoms or groups. Although many of the co-ordinated compounds are stable in aqueous solution, others are decomposed. The spectrum, however, is of the same type, and it is therefore concluded that in these solutions, and in dilute aqueous solutions of simple cupric salts, the cupric atom is surrounded by four molecules of water.

In the present paper, an account is given of work which throws further light on the existence of a molecular structure in solution. It deals with the change in colour from red to blue on adding hydrochloric acid to an aqueous solution of cobalt chloride. The densities and viscosities of a series of solutions, having the same concentration of cobalt chloride but increasing concentrations of hydrochloric acid, have been measured. The same properties for an exactly similar series of solutions without cobalt have also been evaluated,

and from the differences in the values for corresponding solutions it is possible to follow the change which takes place in the state of the cobaltous atom. It is suggested that in the aqueous solution, the cobalt is present as hydrated ions, $Co(H_2O)_6^{..}$, where the cobalt atom is surrounded by six groups, and that as the concentration of hydrochloric acid is increased, these are progressively converted into ions where the cobalt is surrounded by four groups, probably the complex ions, $CoCl_4''$. The existence of complex cobaltous ions in solution is discussed by Hantzsch and Shibata (*Z. anorg. Chem.*, 1912, **73**, 309) and by Kotschubei (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1055).

EXPERIMENTAL.

Determination of Density.—The determination of the density of a liquid is more rapidly and conveniently made with an ordinary specific-gravity bottle than with a pyknometer. Carefully used, this bottle gives reproducible and accurate results. One source of error lies in replacing the stopper in different positions. This was avoided by making a small file mark on the neck of the bottle and on the stopper, and replacing the stopper for each determination so that the marks were in line. Another and more serious error is due to evaporation, which occurs, not only through the hole in the stopper, but more especially through the ground joint. Even when the hole in the stopper is effectively closed, there is a continuous loss in weight so long as the liquid in the bottle is in contact with any portion of the ground surfaces. It would appear that the liquid rises in the fine channels between the roughened faces, and thus reaches the outside round the stopper, where it evaporates. All evaporation is completely prevented by placing over the stopper and the neck of the bottle a small cap, made from glass tubing, which rests on the shoulders of the bottle. Protected in this way, a bottle full of aqueous solution remains unchanged in weight for many hours.

All determinations of density were made with a density bottle of about 25 c.c. capacity, the precautions described above being taken. The relative density was calculated from the formula

$$d_{20°}^{20°} = W'/W - 0·0012(W' - W)/W,$$

where W = weight of water filling the bottle, W' = weight of solution filling the bottle, and $0·0012$ = mean density of air. The maximum error in the determinations is less than one unit in the fourth place of decimals.

Determination of Viscosity.—The viscosity measurements were made in a viscometer of the Ostwald type. In order to provide against evaporation and loss of gas from the strongly acidic solutions

(especially at the higher temperatures at which further measurements will be made), a simplified modification of the apparatus used by Findlay (*Z. physikal. Chem.*, 1912, **79**, 97) was specially made. The viscometer is shown in Fig. 1. It consists of two parts, one being precisely similar to the Ostwald viscometer. The volume of the upper bulb is about 10 c.c. and the diameter of the capillary about 0·4 mm. The narrow limb is continued to form a U-tube with a small bulb of about 2 c.c. capacity. The other part consists of a tube which just fits over the broad limb of the viscometer and is also provided with an exactly similar U-tube. The two parts are held together by a rubber band. This arrangement is simpler and more satisfactory than one having a ground joint as no lubricating material is employed and no contamination of the solution is possible.

FIG. 1.

The apparatus is easily taken apart for emptying and cleaning. It was initially· thoroughly cleansed with chromic acid, and thereafter rinsed with distilled water after each experiment. It was dried by drawing through it a stream of air, filtered through cotton-wool and dried by concentrated sulphuric acid and calcium chloride. With this treatment alone, it was found that after several determinations concordant results ceased to be obtained and this was traced to the presence of grease. The apparatus was therefore also washed with a little pure alcohol or acetone, filtered while boiling.

