

264. *Physicochemical Studies of Complex Formation involving Weak Acids. Part V. Solutions of Complex Cyanides of Silver, Zinc, Cadmium, Mercury, and Nickel.*

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It was shown in Part I (J., 1931, 2332) that the complex cyanides formed by potassium and either silver, zinc, cadmium, nickel, or bivalent iron are but little hydrolysed in solution. This suggests that the metals exist in stable complexes. The presence of these metals in complex anions has been demonstrated by migration experiments (see Hittorf, *Pogg. Ann.*, 1853, **89**, 177; 1856, **98**, 1; Rieger, *Z. Elektrochem.*, 1901, **7**, 871), but investigation of the equivalent conductivities of solutions of complex cyanides has not always led to a definite confirmation of their supposed constitution. For instance, Walden (*Z. anorg. Chem.*, 1900, **23**, 373) found at 25° that $\Lambda_{1024} - \Lambda_{32}$ for $K_2Zn(CN)_4$ and $K_2Cd(CN)_4$ was 14.9 and 15.1 respectively, neither of these values being sufficiently near 20 to indicate the dibasicity of the respective anions.

From *E.M.F.* measurements of cells involving amalgamated zinc

and cadmium electrodes, Euler (*Ber.*, 1903, **36**, 3400) deduced the existence of $\text{Zn}(\text{CN})_4''$ and $\text{Cd}(\text{CN})_4''$, though Kunschert (*Z. anorg. Chem.*, 1904, **41**, 337), in order to account for the potentials of silver electrodes in solutions containing both silver and zinc complex cyanides, found it necessary to postulate the existence of another zinc complex cyanide ion, *viz.*, $\text{Zn}(\text{CN})_3'$. This assumption, however, was based on the belief that the silver was contained in the complex anion, $\text{Ag}(\text{CN})_2'$, which, according to Bodländer and Eberlein (*ibid.*, 1904, **39**, 197), is not strictly true, for they claim the co-existence of yet another anion, $\text{Ag}(\text{CN})_3''$, in all except very dilute solutions.

In the hope that p_{H} measurements would add to our somewhat vague knowledge of complex cyanide ions, the present work was undertaken. An attempt was also made to correlate the p_{H} data with measurements of potential (using the appropriate metal or amalgam) and of conductivity. In extending these studies to complex mercuric cyanide solutions, it was necessary to determine the extent of hydrolysis of such solutions, and this was done by the vapour-pressure method of Harman and Worley (*Trans. Faraday Soc.*, 1924, **20**, 502).

Attempts to use the antimony and tungsten electrodes for the determination of the p_{H} values of cyanide solutions (Britton and Robinson, J., 1930, 1261; Britton and Dodd, J., 1931, 829) have proved fruitless, and resort has now been made to the glass electrode, which is quite serviceable and yields accurate p_{H} values in the presence of cyanides.

1. *Hydrolysis of Potassium Mercuricyanide at 25°*.—Solutions were prepared by mixing mercuric chloride and potassium cyanide in the proportion necessary to produce $\text{K}_2\text{Hg}(\text{CN})_4$ together with the excess of potassium cyanide given in the first column of Table I. The actual concentrations are recorded in cols. 2 and 3. The concentrations of hydrolysed hydrogen cyanide (col. 4) were estimated by Harman and Worley's picric acid method, as described in Part I. Col. 5 gives the calculated amounts of acid liberated by the excess potassium cyanide, the hydrolysis constant K_h being taken as 2.55×10^{-5} . By subtracting these concentrations from the observed concentrations, those of the hydrocyanic acid liberated by the complex were found. The percentage hydrolysis, given in the last column, was calculated on the assumption that the four cyanide groups in the complex anion were capable of hydrolysis. Comparison with the data for other complex anions (Part I) reveals that the mercuricyanide anion undergoes greater hydrolysis, but that this increases with increasing excess of potassium cyanide, contrary to the behaviour of the other complex ions.

TABLE I.

