CCCLXXX.—*Molecular Structure in Solution. Part III. The Electrical Conductivities of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid, with a Note on the Prediction of Crystal Structure.*

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THE densities, viscosities, refractive indices, and surface tensions of a series of solutions containing a constant amount of cobalt chloride with increasing amounts of hydrochloric acid, and the same properties of an exactly similar series of solutions of hydrochloric acid alone have already been determined (this vol., pp. 158, 2039). The differences in the values of each of these properties for corresponding members of the two series throw light upon the change in the state of the cobalt atom in solution with increasing acid concentration. All the results obtained have been fully interpreted by assuming that, in accordance with the theory of the colour of the cobaltous compounds suggested by Hill and Howell (*Phil. Mag.*, 1924, **48**, 833), the cobalt atom is forced out of its association with 6 molecules of water into one with 4 atoms of chlorine.

The electrical conductivities of these solutions have now been examined, and the conclusions drawn from the results are in complete accord with those already indicated.

EXPERIMENTAL.

Determination of Electrical Conductivity.—The electrical conductivities were determined in the usual way by the use of a standard resistance, an alternating current from a small coil, a metre bridge, and a low-resistance telephone. A small U-shaped cell made of resistance glass and having a capacity of about 3 c.c. was employed. It was immersed to below the level of the solution in a thermostat at 20° ± 0·02°. With each solution at least three different known resistances were employed and the point of balance was determined at least four times for each. With each known resistance the mean point of balance was taken and the conductance of the cell calculated. In almost every instance, the values lay within 0·05% of the mean, and in no case did the difference exceed 0·1%.

The cell constant was determined with *N*-potassium chloride solution, prepared from the pure salt (Kahlbaum's), which was first recrystallised and dried. The conductivity of this solution at 20° is 0·10207 mho (Kohlrausch, Holborn, and Diesselhorst, *Wied. Ann.*, 1898, **64**, 417); the actual resistance was found to be 3028 ohms, whence the conductance was 0·0003302 mho and the cell constant 309·1.

Materials.—The solutions used for these determinations were the same as those employed for the measurement of the refractive index and surface tension (*loc. cit.*). A few new solutions were also prepared from the same stock solutions as those previously employed. The water used for preparing these solutions was twice redistilled; its conductivity was negligible compared with that of any of the solutions.

Results.

Conductivities.—The conductivities of the series of solutions of hydrochloric acid alone are given in column 3 of Table I. Previous measurements for concentrated solutions of hydrochloric acid have been made at 18° by Kohlrausch (*Pogg. Ann.*, 1876, **159**, 233) and at 25° by Masson and Green (J., 1908, **93**, 2023). Direct comparison with these is not possible because of the different temperatures employed, but the curve of the values now given lies smoothly between those of the other observers. The values of the conductivity are plotted against the normality of the acid (at 18°) in Fig. 1 (upper curve).

TABLE I.

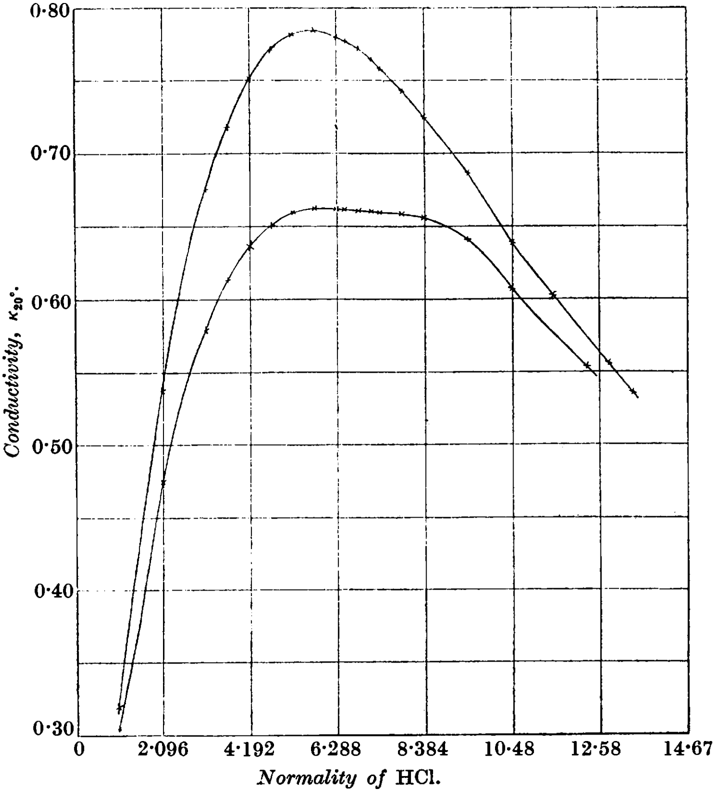
Electrical Conductivities.