A determination of viscosity was made as follows : The small bulbs on the U-tubes were about half-filled with the solution. A fixed amount (16 c.c.) of solution was pipetted into the viscometer. The two portions were assembled, and the apparatus was slipped into two clips fastened to a bar clamped upright in the thermostat. It was thus ensured that the apparatus was perfectly vertical for each experiment. The apparatus was immersed so that only the open ends of the U-pieces were above water. The solution in the small bulbs being under the same conditions as that in the apparatus, and all interchange of air having to take place through the bulbs, the solution under examination suffers no change in composition. It was found that perfectly concordant values were obtained for a large number of consecutive measurements or at long intervals.

The time of flow was measured by means of a stop-watch reading

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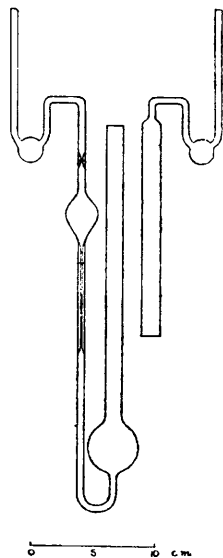
to $\frac{1}{5}$ of a second. The time for water was 376·6 seconds, and this was checked at intervals throughout the measurements and found to be exactly reproducible. All the solutions examined had a time of flow greater than this, so that the maximum error in the determinations of viscosity is less than about 0·05%. In calculating the viscosity coefficient, the value $\eta_{20°} = 0·01005$ for water was used.

Materials. The water used for determining the water constant of the viscometer and for making up the solutions was laboratory-distilled water, filtered, and twice re-distilled with precautions to preclude contamination by dust or grease. The hydrochloric acid was the pure commercial product, and the cobalt chloride was Kahlbaum's purest, free from iron and nickel.

Solutions. Two stock solutions were prepared, one containing 120 g. per litre of $CoCl_2,6H_2O$ in water, and the other containing the same amount per litre in concentrated hydrochloric acid. The acidity of this solution was found to be 10·63N by diluting and titrating against standard sodium hydroxide. From these two solutions a series of solutions was made, each having the same concentration of cobalt chloride, but varying concentrations of hydrochloric acid. This was done by taking x c.c. of the aqueous solution and $(50 - x)$ c.c. of the acid solution, and making up to 50 c.c. with water.

An exactly similar series of solutions containing the same amounts of acid as the foregoing, but no cobalt, was made in precisely the same way from water and a stock solution of hydrochloric acid of the same strength as above (10·63N).

Carefully graduated vessels were used in all cases and the error in composition does not exceed 0·1%. The volumetric handling of the solutions, necessitating the largest error in this work, consequently imposes the limit on the accuracy of the measurements of their densities and viscosities.

All measurements were made in a thermostat, with glass front and back, regulated to $20° \pm 0·01°$.

Results.

Densities.—The relative densities of the two series of solutions, determined as described, are given in Table I. Many previous determinations of the density of hydrochloric acid solutions have been made over a wide range of concentration (see, *e.g.*, Pickering, *Ber.*, 1893, **26**, 277; Lunge and Marchlewski, *Z. angew. Chem.*, 1891, **4**, 133; Lunge, "Technical Chemists' Handbook"). As most of these investigators have expressed their results as absolute densities (d_4^{16}), the values now found are also given in the same

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TABLE I.

Densities.

