XXIII.—*Molecular Structure in Solution. Part IV. The Densities, Viscosities, and Electrical Conductivities of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid at Different Temperatures.*

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The change in colour of aqueous solutions of cobalt chloride from red to blue on addition of hydrochloric acid has already been investigated by examining the physical properties at a constant temperature (20°) of two series of solutions, the one containing a fixed amount of cobalt chloride with increasing concentrations of hydrochloric acid, and the other with exactly the same concentrations of hydrochloric acid alone. By taking the differences between the values for corresponding members of the two series and plotting these against the concentration of acid, it was possible to follow the effect of the increasing acid concentration on the cobalt in solution. The densities and viscosities (J., 1927, 158), refractive indices and surface tensions (*ibid.*, p. 2039), and electrical conductivities (*ibid.*, p. 2843) were determined, and the results indicated that the effect of addition of hydrochloric acid is to throw the cobalt atom out of its association with six molecules of water, $Co(H_2O)_6^{\cdot\cdot}$, which is red, into one with four groups or atoms, probably $CoCl_4''$, which is blue.

It was deemed of interest to examine along similar lines the exactly similar colour change which occurs when an aqueous cobalt solution is heated.

In the presence of hydrochloric acid the change of colour takes place more readily : the higher the concentration of acid, the lower the temperature at which the change occurs. In order to follow the change as far as possible into the blue region, an acidified solution was therefore chosen for the investigation.

The solution employed contained 120 g. of $CoCl_2,6H_2O$ per litre, as did the one series in the previous investigations, and it was also made 4*N* with respect to hydrochloric acid. At room temperature it is red with a distinct violet tinge and has the " muddy " appearance typical of the solutions containing both red and blue forms. At 0° it is bright red and perfectly clear and " clean " ; at 60° it is blue and again quite clear.

The comparison solution was 4*N*-hydrochloric acid alone. The densities, viscosities, and electrical conductivities of these two solutions have been measured at intervals of 5° from 0° to 80°. The determinations thus extend over a range of colour about the same as that in the previous investigations, and since the concentration of cobalt is the same in all, the results are directly comparable.

EXPERIMENTAL.

Solutions.—The solutions were prepared in the same way and from the same materials as for former investigations, and were filtered through fused Jena-glass Gooch crucibles. The concentration of acid was determined by titration against pure dry sodium carbonate, and the concentration of cobalt chloride was checked by estimating the total chlorine in the solution gravimetrically as silver chloride. All concentrations were determined at 18°.

Temperature Control.—All measurements were made in a gas-regulated thermostat with a glass front and back. For the higher temperatures the water was covered with a layer of high-boiling paraffin.

Temperatures below atmospheric were obtained in what is believed to be a novel manner. A stream of water from the mains was run through a constant-level device to secure a fixed head and thence through a copper coil cooled in ice. The steady stream of ice-cold water thus obtained was led through a similar coil immersed in the water filling the thermostat and then discharged into it, the thermostat being fitted with a constant-level arrangement for overflow. In this manner a perfectly even and easily regulated cooling effect was applied to the thermostat, similar to that caused by radiation from thermostats at temperatures above atmospheric. It was counterbalanced by the gas flame working through the regulator in the usual way, and the temperature could be kept constant to within $\pm$ 0·02° as easily as at higher temperatures.

Two standard thermometers were employed, newly calibrated at the National Physical Laboratory to the nearest 0·05°.

Determination of Density.—Densities were determined as in previous investigations with a bottle of about 25 c.c. capacity made of Pyrex glass. For temperatures below atmospheric and also above 60°, a pyknometer was employed. The values adopted for water were those of Thiesen (Landolt and Börnstein, "Tabellen," 1923, 73). For the highest temperatures there may be an error of one unit in the last place of decimals; for the others, it is less than this.

Determination of Viscosity.—Viscosities were determined by means of viscometers of the form previously described. For this series of measurements, they were made of Pyrex glass and were found to be effective in preventing loss through evaporation. The time of flow was taken by means of a stop-watch reading to 0·1 sec., and was reproducible to within this limit in every determination.

Since the minimum time of flow in the whole series was 240 seconds, the results are correct to within 0·1%.