$T = 25^\circ$.	Conc., <i>M</i> .		[HCN] $\times 10^4$.		Hydrolysis of com- plex, %.
	$K_2Hg(CN)_4$	KCN.	Obs.	Calc.	
$K_2Hg(CN)_4$	0.0203	0	7.0	0	0.85
,, + 1 KCN	0.0169	0.01690	11.0	6.4	0.70
,, + 2 ,,	0.0145	0.0290	13.0	8.4	0.77
,, + 4 ,,	0.0110	0.0440	16.0	10.5	1.25
,, + 6 ,,	0.0093	0.0558	18.0	13.2	1.30

2. p_H Measurements by Means of the Glass Electrode.—The method adopted was similar to that of Morton (*J. Sci. Inst.*, 1930, 7, 187), and the apparatus (ballistic galvanometer and condenser) and calibration procedure of the glass electrode were those described by Britton and Robinson (*Trans. Faraday Soc.*, 1932, 28, 531). The calibration of this electrode for use in solutions of high p_H was also confirmed by immersion in potassium cyanide solutions, the p_H values of which were accurately known.

For the titrations, approximately 0.01 *M*-solutions of the sulphates of zinc, cadmium, and nickel, and the chloride and nitrate respectively of mercury and silver, were titrated with 0.1 *M*-potassium cyanide solution. Direct titrations showed that in some cases redissolution of the precipitated simple cyanide in excess potassium cyanide was very slow, and hence equilibrium values of the p_H of the solution could not be obtained. To obviate this difficulty, mixtures of the metallic salt solution with various amounts of potassium cyanide were placed in bottles, which were shaken for several hours or kept over-night, before the p_H of the solution was measured. By this means steady and reproducible p_H values were obtained. In this way several series of solutions were prepared corresponding to increasing excesses of potassium cyanide over the various metallic salts. Each solution was prepared by diluting the required volume of 0.1 *M*-potassium cyanide to 100 c.c. and adding it to 10 c.c. of a 0.1 *M*-salt solution.

Curves illustrating the changes in hydrogen-ion concentration with increase of cyanide are plotted in Fig. 1, whilst the p_H values corresponding to x mols. of potassium cyanide in excess of that required to form $K_2M(CN)_4$ [or $KAg(CN)_2$] are given in Table II.

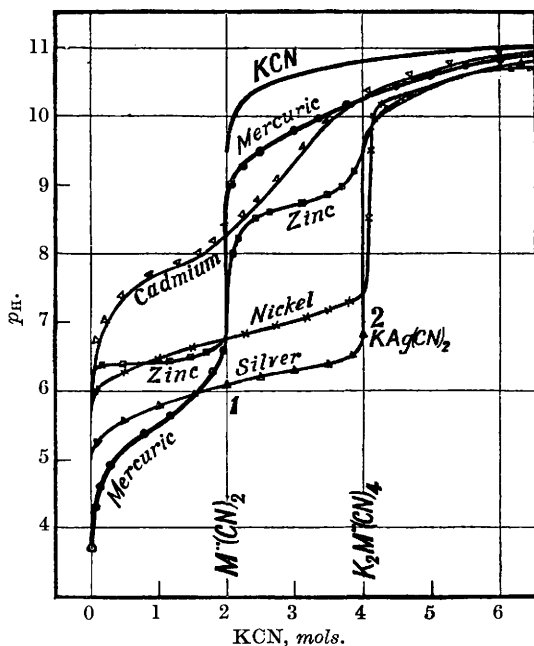
During the addition of the first 2 mols. of potassium cyanide to the solutions of zinc and nickel salts, the respective cyanides were precipitated, but further additions caused redissolution, clear solutions being obtained with 4 mols. Corresponding values for the silver nitrate solution were 1 and 2 mols. respectively. No precipitate separated from either the cadmium sulphate or the mercuric chloride solution.

In Fig. 1 the uppermost curve, labelled KCN, represents the

TABLE II.