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1.	2.	3.	4.	5.	6.
Normality of acid, N.	Relative density of $CoCl_2 + HCl$, $d_{20°}^{20°}$.	Relative density of HCl alone, $d_{20°}^{20°}$.	Relative density (calc.).	Absolute density, $d_{4°}^{20°}$.	Density difference (2—3).
0	1·0582	1·0000	*1·0000*	*0·9982*	0·0582
1·063	1·0755	1·0186	*1·0182*	*1·0168*	0·0569
2·126	1·0926	1·0364	*1·0361*	*1·0346*	0·0562
3·189	1·1092	1·0536	*1·0536*	*1·0518*	0·0556
4·252	1·1261	1·0707	*1·0707*	*1·0689*	0·0554
5·315	1·1420	1·0871	*1·0874*	*1·0852*	0·0549
6·38	1·1575	1·1036	*1·1038*	*1·1016*	0·0539
6·59	1·1602	1·1067	*1·1070*	*1·1048*	0·0535
6·91	1·1639	1·1112	*1·1119*	*1·1093*	0·0527
7·23	1·1678	1·1162	*1·1167*	*1·1142*	0·0516
7·44	1·1704	1·1195	*1·1198*	*1·1176*	0·0509
8·50	1·1830	1·1355	*1·1355*	*1·1337*	0·0475
9·57	1·1957	1·1507	*1·1507*	*1·1488*	0·0450
10·63	1·2100	1·1657	*1·1656*	*1·1637*	0·0443

form in col. 5 of Table I for the sake of comparison.   They agree closely with those already reported in the literature.

The values of the relative densities are plotted against the concentration of acid for the two series of solutions in Fig. 2A.   It is seen that the curve for the solutions of acid only is a smooth one. As for most aqueous solutions, the relative density is expressed approximately by an equation of the form

$$d_{\text{solution}} := d_{\text{water}} + xN + yN^2,$$

where x and y are constants, and N is the normality of the solution. Putting $x = 0·017321$ and $y = -0·00016316$, the values calculated from the expression are given in col. 4 of Table I.   Comparing them with the observed values in col. 3, it is seen that the agreement is very fair throughout the range.   Better agreement is not obtained by inserting a cubic term in the expression.

The curve for the solutions containing cobalt, on the other hand, is not smooth.   It consists of two parts, one (for the lower values) being convex and the other concave to the line joining the extreme values.   The break in the curve is obvious.   It occurs after the maximum colour change, and this circumstance is discussed later.

Many measurements are on record showing breaks in density and viscosity curves, and theoretical conclusions have been drawn from such breaks alone.   In the present instance, however, it is possible, not only to obtain more detailed and trustworthy evidence, but also to follow the course of the change which is the cause of the break.

By subtracting the values for the acid alone from the values for

the solutions of cobalt chloride and hydrochloric acid the influence of the cobalt atom on the molecular structure of the solution is

FIG. 2.

Colour of the cobalt solution.
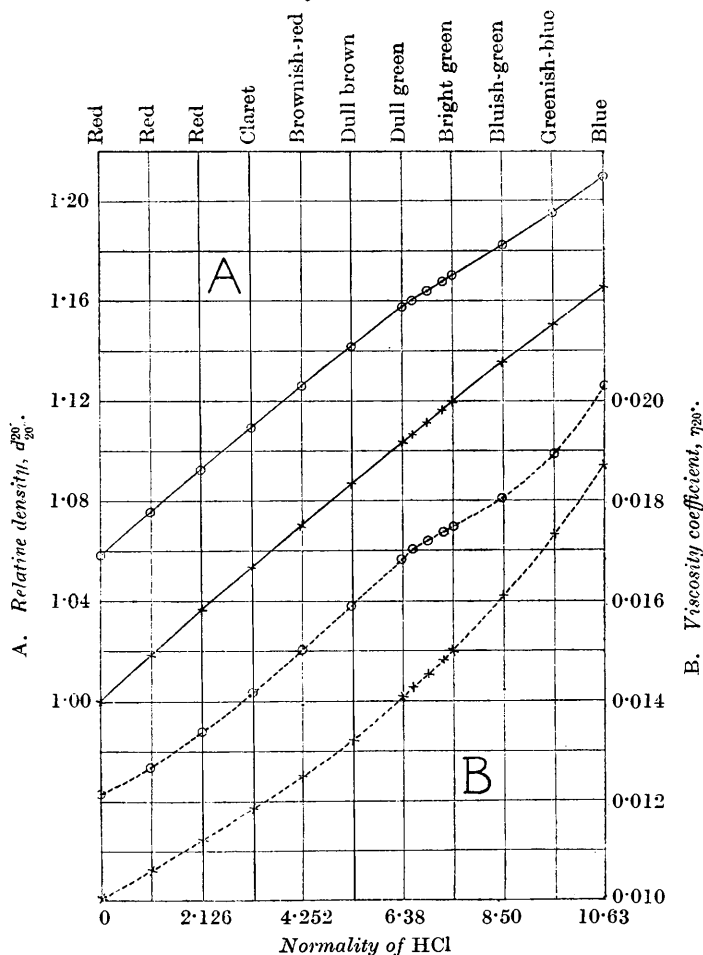
A.   (*Full line curves*).   *Relative density.*
B.   (*Dotted line curves*).   *Viscosity coefficient.*