The values for the viscosity of water at different temperatures given by various observers are not in good agreement. The values used here are the means of those of Hosking (*Phil. Mag.*, 1909, **17**, 502; **18**, 260) and of Bingham and White (*Z. physikal. Chem.*, 1912, **80**, 670) up to 25°; beyond 25°, Hosking gives his results to only three significant figures, and those of Bingham and White are therefore taken, except for 60°, where the given value is evidently too high and the mean is again accepted.

Determination of Conductivity.—Electrical conductivities were determined in the cell already described (*loc. cit.*). For every determination at least four different resistances were used in the circuit, the mean point of balance was taken after several trials, and the conductance of the cell calculated for each. The values were in every instance within 0·1% of the mean.

The cell constant was determined by using *N*-potassium chloride solution prepared from the pure dried salt (Kahlbaum's). Determinations were made at each working temperature from 0° to 25°, over which range the conductivity of this solution is known (Kohlrausch, Holborn, and Diesselhorst, *Wied. Ann.*, 1898, **64**, 417), and almost identical values were obtained for the cell constant. Calculations from the dimensions of the cell showed that the variation over the whole range of temperature should be less than 0·05%, and therefore the mean of the values obtained experimentally was used for all the estimations.

Results.

Densities.—The densities of the two solutions (cobalt chloride with 4*N*-hydrochloric acid, and 4*N*-acid alone) are given in cols. 2 and 4 respectively of Table I. The results at 20°, *viz.*, 1·1209 and 1·0657, are almost identical with those interpolated for the same solutions from the previous investigation, *viz.*, 1·1209 and 1·0656, respectively. The densities are plotted against the temperature in Fig. 1. It is seen that both curves are perfectly smooth and continuous. They are both represented by an equation of the form $d_{t^\circ} = d_{0^\circ}(1 - \alpha t - \beta t^2)$, where α and β are constants. The values of the constants for the two solutions are:

$CoCl_2 + HCl$: $\alpha = 307 \times 10^{-6}$; $\beta = 140 \times 10^{-8}$;
HCl alone: $\alpha = 289 \times 10^{-6}$; $\beta = 142 \times 10^{-8}$;

and the calculated values are given in cols. 3 and 5 respectively. It is seen that the agreement between the observed and the calculated values is very fair; the maximum difference is two units in the last place of decimals, and the average difference is less than one unit in both series.

The density differences (*i.e.*, the differences between the observed densities of the two solutions at each temperature) are given in col. 6 of Table I, and are plotted against the temperature in Fig. 1. The curve is quite smooth and continuous (see later).

TABLE I.

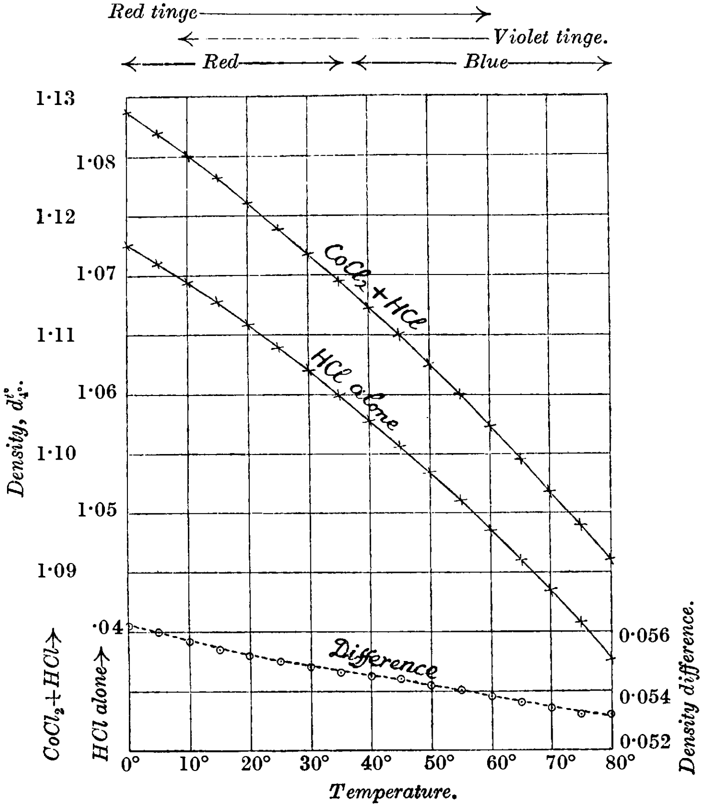
1.	2.	3.	4.	5.	6.
		Density, $d_{4^\circ}^{t^\circ}$.			
	$CoCl_2 + HCl$,		HCl alone,		Difference (2—4).
Temp.	obs.	calc.	obs.	calc.	
0°	1·1287	1·1287	1·0725	1·0725	0·0562
5	1·1269	1·1269	1·0709	1·0709	0·0560
10	1·1250	1·1251	1·0693	1·0693	0·0557
15	1·1231	1·1231	1·0677	1·0675	0·0554
20	1·1209	1·1211	1·0657	1·0657	0·0552
25	1·1188	1·1190	1·0638	1·0638	0·0550
30	1·1167	1·1169	1·0619	1·0618	0·0548
35	1·1144	1·1146	1·0598	1·0598	0·0546
40	1·1122	1·1123	1·0577	1·0577	0·0545
45	1·1100	1·1099	1·0556	1·0555	0·0544
50	1·1075	1·1074	1·0533	1·0532	0·0542
55	1·1050	1·1049	1·0510	1·0509	0·0540
60	1·1021	1·1022	1·0483	1·0484	0·0538
65	1·0995	1·0995	1·0459	1·0459	0·0536
70	1·0967	1·0967	1·0433	1·0433	0·0534
75	1·0940	1·0938	1·0408	1·0407	0·0532
80	1·0910	1·0909	1·0378	1·0380	0·0532

