

CCLXVIII.—*Molecular Structure in Solution. Part II.*
The Refractive Indices and Surface Tensions of
Aqueous Solutions of Cobalt Chloride and Hydro-
chloric Acid.

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THE densities and viscosities of a series of solutions having a fixed concentration of cobalt but increasing concentrations of hydrochloric acid, and also those of an exactly similar series of solutions of the acid alone, have already been determined (this vol., p. 158). It was shown that the differences in the densities of corresponding solutions varied with increasing concentration of acid, the curve exhibiting a point of inflexion. The differences in the viscosities of corresponding solutions also varied, the curve showing a well-defined maximum. The point of inflexion in the one case and the maximum in the other occurred at precisely the same concentration of acid.

The work of Hill and Howell (*Phil. Mag.*, 1924, 48, 833) suggests that in the red pigments and solutions the cobaltous atom is surrounded by six other atoms or groups, whilst in the blue pigments and solutions it is surrounded by four, and the results outlined above were interpreted by assuming that with increasing concentration of acid, the cobalt atom is thrown out of its association with six molecules of water, $\text{Co}(\text{H}_2\text{O})_6^{++}$, into one with four atoms of chlorine, CoCl_4^{--} . It was deemed of interest to determine other physical properties of these solutions in order to ascertain whether they also would show similar variations; the refractive indices and surface tensions have therefore been measured.

EXPERIMENTAL.

Determination of Refractive Index.—The measurements were made with a Pulfrich refractometer. In order that the results should be directly comparable with those already obtained for the densities and viscosities, all determinations were made at 20°.

Since all the solutions were acidic, it was impossible to utilise the usual attachment for temperature regulation. The whole instrument was therefore encased by means of asbestos mill-board cut to shape, and the temperature was kept constant to within $\pm 0.5^\circ$ by regulating a small gas flame placed inside the case. The cell was covered with a watch-glass to prevent loss of acid.

Measurements were made for the D line with a sodium flame, and for the C, F, and G' lines with a hydrogen tube. The refractive index of every solution in the series containing acid only was deter-

mined for each of these lines, but this was impossible with the series containing cobalt since these solutions are coloured. Although the red solutions have strong absorption bands in the blue region, with the concentration of cobalt taken the F and G' lines were transmitted sufficiently well to enable measurements to be made. The refractive index for each of these two lines has therefore been determined for every member of the series of solutions containing cobalt. The blue solutions, however, are much more intense than the red, and with these the C and D lines were completely extinguished. It was therefore possible to determine the refractive index for these two lines only with the solutions at the red end of the series.

Readings could be reproduced to within 1' even with the faintest lines and to within 0.5' with strong ones. The values of the refractive index are therefore all correct to the fourth place of decimals and most of them to within 5 units in the fifth place.

Determination of Surface Tension.—The measurements were made with a Traube stalagmometer. The lower capillary and also a long open tube were passed through a rubber stopper fitted into a small bottle. The stalagmometer was filled with the solution, and a little of this was also placed in the bottle in order to saturate with the vapour the atmosphere in which the drops formed. The apparatus was immersed vertically (against a plumb-line) in a glass-fronted thermostat kept at $20^{\circ} \pm 0.01^{\circ}$. The surface tension was calculated from the formula

$$\gamma_{\text{sol.}} = \gamma_{\text{water}} \times n_w/n_s \times d_s,$$

where n_w and n_s are the number of drops given by water and by the solution respectively, and d_s is the relative density of the solution. The value $\gamma_{20^{\circ}} = 72.69$ for water was employed, and the values of the relative density used were those determined in the previous investigation.

It has been shown (Lohnstein, *Z. physikal. Chem.*, 1908, **64**, 686; 1913, **84**, 410; Harkins and Humphery, *J. Amer. Chem. Soc.*, 1916, **38**, 228; Harkins and Brown, *ibid.*, 1919, **41**, 499) that the simple formula for the surface tension requires a correction factor depending on the ratio of the radius of the tip to the linear dimensions of the drop. If r is the radius of the tip and v the volume of the drop, then when $r/v^{1/3}$ lies between 0.76 and 0.95 the correction is practically constant. In a comparative method of determining surface tension the correction factor would then cancel, leaving the equation given above as a true expression.