Solutions of hydrochloric acid + cobalt chloride shown thus, ⊙.
Solutions of hydrochloric acid only shown thus, ×.

brought to light.   If the arrangement of the atoms or groups around the cobalt atom were the same, whatever the concentration of acid present, the two curves should be parallel and the difference between

the values for corresponding solutions in the two series should evidently be constant.

These values are given in col. 6 of Table I, and are hereafter referred to as density differences, for brevity. It is seen that they vary continuously with the concentration of the acid. The differences are plotted against the concentration of acid in Fig. 3, and the curve can be fully interpreted in the light of the theory already given.

FIG. 3.

Colour of the cobalt solution.

Normality of HCl.
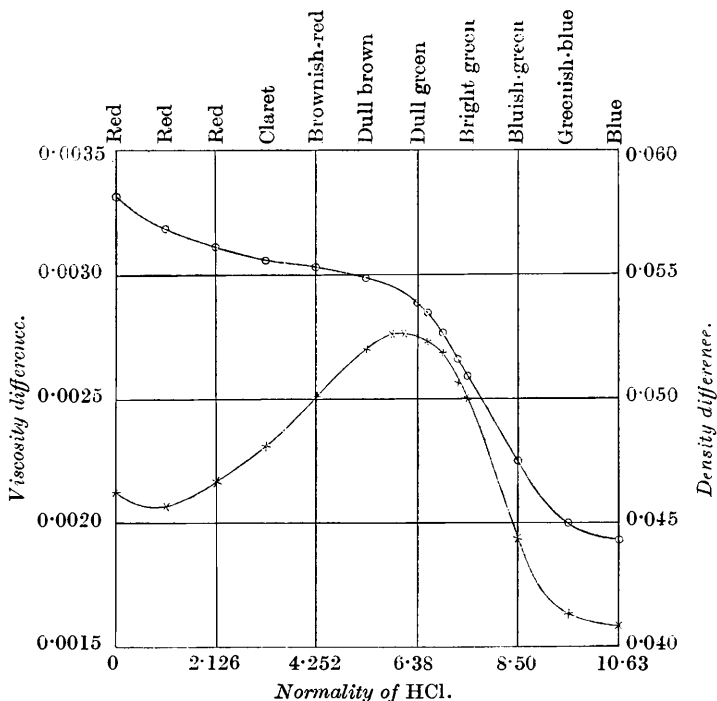
Upper curve : density differences.
Lower curve : viscosity differences.

In the aqueous solution, the cobalt chloride is largely ionised. The cobalt ions are hydrated with six molecules of water, and the solution is therefore red. As the solution is made increasingly acidic, this structure is broken down. The water molecules are crowded out by chlorine ions, and the cobalt atom becomes eventually surrounded by four chlorine atoms, the solution then being blue. Since the final value for the density difference is less than the initial value, the " four "-packing must be less dense than the

" six." There should be a continuous diminution of the difference in density as the change proceeds from the red to the blue form, and this is seen to be so, for the curve falls along its entire course. When the change is complete, further increase in the concentration of acid should have no further effect, *i.e.*, the difference in density between the cobalt solution and one containing the same amount of acid only should become and remain constant.˙ It is seen that this state has practically been reached at the highest concentration of acid employed, for the curve is rapidly flattening out to become parallel to the axis of hydrochloric acid concentration.