TABLE II.

1.	2.	3.	4.	5.	6.
		Viscosity coefficient, η_{t°.			
	$CoCl_2 + HCl$,		HCl alone,		Difference (2—4).
Temp.	obs.	calc.	obs.	calc.	
0°	0·02358	0·02358	0·01958	0·01958	0·00400
5	0·02077	0·02077	0·01729	0·01727	0·00348
10	0·01842	0·01845	0·01533	0·01535	0·00309
15	0·01647	0·01650	0·01375	0·01375	0·00272
20	0·01486	0·01486	0·01241	0·01241	0·00245
25	0·01345	0·01346	0·01125	0·01126	0·00220
30	0·01225	0·01226	0·01028	0·01028	0·00197
35	0·01120	0·01122	0·009419	0·009419	0·001781
40	0·01031	0·01031	0·008649	0·008672	0·001661
45	0·009519	0·009503	0·008012	0·008014	0·001507
50	0·008821	0·008793	0·007443	0·007431	0·001378
55	0·008191	0·008164	0·006923	0·006916	0·001268
60	0·007608	0·007602	0·006448	0·006455	0·001160
65	0·007102	0·007097	0·006041	0·006040	0·001061
70	0·006654	0·006643	0·005667	0·005667	0·000987
75	0·006218	0·006234	0·005321	0·005329	0·000897
80	0·005844	0·005861	0·005003	0·005021	0·000841

Viscosities.—The viscosities of the two solutions are given in Table II, cols. 2 and 4, and plotted against temperature in Fig. 2 : both curves are again smooth and continuous. The results at 20°, *viz.*, 0·01486 and 0·01241, may be compared with those calculated for the same solutions from the results obtained in previous investigations, *viz.*, 0·01487 and 0·01240, respectively.

FIG. 1.