The diameter of the tip of the stalagmometer used for these experiments was 0.87 cm. The volumes of the largest drops (given

by water) and of the smallest (given by the most concentrated acid solution) were determined by weighing and found to be 0.1268 c.c. and 0.1021 c.c., respectively. The extreme values of the ratio $r/v^{\frac{1}{2}}$ are therefore 0.865 and 0.930. Since these fall within the limits for the constancy of the correction factor, the simple equation used for the calculation is sufficiently accurate.

With the solution yielding the smallest drops, each drop corresponded to 18 divisions on the scale. Since the determinations could be reproduced to within 0.5—1.0 division, the measurements are correct to within about ± 3 units in the second place of decimals. At least two determinations were made for each solution and the mean was taken.

The tip of the stalagmometer was freed from grease by being dipped in chromic acid solution before each determination and the whole apparatus was similarly cleansed at intervals. The drop number for water was checked from time to time and found to remain quite constant at 55.55 drops.

Materials.—As in the previous investigation, the hydrochloric acid employed was the pure commercial product and the cobalt chloride was Kahlbaum's purest, free from iron and nickel. All the water used was the laboratory distilled water, redistilled with precautions to preclude contamination by dust or grease.

Solutions.—Three stock solutions were prepared: cobalt chloride in water (120 g. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ per litre), cobalt chloride in concentrated hydrochloric acid (120 g. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ per litre), and hydrochloric acid in water. Their concentrations were adjusted to exactly the same values as those employed in the previous investigation. All the other solutions were prepared from these by dilution in the manner already described (*loc. cit.*).

Note on the Density of Aqueous Hydrochloric Acid.—It was not stated in the previous paper that in preparing the stock solution of hydrochloric acid by diluting the fuming acid, the solutions were cooled in iced water to minimise loss of acid. The stock solution was therefore 10.63*N* at $0^\circ = 32.88\%$ of HCl (by weight). In the present investigation, a solution of the acid having exactly the same density was found by titration against pure sodium carbonate to be 10.48*N* at 18° . The solution therefore contained 32.80% of HCl, a figure in good agreement with that previously found. The densities of the series of solutions prepared by diluting the stock solution were checked and found to agree with those obtained previously to within 1 unit in the fourth place of decimals.

In order to complete the series of values up to the fuming acid, the densities and viscosities of three more concentrated solutions have been determined; these are shown in Table I together with

the true normality of the solution at 18° and the composition by volume and by weight. The concentrations are correct to 0.2%, the densities to within 2 units in the fourth place of decimals and the viscosities to within 0.1%.

TABLE I.

Densities and Viscosities of Aqueous Solutions of Hydrochloric Acid.

Concentration of HCl.			Relative density, d_{20}^{20} .	Absolute density, d_4^{20} .	Viscosity, η_{20} .
Normality, N_{18} .	% by vol.	% by weight.			
0	0	0	1.0000	0.9982	0.01005
1.048	3.821	3.757	1.0186	1.0168	0.01065
2.096	7.642	7.385	1.0364	1.0346	0.01125
3.144	11.46	10.89	1.0536	1.0518	0.01187
4.192	15.28	14.29	1.0707	1.0689	0.01251
5.240	19.11	17.59	1.0871	1.0852	0.01323
6.288	22.93	20.80	1.1036	1.1016	0.01408
6.498	23.69	21.43	1.1067	1.1048	0.01430
6.812	24.84	22.37	1.1112	1.1092	0.01452
7.126	25.98	23.30	1.1162	1.1142	0.01482
7.336	26.75	23.91	1.1195	1.1176	0.01500
7.860	28.66	25.43	1.1275	1.1255	0.01555
8.384	30.57	26.94	1.1355	1.1335	0.01611
9.432	34.39	29.90	1.1507	1.1487	0.01731
10.48	38.21	32.80	1.1657	1.1637	0.01870
11.48	41.86	35.53	1.1789	1.1768	0.02004
12.83	46.78	39.14	1.1957	1.1935	0.02183
13.38	48.78	40.61	1.2020	1.1998	0.02266

The curve obtained on plotting the densities against the % of HCl by weight is almost a straight line up to 33%, being only very slightly concave to the axis of concentration. The last three values, however, fall below the extended curve, which is in agreement with the values recorded by other observers (Landolt and Bornstein's Tables, 1923, p. 394).