1.	2.	3.	4.
	Conductivity of		
Normality of HCl, N_{18°.	$CoCl_2$+ HCl, κ_{20°.	HCl alone, κ_{20°.	Diff., 2—3.
0	0·06358	—	+0·0636
1·048	0·3053	0·3196	−0·0143
2·096	0·4742	0·5375	−0·0633
3·144	0·5797	0·6760	−0·0963
3·668	0·6132	0·7190	−0·1058
4·192	0·6361	0·7508	−0·1147
4·716	0·6503	0·7715	−0·1212
5·240	0·6599	0·7823	−0·1224
5·764	0·6624	0·7854	−0·1230
6·288	0·6624	0·7799	−0·1175
6·498	0·6618	0·7771	−0·1153
6·812	0·6611	0·7728	−0·1117
7·126	0·6605	0·7647	−0·1042
7·336	0·6599	0·7585	−0·0986
7·860	0·6584	0·7434	−0·0850
8·384	0·6556	0·7258	−0·0702
9·432	0·6408	0·6874	−0·0466
10·48	0·6068	0·6389	−0·0321
11·48	—	0·6021	—
12·26	0·5530	0·5749	−0·0219
12·83	—	0·5564	—
13·38	—	0·5357	—

The results obtained with the series of solutions of cobalt chloride and hydrochloric acid are given in column 2 of Table I, and plotted against the normality of the acid in Fig. 1 (lower curve). The two curves are very different in form: that for the acid only rises to a sharp maximum, whereas that for the solutions containing cobalt is greatly flattened at its maximum.

The differences in conductivity between corresponding solutions in the two series are given in col. 4 of Table I and are plotted against the normality of the acid in Fig. 2. It is seen that the conductivity-differences curve is almost the exact complement of the viscosity-differences curve, which is also reproduced for comparison; the minimum of the one occurs at the same concentration of acid as the maximum of the other. There is one point of difference, *viz.*, that whereas the viscosity-differences curve first falls slightly before rising to its maximum, the conductivity-differences curve falls continuously to its minimum. The same reasoning which accounted for the form of the first (this vol., p. 168) also explains that of the second, including this respect in which they differ.

FIG. 1.



Upper curve : Solutions of hydrochloric acid only.
Lower curve : Solutions of hydrochloric acid + *cobalt chloride.*

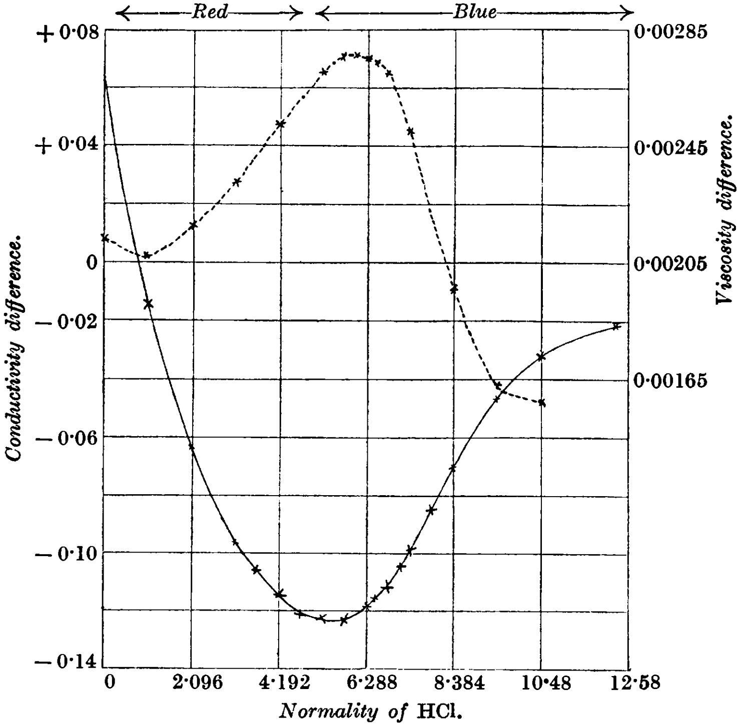
The effect of increasing the concentration of acid is to throw more and more of the cobalt out of its association with 6 molecules of water, $Co(H_2O)_6^{\cdot\cdot}$, into one with 4 atoms of chlorine, $CoCl_4''$. When this transition is complete, continued increase in the concentration of acid would be without further effect, and the difference in physical properties between the solutions containing cobalt and the corresponding solutions of acid alone should become and remain constant. It is seen that the conductivity-differences curve, like the viscosity-differences curve, flattens out at the highest concentrations of acid to become parallel to the axis of concentration, indicating that this transition is practically complete. Moreover, both curves exhibit this characteristic at approximately the same concentration of acid.