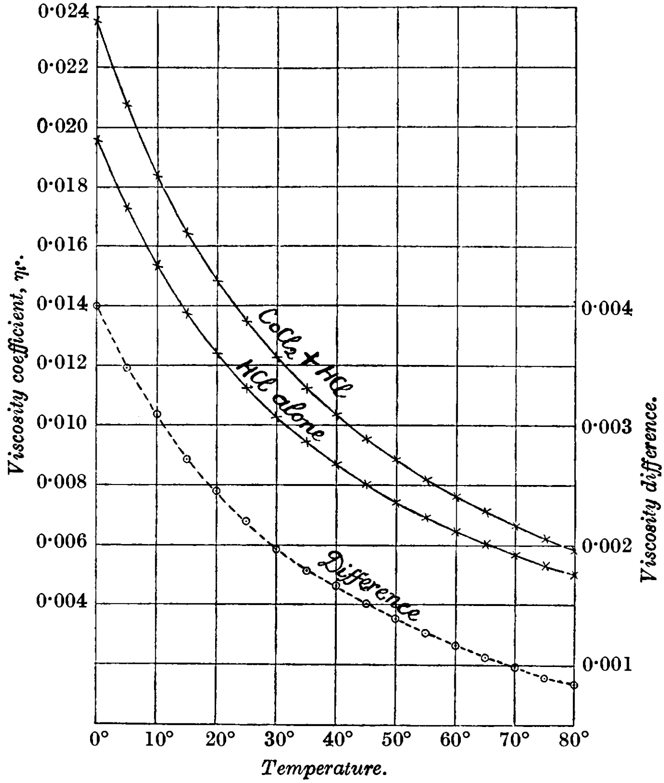


Colour of the cobalt solution in transmitted light.

Many equations have been suggested by different observers to express the relation between viscosity and temperature. Most of them give good agreement for non-associated, but not for associated liquids. The most satisfactory (see Thorpe and Rodger, *Phil. Trans.*, 1894, *A*, **185**, 397) is the second expression proposed by Slotte (*Beibl.*, 1892, **16**, 182), *viz.*, $\eta_{t^\circ} = \eta_{0^\circ}/(1 + \beta t)^n$, which has been shown to reproduce the observed values for non-associated liquids with great accuracy over wide ranges of temperature and to give good agreement for many associated liquids also. It is now shown that the equation also applies to solutions, even to those containing complexes.

The equation is preferably written in the form $\eta_{t_1^\circ}/\eta_{t_2^\circ} = [(t_1 + k)/(t_2 + k)]^{-C}$, where k and C are constants. It is most conveniently applied to a series of values over a wide range of temperature by

FIG. 2.

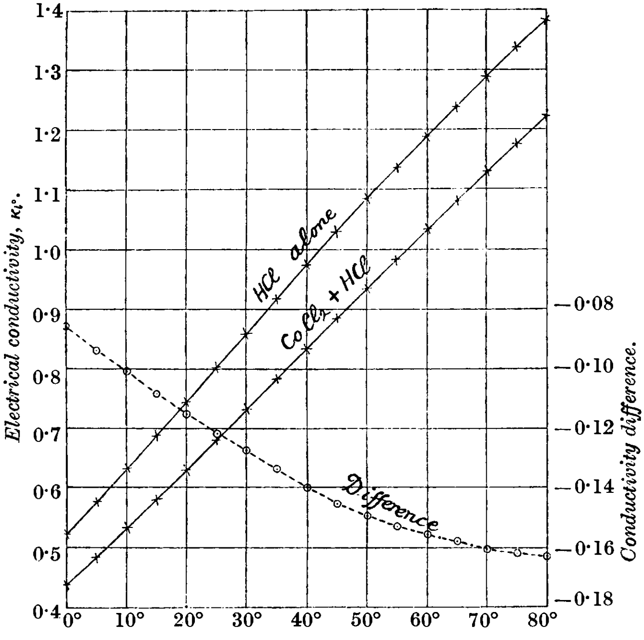


plotting the logarithms of the viscosities against the logarithms of $(t + k)$ for different values of k. A few attempts soon fix that value of k which gives a perfectly straight line, and the slope of this line gives C. The calculated values are then readily obtained from the expression $\log \eta_{t^\circ} = K - C \log (t + k)$, where $K = \log \eta_{0^\circ} + C \log k$. The values of the constants (k being given only to the nearest whole number) for the two solutions are

$CoCl_2 + HCl$: $k = 68$; $C = 1{\cdot}790$;
HCl alone : $k = 64$; $C = 1{\cdot}678$;

and the calculated viscosities are given in cols. 3 and 5 of Table II. It is seen that the agreement is very good; the maximum deviations are 0·34% and 0·27%, and the average deviations only 0·15% and 0·08% in the two series, respectively. Still more concordant values would doubtless result if the accepted viscosities for water were more trustworthy and if slight adjustments were made in the constants. The viscosity differences are given in col. 6 of Table II and are plotted against the temperature in Fig. 2; the curve is smooth and continuous (*vide infra*).

FIG. 3.