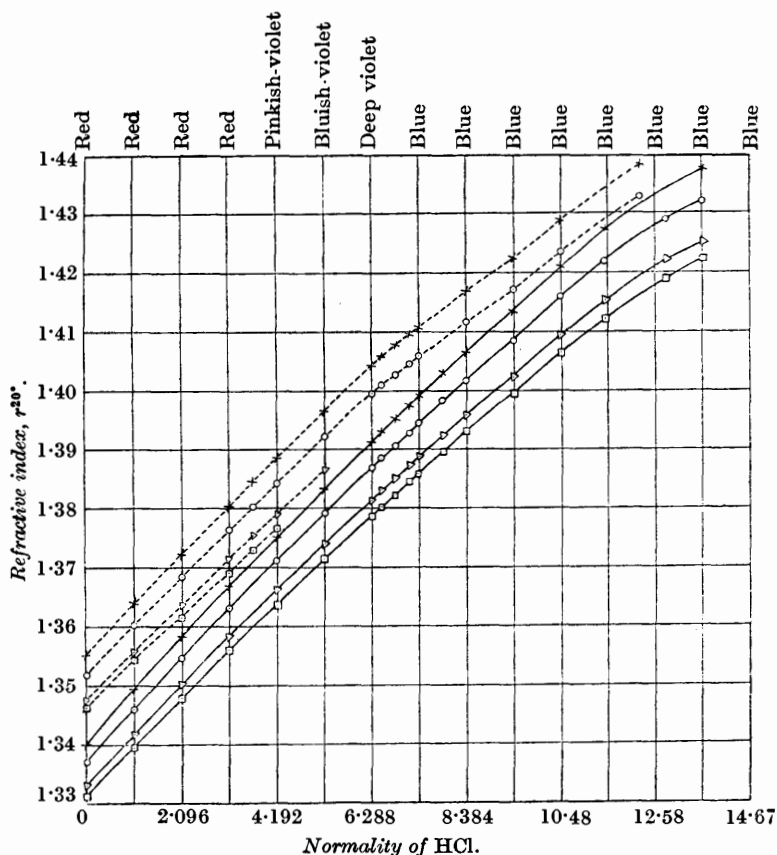
Results.

Refractive Indices.—The values of the refractive indices of the solutions of hydrochloric acid only, measured as already described, are given in Table II, and plotted against the normality of the solution in Fig. 1. It is seen that almost throughout their entire length all four curves exhibit a gradual increase of concavity to the axis of concentration. They fall more rapidly near the end, the values for the two highest concentrations of acid being lower than those anticipated from the general course of the curves. Each of the curves is expressed with very fair accuracy by an equation of the form

$$r_{\text{sol.}} = r_{\text{water}} + xN - yN^2,$$

where N is the normality of the solution and x and y are constants.

FIG. 1.

Colour of the cobalt solution in transmitted light.*Dotted line curves : Solutions of hydrochloric acid + cobalt chloride.**Full-line curves : Solutions of hydrochloric acid only.*

Refractive index for the G' line shown thus : X.

" " " F " " " O.

" " " D " " " Δ.

" " " C " " " □.

The values calculated from the equations

$$r_C^{20} = 1.33117 + 0.008090N_{18} - 0.0000862N_{18}^2$$

$$r_D^{20} = 1.33299 + 0.008330N_{18} - 0.0001000N_{18}^2$$

$$r_F^{20} = 1.33703 + 0.008630N_{18} - 0.0001083N_{18}^2$$

$$r_G^{20} = 1.34017 + 0.008850N_{18} - 0.0001129N_{18}^2$$

are given in italics in the columns next to the observed values in

TABLE II.

Refractive Indices of Aqueous Solutions of Hydrochloric Acid.