It is seen that the diminution of the difference in density, although continuous, does not take place evenly throughout the change from red to blue. The change is at first very gradual, and then (at a point corresponding to the abrupt change in the viscosity-differences curve, which will be discussed later) it takes place very rapidly. This also is explicable and is attributed to two causes.

First, as the change from the six- to the four-packing proceeds, the balance between the undissociated cobalt chloride and its ions is disturbed, and more salt therefore becomes ionised. The newly-liberated cobalt ions are immediately hydrated. The water used up for this purpose was previously free, but is now bound in close union with the cobalt atom, thus making the solution denser and counteracting the diminution due to the formation of the four- from the six-packing.

Secondly, and more important, is the effect of the electrical attraction between the ions. The $Co(H_2O)_6^{..}$ ions present in the aqueous solution carry a double positive charge. The $CoCl_4''$ ions produced by the action of the acid carry a double negative charge. As the concentration of acid is increased, the amount of the negatively charged ion also increases. There will evidently be a great attraction between these oppositely charged ions. This will result in a closer association of the constituents of the solution, tending to make it more dense and thus counteracting the general diminution in density due to the looser packing of the four- than the six-grouping. This effect will continue to become more and more marked until the amounts of both ions present are the same, when the attraction between them will be a maximum. It is seen that, for the first part of its course, the curve does actually become increasingly less steep.

After one-half of the cobalt ions have undergone the change from the sixfold to the fourfold association, continued increase in the strength of the acid produces a far greater diminution in the density difference. The continued production of $CoCl_4''$ ions from the $Co(H_2O)_6^{..}$ ions not only causes, in itself, a diminution of the density

difference, but, whereas it formerly increased the attraction between the two kinds of ions by making their number more nearly equal, and thus tended to counterbalance the decrease in the density difference, it now makes the numbers of the two kinds of ions more and more unequal, thus lessening the attraction between them and causing the density difference to decrease far more rapidly.   It is seen that the curve which begins by falling less and less steeply now falls extremely sharply.

It is therefore suggested that the point at which the curve under-goes inflexion corresponds (very approximately) to a solution having equal amounts of the two kinds of ions, i.e., having equal numbers of cobalt atoms with the six- and four-groupings.

It is to be noted that this point does not correspond with the maximum colour change.   The solution has already changed colour before the curve exhibits inflexion.   This is in accordance with the fact already pointed out by Hill and Howell (loc. cit.) that the absorption spectra of blue cobalt solutions show that both forms (red and blue) may be present together.   Thus the absorption spectrum of cobalt chloride in magnesium chloride solution clearly shows the presence of the red association although the solution appears quite blue.   Indeed, since the blue form is far more intense than the red, the solution may have considerably more of the red form than of the blue, and still be perfectly blue to the eye.   In the present instance, it is seen clearly that the colour change has already taken place before even half of the cobalt has changed from the six- to the four-association.

Viscosities.—The viscosity coefficients of the two series of solutions, determined as already described, are in Table II.   Previous deter-minations of the viscosity of solutions of hydrochloric acid alone have been made by Reyher (*Z. physikal. Chem.*, 1888, **2**, 744), and of aqueous solutions of cobalt chloride alone by Wagner (*ibid.*, 1890, **5**, 31) and by Green (J., 1908, **93**, 2023).

The results given in Table II are plotted in Fig. 2B.   It is seen that the values for hydrochloric acid lie on a perfectly smooth curve, which, however, cannot be even approximately represented by an expression of the type found to hold good for the density curve, or by one having a cubic term.

The curve for cobalt chloride and hydrochloric acid evidently consists of two distinct parts, both of which are concave to the line joining the extreme values.   The break occurs at precisely the same concentration as that in the corresponding density curve, and is far more pronounced.   If the cobalt atom were similarly associated in all these solutions, the two curves should be parallel, i.e., the viscosity differences should be constant.

TABLE II.

Viscosities.