Electrical Conductivities.—The conductivities of the two solutions are given in Table III, cols. 2 and 4. The results at 20° may be compared with those for the same solutions read from the curves obtained in the previous investigations; the figures are 0·6287 and 0·7440, as against 0·6290 and 0·7430. The result for hydrochloric acid at 25°, 0·8014, agrees well with that of Green (J., 1908, **93**, 2023), who found 0·8016 for the same solution.

The conductivities are plotted against temperature in Fig. 3, and it is seen that both curves are again quite smooth and continuous. They may both be represented by an equation of the

TABLE III.

1.	2.	3.	4.	5.	6.
	Electrical conductivity, κ_{t°.				
	$CoCl_2$ + HCl,		HCl alone,		
Temp.	obs.	calc.	obs.	calc.	Difference (2—4).
0°	0·4360	0·4360	0·5217	0·5217	−0·0857
5	0·4827	0·4827	0·5766	0·5763	−0·0939
10	0·5310	0·5306	0·6318	0·6319	−0·1008
15	0·5788	0·5794	0·6873	0·6881	−0·1085
20	0·6287	0·6290	0·7440	0·7449	−0·1153
25	0·6795	0·6792	0·8014	0·8018	−0·1219
30	0·7310	0·7297	0·8587	0·8589	−0·1277
35	0·7818	0·7806	0·9157	0·9157	−0·1339
40	0·8317	0·8315	0·9719	0·9722	−0·1402
45	0·8823	0·8822	1·028	1·028	−0·1457
50	0·9334	0·9328	1·083	1·083	−0·1496
55	0·9818	0·9827	1·135	1·137	−0·1532
60	1·032	1·032	1·188	1·189	−0·156
65	1·080	1·081	1·238	1·240	−0·158
70	1·128	1·129	1·289	1·289	−0·161
75	1·175	1·175	1·337	1·337	−0·162
80	1·222	1·220	1·385	1·382	−0·163

form $\kappa_{t^\circ} = \kappa_{0^\circ}(1 + \alpha t + \beta t^2 - \gamma t^3)$, where α, β, and γ are constants. The values of the constants for the two solutions are

$CoCl_2$ + HCl : $\alpha = 0{\cdot}02116$; $\beta = 5915 \times 10^{-8}$; $\gamma = 5320 \times 10^{-10}$;
HCl alone : $\alpha = 0{\cdot}02073$; $\beta = 4442 \times 10^{-8}$; $\gamma = 5748 \times 10^{-10}$;

and the calculated conductivities are given in cols. 3 and 5, respectively, of Table III. It is seen that the agreement is very good; the maximum deviations are 0·19% and 0·18%, respectively, and the average deviation is only 0·07% in each series. The conductivity differences are given in col. 6 of Table III and are plotted against the temperature in Fig. 3. It is seen that the curve is smooth and continuous (*vide infra*).

Discussion of Results.

In the previous series of experiments (*loc. cit.*) on the effect of the addition of hydrochloric acid to cobalt chloride in solution, the curves for the solutions of hydrochloric acid alone were all smooth and continuous and could be represented by comparatively simple expressions, but those for cobalt chloride with hydrochloric acid exhibited discontinuity, the differences curves being characterised by marked inflexion.

Thus, the density-differences curve exhibited a point of inflexion; the density difference at the concentration of acid at which the inflexion occurs, as read from the line joining the values at the extreme ends of the series, is 0·0503, whereas the actual value is 0·0544, which is 8% greater. Similarly, the viscosity-differences curve exhibited a maximum; the difference read from the straight line is 0·00182, and the actual value is 0·00276, which is 51% higher. Again, the conductivity differences curve exhibited a minimum, the differences being respectively + 0·0095 and − 0·1230, which is 1395% lower.

In this series of experiments, on the other hand, the curves for these three properties of the solutions of hydrochloric acid both alone and with cobalt chloride are smooth and may be represented with nearly equal accuracy by simple expressions. Consequently the differences curves are also smooth. It follows that, although the colour change on the addition of hydrochloric acid to cobalt chloride solution and that on heating the solution appear precisely similar, the mechanism underlying the change is profoundly different.

The curves obtained in the previous investigations could be interpreted only on the hypothesis that on continued addition of hydrochloric acid to the cobalt chloride solution, the positively charged cobalt ions were progressively converted into negatively charged complex ions and that the point of inflexion (maximum or minimum) on the differences curves occurred when equal numbers of each were present and the attraction between them was consequently greatest.