M.	z.	Conc., $M \times 10^4$.		p_H .	$[CN^-]$		$[HCN] \times 10^4$		$[ON^-] \times 10^4$.	$[CN^-] / [KCN]$.
		$K_2M(CN)_z$.	KCN.		$[HCN]$	Complex.	KCN.	$[HCN] \times 10^4$.		
Ag	0.5	9.09	4.54	10.40	12.02	0	3.23	3.23	3.88	0.9
	1.0	9.09	9.09	10.65	21.38	0	4.55	4.55	9.72	1.1
	1.5	9.09	13.63	10.78	28.84	0	5.59	5.59	16.13	1.2
	2.0	9.09	18.18	10.85	33.88	0	6.36	6.36	21.59	1.2
Zn	0.5	9.09	4.54	10.19	7.41	1.64	3.23	4.86	3.60	0.8
	1.0	9.09	9.09	10.44	13.18	1.45	4.55	6.00	7.91	0.9
	1.5	9.09	13.63	10.56	17.40	1.35	5.59	6.94	12.07	0.9
	2.0	9.09	18.18	10.66	21.88	1.20	6.36	7.56	16.55	0.9
Cd	0.5	9.13	4.56	10.50	15.14	1.46	3.15	4.61	6.98	1.5
	1.0	9.13	9.13	10.66	21.88	1.02	4.56	5.58	1.22	1.3
	1.5	9.13	13.69	10.79	29.50	0.99	5.61	6.60	1.95	1.4
	2.0	9.13	18.25	10.88	36.31	0.48	6.39	6.87	2.49	1.4
Hg	0.5	6.94	3.47	10.12	6.31	2.14	2.81	4.95	3.12	0.9
	1.0	6.71	6.71	10.20	7.59	1.88	3.93	5.81	4.40	0.7
	1.5	6.50	9.75	10.28	9.12	1.87	4.68	6.55	5.97	0.6
	2.0	6.30	12.60	10.34	10.50	1.95	5.29	7.24	7.58	0.6
Ni	0.5	9.09	4.54	10.34	10.47	0.36	3.23	3.59	3.76	0.8
	1.0	9.09	9.09	10.52	15.85	0.76	4.55	5.31	8.42	0.9
	1.5	9.09	13.63	10.66	21.88	0.80	5.59	6.39	13.98	1.0
	2.0	9.09	18.18	10.78	28.84	0.87	6.36	7.23	20.86	1.1

FIG. 1.



p_H variations that would have been established if the reactions of the various salts with potassium cyanide had consisted simply of double decompositions and the excess of the alkali cyanide had

remained, as such, in solution. It will be seen that, for both silver and nickel, there was a steady increase in p_H from 5.0 to 6.5 and from 6.0 to 7.3, respectively, during the addition of the cyanide required to form solutions of $KAg(CN)_2$ and $K_2Ni(CN)_4$. Immediately the complex silver cyanide had been formed, further addition produced a sudden increase in p_H , but with nickel this increase was very slightly delayed. Reference to Part I shows that $KAg(CN)_2$ does not hydrolyse in solution, and that the hydrolysis of $K_2Ni(CN)_4$ is negligibly small: this is reflected in the fact that the p_H values prevailing during the redissolution of these cyanides are in the region of neutrality.

The zinc and mercuric curves indicate that considerable increases in p_H occurred when the stoichiometric amounts of potassium cyanide had been added to form the heavy-metal cyanides. The second section of the zinc curve, corresponding to dissolution of zinc cyanide, shows that the mother-liquor was buffered just below p_H 9, the formation of the complex $K_2Zn(CN)_4$ being indicated by an inflexion. The corresponding section of the mercury curve is not marked by an inflexion, but the range of p_H values of the solutions in which the complex salt was being formed is much lower than that which would have obtained if the potassium cyanide had not entered into combination with the mercuric cyanide. The hydrogen-ion concentration prevailing during the precipitation of zinc cyanide is similar to that set up in an alkali titration of a zinc salt solution (see Britton and Robinson, *loc. cit.*), and the buffered curve of the second half of the reaction, being somewhat lower than p_H 9.32 (the p_{K_a} of hydrogen cyanide), shows that the ratio of the concentration of free hydrocyanic acid to that of cyanide ions was relatively high. Both observations reveal hydrolysis, in the first place of the precipitated zinc cyanide, and in the second, of the complex cyanide that was being formed. The latter conforms with the hydrolysis measurements, that of a 0.02M- $K_2Zn(CN)_4$ solution being 0.5%.