Conc. of HCl,		$r_{\text{C}}^{20^\circ}$.		$r_{\text{D}}^{20^\circ}$.		$r_{\text{F}}^{20^\circ}$.		$r_{\text{G}}^{20^\circ}$.	
N_{18}^* .	%.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
0	0	1.33117	1.33117	1.33299	1.33299	1.33703	1.33703	1.34017	1.34017
1.048	3.757	1.33938	1.33956	1.34173	1.34161	1.34599	1.34595	1.34944	1.34933
2.096	7.385	1.34786	1.34775	1.35007	1.35001	1.35464	1.35464	1.35824	1.35823
3.144	10.89	1.35594	1.35575	1.35815	1.35819	1.36305	1.36309	1.36684	1.36687
4.192	14.29	1.36357	1.36357	1.36603	1.36615	1.37111	1.37130	1.37521	1.37529
5.240	17.59	1.37135	1.37120	1.37387	1.37389	1.37922	1.37927	1.38339	1.38344
6.288	20.79	1.37863	1.37863	1.38127	1.38142	1.38686	1.38701	1.39121	1.39136
6.498	21.43	1.38027	1.38010	1.38304	1.38291	1.38850	1.38853	1.39302	1.39291
6.812	22.37	1.38230	1.38228	1.38503	1.38509	1.39059	1.39079	1.39517	1.39522
7.126	23.30	1.38442	1.38444	1.38713	1.38727	1.39281	1.39303	1.39745	1.39751
7.336	23.91	1.38592	1.38589	1.38867	1.38872	1.39449	1.39451	1.39903	1.39901
7.860	25.43	1.38962	1.38945	1.39238	1.39229	1.39830	1.39817	1.40305	1.40276
8.384	26.94	1.39294	1.39295	1.39572	1.39580	1.40169	1.40176	1.40646	1.40643
9.432	29.90	1.39945	1.39981	1.40218	1.40266	1.40851	1.40879	1.41350	1.41360
10.48	32.80	1.40654	1.40649	1.40950	1.40931	1.41600	1.41557	1.42111	1.42052
11.48	35.53	1.41224	1.41269	1.41542	1.41544	1.42209	1.42183	1.42743	1.42688
12.83	39.14	1.41907	—	1.42232	—	1.42915	—	1.43454	—
13.38	40.61	1.42203	—	1.42522	—	1.43222	—	1.43784	—

Table II. It is seen that the agreement is quite good up to a concentration of 10N.

The refractive indices of the solutions containing cobalt are given in Table III and plotted against the normality of the acid in Fig. 1 with those for the solutions of acid only. It is seen that the curves are not smooth. There is an obvious break in the continuity, and each curve ultimately tends to become parallel with the corresponding curve for the solutions of acid only.

TABLE III.

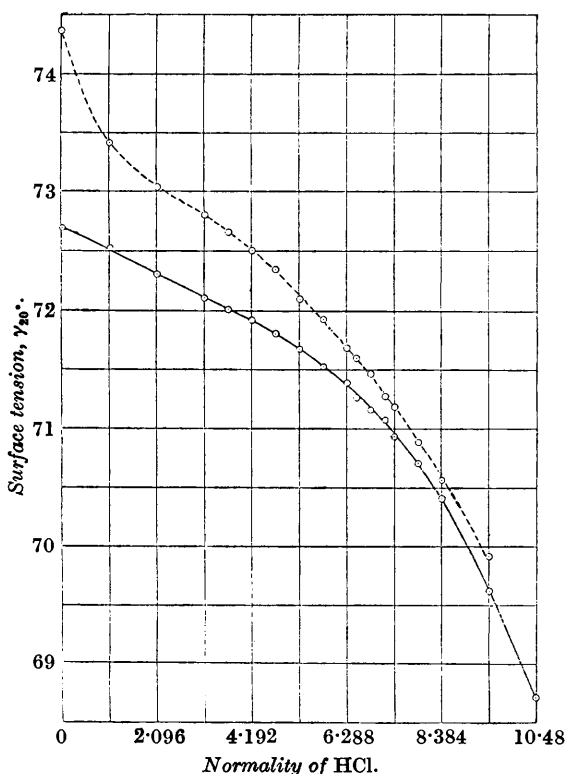
Refractive Indices of $\text{CoCl}_2 + \text{HCl}$ Solutions and Differences from Corresponding HCl Solutions.