Since all the curves obtained in the present investigation are smooth, it follows that there is no change (or, at most, a negligibly small change) in the numbers of oppositely charged cobalt ions. The mechanism of the colour change which occurs on cooling or heating these acid solutions must therefore be different from that brought about by alteration of acid concentration (see above), and must be explained by the addition or subtraction, respectively, of two groups to or from each kind of ion without changing its charge. This can be effected only by addition or subtraction of water molecules, and the phenomenon is therefore one of hydration and dehydration according to the scheme

$$\begin{array}{c} \xrightarrow{\text{heating}} \\ \text{Red}\left\{\begin{array}{lcl} \mathrm{Co(H_2O)_6^{\cdot\cdot}} & \rightleftarrows & \mathrm{Co(H_2O)_4^{\cdot\cdot}} \\ \mathrm{CoCl_4(H_2O)_2''} & \rightleftarrows & \mathrm{CoCl_4''} \end{array}\right\}\text{Blue} \\ \xleftarrow[\text{cooling}]{} \end{array}$$

The first explanation suggested to account for the change of colour of cobalt solutions, not only on heating, but also on addition of alcohol, acid, and certain salts, was that of hydration (von Babo, *Jahresber.*, 1857, 72; Schiff, *Annalen*, 1859, **110**, 203). Many investigations on the absorption spectra of cobalt solutions led to the same conclusion (Russell, *Proc. Roy. Soc.*, 1881, **32**, 258; Hartley, *Trans. Roy. Dublin Soc.*, 1900, **7**, 253; J., 1903, **83**, 401; Jones and Uhler, *Amer. Chem. J.*, 1907, **37**, 126), and the formation of definite aquo-complexes has been postulated (Hantzsch, *Z. anorg. Chem.*, 1927, **159**, 273; **166**, 237; Gróh and Schmid, *ibid.*, **162**, 321).

The present investigations, however, show that the mechanism of the change of colour on addition of acid is different from that on heating, yet the two are explained and harmonised on the general theory of colour based on the number of groups surrounding the cobalt atom (Hill and Howell, *Phil. Mag.*, 1924, **48**, 833; compare Hantzsch and Shibata, *Z. anorg. Chem.*, 1912, **73**, 309; Hantzsch, *loc. cit.*).

It may be noted that this work shows that not only the kation but also the complex anion is hydrated. Indeed, with a solution containing approximately equal numbers of the two kinds of ions, the change of colour to red (hydration chiefly of the anion) on cooling is far more rapid than the change to blue (dehydration of the kation) on heating.

Although the differences curves obtained on addition of hydrochloric acid to cobalt chloride solution differ essentially in form from those obtained on heating the solution, there is one feature in which they all resemble one another, namely, that they all tend eventually to become parallel to the axis of acid concentration or of temperature, showing that the change of the cobalt atom to the blue configuration is nearing completion. No further change being then possible, the physical properties of the cobalt solution compared with those of the acid alone become and remain constant. It is evident from the form of the curves obtained in this work, that dehydration of the cobalt ions would not be complete even at 100°.

Summary.

1. The densities, viscosities, and electrical conductivities of two aqueous solutions, one containing 120 g. of $CoCl_2,6H_2O$ per litre with hydrochloric acid ($4N$) and the other hydrochloric acid ($4N$) alone, have been determined at intervals of 5° from 0° to 80° and plotted against the temperature.
2. The curves of each of the properties are smooth for both the solutions and expressions have been found for them which give good agreement with the observed values.
3. The three differences curves are also smooth, unlike those obtained on continued addition of hydrochloric acid to cobalt chloride solution at constant temperature.
4. It is therefore concluded that the relative number of oppositely

charged cobalt ions in the solution is unchanged over the whole range of temperature and therefore during the colour change.

5. Since the colour is determined by the number of groups surrounding the cobalt atom, it follows that the change must be due to addition and subtraction of water molecules, leaving the charge of the ion unaltered.

6. The change of colour is therefore due to hydration and dehydration on cooling and heating respectively.

7. Both kation and anion are hydrated, gaining or losing two molecules of water on cooling or heating respectively, so that the total number of groups surrounding the cobalt atom is six when red and four when blue.

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