The p_H corresponding to the reaction of 2 mols. of potassium cyanide with 1 mol. of cadmium sulphate lies chiefly between 7 and 8, the range within which cadmium salts undergo precipitation on treatment with alkali (Britton, J., 1925, 127, 2148). Actually no precipitate separated from these solutions except on prolonged standing. Joannis (*Compt rend.*, 1881, 93, 272), Loebe (*Diss.*, Berlin, 1902), and Corbet (J., 1926, 3190) have found, however, that by using more concentrated reactants basic cadmium cyanide is precipitated; the formation of this basic cyanide would account for the p_H curve given by the second stage of the reaction being buffered between p_H 8 and 10 owing to the free hydrocyanic acid present in the solutions. Much of this hydrolysed acid must have eventually

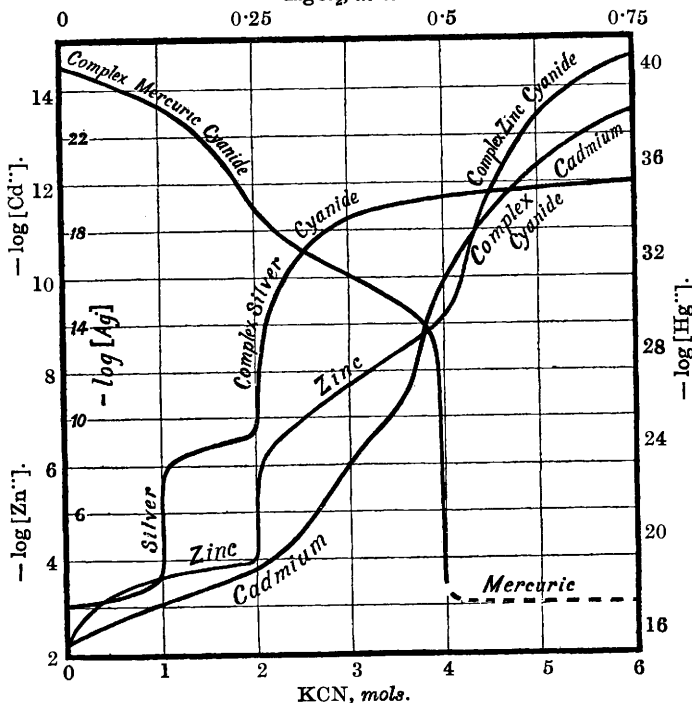
entered into combination to form the complex salt, for not only did the mother-liquor attain p_H 10 with less potassium cyanide than in several other cases, but the extent of hydrolysis of the complex cadmium cyanide immediately it had been formed was only 0.53%. (Subsequent determinations of the concentration of free hydrocyanic acid by the vapour pressure method have confirmed these statements.)

The p_H values of the solutions containing the complex cyanides and varying excesses of potassium cyanide were the outcome of the dissociation of hydrolysed hydrocyanic acid and cyanide ions. Such equilibria may be represented by the expression $p_H = p_{K_a} + \log [CN^-]/[HCN]$, p_{K_a} being 9.32 (Britton and Robinson, *loc. cit.*). Values of $[CN^-]/[HCN]$ corresponding to the addition of various molecular proportions of potassium cyanide are recorded in col. 4 of Table II. It is, however, possible to calculate the concentrations of free hydrogen cyanide of the solutions on the basis of the previous hydrolysis measurements (Part I and foregoing section), and therefore to calculate the actual concentration of cyanide ions of the various solutions. These are given in the penultimate column of Table II, whilst the last column gives the values of the ratio $[CN^-]/[KCN]$, $[KCN]$ being the concentration of potassium cyanide in excess of the complex salts that have tacitly been assumed to be present in the solutions. With the exception of the figures for the cadmium solutions, the values approximate to unity, which, in view of the appreciable differences caused by slight errors in the p_H measurements, may be considered to offer some confirmation of the existence of the ions $Ag(CN)_2^-$, $Zn(CN)_4^{2-}$, $Hg(CN)_4^{2-}$, and $Ni(CN)_4^{2-}$. The divergences from unity are more pronounced in the case of the cadmium solutions, and suggest that other complex cadmium ions, possibly $Cd(CN)_3^-$, existed in the solutions, requiring less potassium cyanide for their formation.