It is seen that the conductivity differences at the end of the series (blue solutions) are smaller than those at the beginning (red solutions). The curve does not, however, fall evenly from the initial to the final value, but exhibits a very deep minimum, just as the viscosity-differences curve similarly shows a well-defined maximum. Since the red and the blue ions, $Co(H_2O)_6^{\cdot\cdot}$ and $CoCl_4''$, are oppositely charged, there will undoubtedly be combination between them where they are present together in solution; they will not remain wholly as free ions. The combination of these ions will result in further dissociation of the compounds from which they are derived, thus liberating chlorine ions and hydrogen ions respectively. These, however, will not remain free, the ionisation being depressed by the hydrochloric acid already present in high concentration, so that the conductivity of the solution will diminish. The greater the combination, the less will be the conductivity of the solution; therefore, as transformation of the red $Co(H_2O)_6^{\cdot\cdot}$ into the blue $CoCl_4''$ proceeds, the conductivity-differences curve falls sharply. The combination will evidently be greatest when these two oppositely charged ions are present in equal amounts, so that the conductivity differences should decrease up to this point. Thereafter, continued transformation of the $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions will result in an increasing surplus of free $CoCl_4''$ and the conductivity differences should increase again up to a constant value. This is seen to be so and it is therefore suggested that the minimum of the conductivity-differences curve occurs when half the cobalt is present as $Co(H_2O)_6^{\cdot\cdot}$ and half as $CoCl_4''$.

The viscosity-differences curve exhibits an initial decrease before rising to its maximum, whereas the conductivity-differences curve falls sharply to its minimum. When discussing the viscosity-differences curve (*loc. cit.*), it was pointed out that the first effect of the addition of hydrochloric acid is to depress the ionisation of the cobalt chloride because of the addition of a common ion. There is thus at first a decrease in the number of the viscous $Co(H_2O)_6^{\cdot\cdot}$ ions, resulting in a decrease of viscosity. This effect is soon overwhelmed by the conversion of $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions, so that the curve exhibits only a small dip and then rises rapidly. The two effects are thus opposed when the viscosity of the solutions is concerned; but they operate together when the conductivity is considered. Both the initial depression of ionisation and (as discussed above) the conversion of $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions result in a decrease of conductivity, so that the conductivity-differences curve falls continuously to its minimum.

Fig. 2.

Colour of the cobalt solution in transmitted light.



Full curve: Conductivity differences.
Broken curve: Viscosity differences.

It may readily be shown that the curve of the differences of specific resistance is quite different in form from that of the differences of specific conductance. It is very similar to the density-differences and refractive-index-differences curves found previously (*loc. cit.*), in that it exhibits a point of inflexion at the same concentration of acid and then falls, eventually becoming parallel to the axis of concentration, just as these do, and at about the same concentration of acid. It differs from them in first rising to a maximum, whereas they fall continuously from the beginning; and this difference is explained in exactly the same way as that between the conductivity-differences and viscosity-differences curves.

Note on the Prediction of Crystal Structure.

When the metallic atom of a colourless insoluble compound is replaced, wholly or partly, by cobalt, a pigment is obtained which may be either blue or red, and it has been shown (Hill and Howell, *loc. cit.*), by carrying out this replacement in compounds of known crystal structure, that when the metallic atom is surrounded by *four* other atoms or groups, the resulting pigment is *blue*, and when surrounded by *six*, the pigment obtained is *red*. Thus, when the magnesium atom in spinelle (magnesium aluminate, where it is surrounded by four oxygen atoms) is replaced by cobalt, a blue pigment (cobalt blue) is obtained, but when the magnesium atom in magnesium oxide (where it is surrounded by six oxygen atoms) is similarly replaced, a red pigment (cobalt pink) is produced.