Normality of acid, N_{18}^* .	$r_{\text{C}}^{20^\circ}$.	Differ- ence $\times 10^5$.	$r_{\text{D}}^{20^\circ}$.	Differ- ence $\times 10^5$.	$r_{\text{F}}^{20^\circ}$.	Differ- ence $\times 10^5$.	$r_{\text{G}}^{20^\circ}$.	Differ- ence $\times 10^5$.
0	1.34621	1504	1.34744	1445	1.35172	1469	1.35524	1507
1.048	1.35437	1499	1.35564	1391	1.36019	1420	1.36390	1446
2.096	1.36147	1361	1.36367	1360	1.36844	1380	1.37236	1412
3.144	1.36899	1305	1.37142	1327	1.37646	1341	1.38056	1372
3.668	1.37283	1308	1.37541	1332	1.38039	1331	1.38463	1361
4.192	1.37655	1298	1.37906	1303	1.38435	1324	1.38864	1343
4.716	—	—	1.38294	1299	1.38828	1312	1.39270	1340
5.240	—	—	1.38670	1283	1.39225	1303	1.39673	1334
6.288	—	—	—	—	1.39957	1271	1.40415	1294
6.498	—	—	—	—	1.40093	1243	1.40568	1266
6.812	—	—	—	—	1.40269	1210	1.40767	1250
7.126	—	—	—	—	1.40449	1168	1.40932	1187
7.336	—	—	—	—	1.40583	1134	1.41065	1162
8.384	—	—	—	—	1.41169	1000	1.41693	1047
9.432	—	—	—	—	1.41726	875	1.42268	918
10.48	—	—	—	—	1.42366	766	1.42913	802
12.26	—	—	—	—	1.43301	641	1.43853	673

If the cobalt atom were similarly associated in all these solutions, the refractive index should change regularly with increasing con-

centration of acid, as it does with the solutions of acid alone. Since this is not so, it follows that the cobalt atom undergoes a change in its association as the concentration of acid is increased; a suggestion as to the nature of this change has been given on p. 2039 and its course may be followed by considering the differences of the refractive indices of corresponding solutions. The values

FIG. 2.

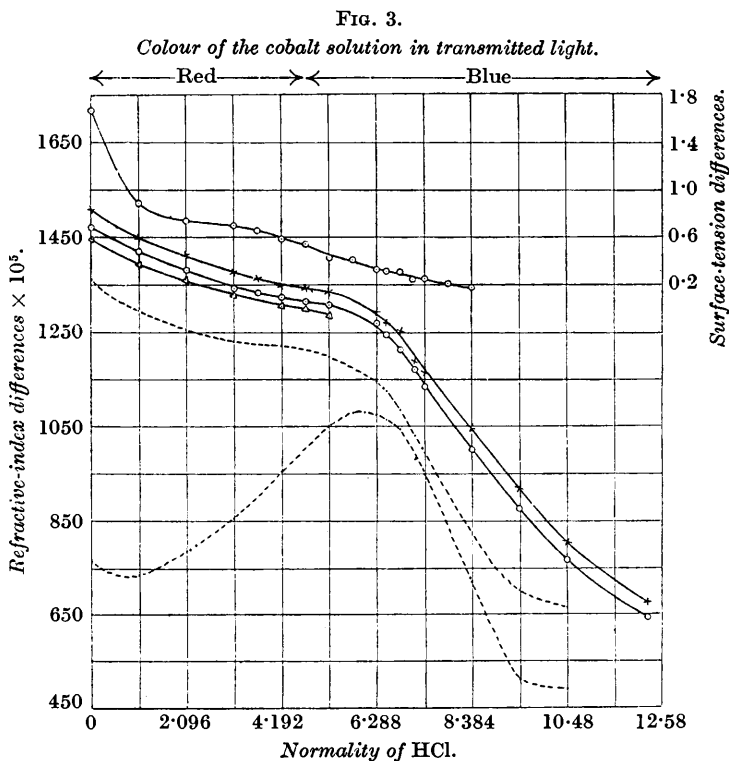


Upper curve : Solutions of hydrochloric acid + cobalt chloride.
Lower curve : Solutions of hydrochloric acid only.

obtained on subtracting the refractive indices of the solutions of hydrochloric acid alone from those of the corresponding solutions containing cobalt are given in Table III and plotted against the normality of the acid in Fig. 3.