3. *Metal-ion Concentrations.*—In order to study the reactions involved, several series of solutions of the same concentration were prepared, mechanically shaken, and kept over-night; the *P.D.*'s of the cells $M|MX + xKCN|Satd. KNO_3|N\text{-Calomel}$ were then measured at room temperature. For the silver reaction, 50 c.c. portions of 0.01*M*-silver nitrate solution were treated with various volumes of 0.1*M*-potassium cyanide and each mixture was allowed to attain equilibrium before insertion in the cell. In this case the standard half-element was $Ag|0.1M\text{-}AgNO_3$. Owing to the reduction of mercuric chloride which occurs at a mercury interface, the mercury potential measurements took the form of a potentiometric back-titration of 110 c.c. of 0.04477*M*-potassium cyanide with 0.1*M*-mercuric chloride solution.

The silver electrode consisted of silver wire sealed into a glass tube, the exposed end of which was covered with a crystalline layer of the metal. This was deposited from a silver nitrate solution by passing a current of a few milliamps. for 3—4 hours. The normal electrode potential on the hydrogen scale was 0.800 volt. The zinc and cadmium electrodes consisted of fairly dilute amalgams, freshly prepared by electrodeposition from their respective sulphate solutions at pure mercury cathodes. The zinc amalgam gave a potential, E_h , against 0.005M-zinc sulphate solution of -0.786 volt, whilst the cadmium

FIG. 2.
HgCl₂, mols.



amalgam in 0.005M-cadmium sulphate solution at 14° gave $E_h = -0.404$. The degree of dissociation of each solution being taken as 0.633, normal electrode potentials are found to be -0.722 volt and -0.340 volt respectively for the amalgams employed in these measurements. The mercury electrode consisted of a U-tube with unequal arms, the bend of which was filled with pure mercury. The short arm was immersed in the solution undergoing titration. The value, $+0.856$ volt, was used as the normal electrode potential of mercury in regard to mercuric ions, it having been calculated by

Luther's rule from $E_{2\text{Hg}} \rightarrow \text{Hg}_2^{2+} = 0.80$ (Lewis and Randall, "Thermodynamics") and $E_{\text{Hg}_2^{2+} \rightarrow 2\text{Hg}^+} = 0.913$ (Carter and Robinson, J., 1927, 267).

Fig. 2 gives the metal-ion concentrations set up throughout these reactions. The ordinates on the left give the logarithms of those concentrations corresponding to the silver, zinc, and cadmium reactions, calculated from the observed *E.M.F.*'s by means of the Nernst formula. The quantities of potassium cyanide added are given by the lower abscissa. The upper abscissa and the right-hand ordinate refer to the back-titration with mercuric chloride. Typical *E.M.F.*'s set up by solutions containing the different complex cyanides and various excesses of potassium cyanide are recorded in Table III.

TABLE III.