For comparison of their absorption spectra, pigments were prepared, not only from compounds of known crystal structure, but also from a number the structure of which was at that time unknown. From the colour of the pigment obtained, it was possible to predict the structure of the compound from which it was derived. Since that work was published, two of the compounds have been submitted to *X*-ray analysis by different observers, and the structure is in both instances in accord with that predicted from the colour of the corresponding cobalt pigment. The structures of cobalt oxide and cobalt fluoride have also been subsequently determined and are in agreement with the predictions from the theory.

Zinc orthosilicate. If the zinc atom in zinc orthosilicate is replaced by cobalt, a *blue* pigment is obtained. It follows from the theory that in the pigment the cobalt atom is surrounded by *four* other atoms or groups, and therefore that the zinc atom in the original compound is similarly situated. The crystal structure of willemite (zinc orthosilicate) has recently been determined by Zachariasen (*Norsk. Geol. Tidsskr.*, 1926, **9**, 65), who showed it to be isomorphous with phenacite (beryllium orthosilicate), the crystal structure of which was elucidated by W. L. Bragg (*Proc. Roy. Soc.*, 1927, *A*, **113**, 642), who established that the beryllium atom is between four oxygen atoms. It follows that in zinc orthosilicate the zinc atom is similarly placed, as predicted from the theory.

Magnesium orthosilicate. If the magnesium atom in magnesium orthosilicate is replaced by cobalt, a *red* pigment is produced, so that, according to the theory, the magnesium atom in this compound is surrounded by *six* other atoms. This prediction has been verified by the work of W. L. Bragg and Brown (*Z. Krist.*, 1926, **63**, 538) on olivine (magnesium orthosilicate).

Cobalt oxide. It is well known that when cobalt oxide is melted in the electric furnace, it crystallises in rose-coloured needles (Moissan, *Compt. rend.*, 1892, **115**, 1034; *Bull. Soc. chim.*, 1893, **9**, 955; *Ann. Chim. Phys.*, 1895, **4**, 136). Although the crystal structure of the compound was unknown, the theory enabled us to predict that, since the compound was of the *red* form, the cobalt atom should be surrounded by *six* oxygen atoms, and verification was forthcoming in the work of Goldschmidt, Barth, and Lunde (*Skrifter Norske Videnskaps Akad.*, No. 7, 1925), of Natta and Reina (*Atti R. Accad. Lincei*, 1926, **4**, 48), and of Bravo (*Anal. Fís. Quím.*, 1926, **24**, 611), who found that the compound possesses the rock-salt structure, *i.e.*, the cobalt atom is between six oxygen atoms.

Cobalt fluoride. Since anhydrous cobaltous fluoride is *red* (Poulenc, *Compt. rend.*, 1892, **114**, 1426), it could be predicted that the cobalt atom should lie between *six* fluorine atoms. Actually, it has been found (Ferrari, *Atti R. Accad. Lincei*, 1926, **3**, 324) to have the same crystal structure as rutile, in which the titanium atom is surrounded by six oxygen atoms (Vegard, *Phil. Mag.*, 1916, **32**, 65, 505; 1917, **33**, 395; 1926, **1**, 1151; Williams, *Proc. Roy. Soc.*, 1917, **93**, 418; Greenwood, *Phil. Mag.*, 1924, **48**, 654).

Summary.

1. The electrical conductivities of a series of solutions containing a constant amount of cobalt chloride and increasing amounts of hydrochloric acid have been determined.

2. The same properties of an exactly similar series containing hydrochloric acid only have also been determined.

3. The curve of the differences of conductivity of corresponding solutions plotted against the concentration of acid is almost the exact complement of the viscosity-differences curve found in a previous investigation. It exhibits a minimum at the same concentration of acid where the other curve exhibits a maximum. It differs in falling constantly to the minimum, whereas the viscosity-differences curve first falls slightly before rising to its maximum. Both its resemblance to and difference from the viscosity-differences curve are fully explained on the same reasoning as that employed in previous investigations.

4. It is noted that the crystal structure of compounds which yield pigments when the metallic atom is replaced by cobalt can be predicted from the colour of the pigment so obtained. The structures of two compounds (zinc and magnesium orthosilicates) have been determined since the theory of the colour of the cobaltous

compounds was suggested, and they verify the predictions made from the theory. The structures of cobalt oxide and cobalt fluoride are similarly in accordance with prediction from the theory.

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