The resulting curves are precisely similar to the curve obtained in the previous investigation by plotting the density differences against the concentration of acid. They exhibit well-marked inflexions at the same concentration of acid as the inflexion of the

density-differences curve and as the maximum of the viscosity-differences curve (both of which are reproduced in Fig. 3 for comparison). It is seen that towards the end of its course each curve is flattening out (although not as sharply as the density-differences curve) to become parallel to the axis of concentration, thus indicat-



Upper full-line curve : Surface-tension differences.

Lower full-line curves : Refractive-index differences.

For the G' line, shown thus : ×.

" " F " " " ⊙.

" " D " " " △.

Upper dotted-line curve : Density differences.

Lower dotted-line curve : Viscosity differences.

ing that the change to the CoCl_4'' configuration is nearing completion, where further increase in the concentration of acid could no longer affect the state of the cobalt atom.

The refractive index of the blue form is evidently less than that of the red. As the concentration of acid is increased and the change from red to blue proceeds, the curve falls continuously but not regularly. The diminution of the difference of refractive index,

like that of the density difference, takes place at first very gradually and then very rapidly. The suggestion offered to account for this feature in the density-differences curve also explains the same form of the refractive index-differences curve. The $\text{Co}(\text{H}_2\text{O})_6^{++}$ ions are progressively converted into CoCl_4^{--} ions, and as these are oppositely charged there is a powerful attraction between them. Evidently this attraction will be a maximum when equal numbers are present in the solution, and it is suggested that this condition obtains at the point of inflexion.

Surface Tensions.—The values of the surface tensions for the two series of solutions are given in Table IV and plotted in Fig. 2. Previous determinations of the surface tension of some aqueous solutions of hydrochloric acid alone have been made by Volkmann (see Landolt and Bornstein's Tables, 1923, p. 238) using the capillary-rise method. The values are in fair agreement with those now reported, which lie on a smooth curve. An equation has not been found to express the whole curve, but if the logarithm of the

TABLE IV.
Surface Tensions.

1.	2.	Surface tension of			6.
Conc. of HCl, N_{18}° .	%.	CoCl ₂ + HCl.	HCl alone.		Difference, (3—5).
		γ_{20}° .	γ_{20}° (obs.).	γ_{20}° (calc.).	
0	0	74.36	72.69	—	1.67
1.048	3.757	73.41	72.52	—	0.89
2.096	7.385	73.04	72.30	—	0.74
3.144	10.89	72.80	72.10	72.10	0.70
3.668	12.63	72.66	72.00*	72.01	0.65
4.192	14.29	72.50	71.91	71.92	0.58
4.716	15.97	72.34	71.80*	71.80	0.54
5.240	17.59	72.09	71.67	71.67	0.42
5.764	19.20	71.92	71.52	71.52	0.40
6.288	20.79	71.68	71.38	71.36	0.32
6.498	21.43	71.59	71.26	71.28	0.31
6.812	22.37	71.46	71.15	71.16	0.30
7.126	23.30	71.27	71.07	71.03	0.24
7.336	23.91	71.18	70.92	70.94	0.24
7.860	25.43	70.88	70.70	70.68	0.20
8.384	26.94	70.56	70.40	70.39	0.17
9.432	29.90	69.91	69.62	69.66	0.25
10.48	32.80	—	68.71	68.71	—

(Column 2 refers only to the solutions of hydrochloric acid alone.)