1. Normality of acid, N.	2. Viscosity coeff. of $CoCl_2 + HCl$, $\eta_{20°}$.	3. Viscosity coeff. of HCl alone, $\eta_{20°}$.	4. Viscosity difference (2—3).
0	0·01218	0·01005	0·00213
1·063	0·01272	0·01065	0·00207
2·126	0·01342	0·01125	0·00217
3·189	0·01418	0·01187	0·00231
4·252	0·01502	0·01251	0·00251
5·315	0·01593	0·01323	0·00270
* 5·85	0·01640	0·01364	0·00276
* 6·11	0·01662	0·01386	0·00276
6·38	0·01683	0·01408	0·00275
6·59	0·01703	0·01430	0·00273
6·91	0·01721	0·01452	0·00269
7·23	0·01738	0·01482	0·00256
7·44	0·01750	0·01500	0·00250
8·50	0·01805	0·01611	0·00194
9·57	0·01894	0·01731	0·00163
10·63	0·02028	0·01870	0·00158

* The values of the viscosity coefficients for these two concentrations are read from the viscosity curves shown in Fig. 2B.

It is seen, however, from the values of the viscosity differences, given in col. 4 of Table II, that they show a remarkable variation. The values are plotted against the normality of the acid in Fig. 3. The curve first exhibits a very small dip. The first effect of the acid on the solution is to decrease the ionisation of the cobalt chloride owing to the addition of a common ion. This results in a decrease of the number of cobalt ions present. These hydrated ions may reasonably be assumed to be comparatively highly viscous and the reduction in their number therefore leads to an initial decrease in the viscosity difference.

This initial effect of the acid is, however, soon overwhelmed by the increase in ionisation resulting from the transformation of the $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions by the action of the acid. The presence of these two kinds of ions, oppositely charged, causes an increase in the viscosity of the solution. Their electric fields, causing a strong attraction between them, retard their movement past one another, thus causing the solution to become more viscous. Increase in the concentration of the acid causes further transformation of the one type of ion into the other. The viscosity-differences curve therefore rises rapidly, and this in spite of the fact that the corresponding density curve is falling. As already noted when discussing the density changes, the attraction between the ions should be a maximum when there are equal numbers of each. It is seen that the curve rises to a maximum. It is suggested that at the maximum there are equal numbers of the two kinds of ions

present, and it should be noted that the maximum in the viscosity-differences curve corresponds exactly with the point of inflexion in the density-differences curve, which was accounted for by the same reasoning.

Continued increase in the concentration of acid causes continued transformation of the cobalt atom from the six- to the four-packing. This results in the number of ions of each kind becoming increasingly unequal, in the attraction between them becoming thereby diminished, and therefore in the viscosity difference decreasing continuously. It is seen that the curve falls sharply from the maximum.

When the whole of the cobalt has assumed the new configuration, further increase in the concentration of the acid should produce no change in the viscosity difference. It is seen that, as with the density-differences curve, so also the viscosity-differences curve flattens out and indicates that, with the highest concentration of acid employed, the change to the four-configuration is practically complete.

It is also to be noted that whilst the density-differences curve indicates that the density of the four-configuration is less than that of the six-, the viscosity-differences curve shows that its viscosity is also less.

It is proposed to make further similar measurements at different temperatures and with different concentrations of cobalt, and also to determine other physical constants for these solutions.

Summary.

1. The densities and viscosities of a series of aqueous solutions containing a constant amount of cobalt chloride and varying amounts of hydrochloric acid have been determined.

2. The densities and viscosities of an exactly similar series containing hydrochloric acid only have also been measured.

3. From the differences in values for corresponding solutions, the effect of the acid on the cobalt in solution can be followed.

4. The curve showing the differences in density exhibits a point of inflexion, and that showing the differences in viscosity a maximum, both well-defined and at the same concentration of acid.

5. The general form of the curves and these two important characteristics are explained by attributing the action of the acid to the forcing of the cobalt atom out of its association with six molecules of water into an association with four atoms of chlorine.

6. The change of colour from red to blue and the point at which it occurs are accounted for.

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