* These two values are read from the curve shown in Fig. 2.

difference, Δ , between the surface tension of water and that of each solution be plotted against the concentration of the solution, all the points except the first three lie on a perfectly straight line. The equation to the line is

$$\log \Delta = 0.1130N_{18}^{\circ} - 0.5850$$

where $\Delta = \gamma_{\text{water}} - \gamma_{\text{sol.}}$, and N_{18° is the normality of the solution at 18° . The values of the surface tension calculated from this expression are given in column 5 of Table IV. Comparing them with the observed values in column 4, it is seen that the agreement is within the limits of experimental error.

It was found impossible to get very concordant values of the drop number with the more concentrated acid solutions. They indicate, however, that the surface tensions of these solutions are progressively higher than those anticipated from the general course of the curve. It will be recalled that the densities of these solutions were lower than demanded by the form of the density curve.

The curve for the solutions containing cobalt, on the other hand, obviously consists of two parts, the first (for lower concentrations of acid) being convex to the axis of concentration, and the second (for higher concentrations of acid) being concave to this axis, and eventually becoming parallel to the curve for the solutions of acid alone.

The change in the association of the cobalt atom may again be followed by examining the differences of the surface tensions of the solutions containing cobalt and the corresponding solutions containing acid only. These differences are given in column 6 of Table IV and are plotted against the normality of acid in Fig. 3. It is seen that the curve is again of the same type as the density-differences curve and the refractive index-differences curves, but it differs from these in two important particulars.

The first of these is that the curve falls away rapidly from the initial value, whereas both the density-differences and the refractive index-differences curves fall off gently from the beginning. This characteristic of the surface tension-differences curve is readily explained. It is seen from the values of the surface tensions in Table IV and from the curves in Fig. 2 that the first solution in the series containing cobalt (*i.e.*, aqueous cobalt chloride alone) has a surface tension greater than that of water; so also have the solutions immediately following. That is, the cobalt atom in its red association, $\text{Co}(\text{H}_2\text{O})_6^{++}$, raises the surface tension of water. It follows from the Gibbs equation that the concentration of this ion in the surface layer is less than that in the bulk of the solution.

It is evident from the curves in Fig. 2 that the blue solutions (those having a high concentration of acid) have a surface tension only slightly higher than the corresponding solutions containing acid alone. Assuming that the whole of the acid is "free" in these cobalt solutions, as in the solutions of acid alone, it follows that the cobalt atom in its blue association, CoCl_4^{--} , also raises the surface tension of water, but to a far smaller extent than does the

red $\text{Co}(\text{H}_2\text{O})_6^{++}$. It is quite probable, however, since the acid is not wholly free but partly bound in the form of these complex ions, that the surface tension of the blue solutions is actually less than that of solutions of acid alone having a concentration equal to that of the "free" acid. In this event, the blue form, CoCl_4^{--} , lowers the surface tension of water, and in accordance with the Gibbs equation its concentration in the surface layer is *greater* than in the bulk.

Even if the blue form raises the surface tension, it follows that for a given bulk concentration of cobalt, its concentration in the surface layer would be greater than that of the red form. When, therefore, the first introduction of acid to the cobalt solution results in the conversion of some $\text{Co}(\text{H}_2\text{O})_6^{++}$ ions into CoCl_4^{--} ions, the same change takes place in the surface layer to a far greater degree. The increase in concentration of the blue form is therefore far greater in the surface layer than in the bulk of the solution. The surface tension, which is a purely surface phenomenon, is a measure of this change, so that the surface tension-differences curve falls rapidly with the initial increases in acid concentration, whereas the density-differences curve and the refractive index-differences curves, indicating the effect in the bulk of the solution, fall away gradually.

The second particular in which the surface tension-differences curve differs from the others is that it exhibits its inflexion at a different concentration of acid. This also is to be expected and is explicable on the same reasoning. It has been suggested that the point of inflexion in the density-differences curve and in the refractive index-differences curves and also the maximum in the viscosity-differences curve occur when the solution contains equal amounts of the two kinds of ions, $\text{Co}(\text{H}_2\text{O})_6^{++}$ and CoCl_4^{--} , since the attraction between them will then be greatest. It is now suggested that the point of inflexion in the surface tension-differences curve corresponds to the concentration of acid at which the same conditions obtain in the surface layer. Since the blue form accumulates in the surface layer to the exclusion of the red form, it follows that there will be equal amounts of each in the surface layer before this state is reached in the bulk of the solution. The surface tension-differences curve should therefore exhibit inflexion before the corresponding curves for the other properties which are dependent on the conditions in the bulk. It is seen from Fig. 3 that this is so.

It should be noted that although replacement of half the red form by the blue occurs in the surface layer sooner than in the bulk, the complete replacement cannot occur until this change is also

complete in the bulk. So long as any of the red form remains in the solution, a corresponding amount will be present in the surface layer, and it is not until all the red form has been converted in the solution that the same state is reached in the surface layer. The surface tension-differences curve should therefore not flatten out and become parallel to the axis of concentration sooner than the other curves, but at the same concentration of acid. It is seen from Fig. 3 that the curve falls continuously from the point of inflexion and has not become parallel over the range examined, but there are indications that this condition will be reached as with the other curves.

The Colour Change.—In the previous investigation, the colours of the cobalt solutions recorded were those observed by viewing thin layers against a white ground. In the present paper the colours of layers 5 cm. thick viewed in transmitted daylight are given at the head of Fig. 1.

The solutions having an acid concentration up to 3.144*N* are definitely red when examined in either thin or thick layers. Those having a concentration greater than 6.288*N* are green in very thin layers, but definitely blue with no trace of green in thicker layers. This dichroism is very marked.

Whereas these definitely red and blue solutions are clear and "clean," those lying within the limits stated are dull and "muddy" in appearance. In thin layers, the colour is indefinite. Thus the 4.192*N*-solution was previously described as brownish-red; in a thick layer, however, it is pinkish-violet, being definitely reddish with a tinge of blue. The 5.240*N*-solution, which is the most indefinite, was called a dull brown, but would have been better described as a dull amethyst, for even in thin layers it has a distinct blue tinge. In thicker layers the solution is definitely blue with a faint tinge of red. The 6.288*N*-solution is a very deep violet. The change in colour is therefore gradual and extends over a fair range of acid concentration. The 4.192*N*-solution being more red than blue, and the 5.240*N*-solution being more blue than red, the maximum colour change occurs between these concentrations of acid, as indicated at the head of Fig. 3. The 4.716*N*-solution, mid-way in acid concentration between these two, appears to be very nearly half red and half blue.

It was pointed out in the previous investigation that the point of inflexion in the density-differences curve and the maximum in the viscosity-differences curve do not coincide with the maximum change in colour, but at a considerably higher concentration of acid. The same is now seen to be true for the refractive index-differences curve. The colour change therefore takes place before

even half the cobalt has been transformed from the red to the blue association and this is in accordance with the fact already pointed out, that the blue form is far more intense than the red.

It should be noted that the concentration of acid at which the two forms are in equal amount in the surface layer, as indicated by the surface tension-differences curve, also does not correspond to the concentration at which the change of colour occurs.

Summary.

1. The refractive indices and surface tensions of a series of aqueous solutions containing a constant amount of cobalt chloride and increasing amounts of hydrochloric acid have been determined.

2. The same constants of an exactly similar series containing hydrochloric acid alone have also been measured.

3. The differences in the values for corresponding solutions bring to light the effect of the acid on the cobalt in solution.

4. The curve showing the differences in refractive index plotted against the concentration of acid is exactly similar to that of the density differences found in a previous investigation. The point of inflexion in both occurs at the same concentration of acid and is accounted for on the same reasoning.

5. The curve showing the differences in surface tension is also similar, but has a sharp initial fall and exhibits its point of inflexion at a lower concentration of acid. These two differences are wholly explained by the facts (*a*) that the surface tension is a measure of the conditions prevailing in the surface layer while the other properties are a measure of those in the bulk of the solution, and (*b*) that the relative concentrations of the red and the blue cobalt ions in the surface layer are different from those in the bulk under any given conditions.

6. The change in colour of the cobalt solutions with increasing acid concentration is discussed.

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