$[\text{KAg}(\text{CN})_2]$ $\times 10^3$.	$[\text{KCN}]$ $\times 10^2$.	$\frac{[\text{KCN}]}{[\text{KAg}(\text{CN})_2]}$.	<i>E.M.F.</i> at 15°.	$-\log [\text{Ag}^+]. \bar{K} \times 10^{22}$.	
9.28	1.41	1.5	-1.0634	19.72	5.26
6.12	2.45	4.0	-1.0996	20.36	4.26
5.42	3.25	6.0	-1.1162	20.65	4.35
4.86	3.89	8.0	-1.1302	20.90	3.94
4.42	4.42	10.0	-1.1378	21.03	4.13
4.03	4.81	11.9	-1.1440	21.14	4.17
3.71	5.20	14.0	-1.1506	21.25	4.05
3.44	5.51	16.0	-1.1542	21.32	4.25

$[\text{K}_2\text{Zn}(\text{CN})_4]$ $\times 10^3$.	$[\text{KCN}]$ $\times 10^3$.	$\frac{[\text{KCN}]}{[\text{K}_2\text{Zn}(\text{CN})_4]}$.	<i>E.M.F.</i> at 12.5°.	$-\log [\text{Zn}^{2+}]. \bar{K} \times 10^{20}$.	
9.09	3.74	0.4	-1.344	11.94	2.47
9.09	8.20	0.9	-1.390	13.55	1.40
9.09	8.42	0.9	-1.395	13.72	1.05
9.09	17.11	1.9	-1.429	14.95	1.06
7.41	25.08	3.4	-1.410	14.57	14.4
4.76	27.86	5.8	-1.434	15.10	10.1
2.91	36.17	12.4	-1.437	15.20	37.0

$[\text{K}_2\text{Cd}(\text{CN})_4]$ $\times 10^3$.	$[\text{KCN}]$ $\times 10^3$.	$\frac{[\text{KCN}]}{[\text{K}_2\text{Cd}(\text{CN})_4]}$.	<i>E.M.F.</i> at 14°.	$-\log [\text{Cd}^{2+}]. \bar{K} \times 10^{20}$.	
9.13	3.56	0.4	-0.952	11.53	5
9.13	8.02	0.9	-0.980	12.51	14
9.13	8.24	0.9	-0.962	11.92	61
9.13	16.93	1.9	-1.013	13.67	19
7.44	15.83	2.1	-0.982	12.74	156
4.78	27.77	5.8	-1.012	13.69	256
2.92	26.55	9.0	-1.022	14.07	143

$[\text{K}_2\text{Hg}(\text{CN})_4]$ $\times 10^2$.	$[\text{KCN}]$ $\times 10^2$.	$\frac{[\text{KCN}]}{[\text{K}_2\text{Hg}(\text{CN})_4]}$.	<i>E.M.F.</i> at 12°.	$-\log [\text{Hg}^{2+}]. \bar{K} \times 10^{44}$.	
6.25	0.579	0.09	-0.455	35.45	6.4
6.06	0.860	0.14	-0.473	36.04	8.3
5.88	1.12	0.19	-0.487	36.48	8.9
5.71	1.37	0.24	-0.497	36.83	9.2
5.56	1.61	0.29	-0.505	37.10	9.5
0.833	0.772	0.93	-0.459	35.59	110
0.678	1.46	2.15	-0.492	36.72	127
0.435	2.54	5.85	-0.520	37.66	213

The silver and zinc curves show that appreciable diminutions in metal-ion concentration occurred when the quantities of potassium cyanide were those required to effect the complete precipitation of the respective cyanides. With more alkali cyanide, which gradually brought about their dissolution, there was a gradual change in ion concentration up to 2 mols. and a little more than 4 mols. respectively, rapid changes then being set up again. The second step of the silver curve corresponds to equilibria between the silver ions arising from the slight amount of silver cyanide in solution and the soluble complex salt formed with the added potassium cyanide: $2\text{AgCN} \rightleftharpoons \text{Ag}^+ + \text{Ag}(\text{CN})_2'$. If each portion of the 1 mol. of potassium cyanide in excess of the first added to 1 mol. of silver nitrate immediately converts an equivalent amount of silver cyanide into $\text{KAg}(\text{CN})_2$, then, by assuming that the complex cyanide (now in solution) is completely dissociated, $\text{KAg}(\text{CN})_2 \rightarrow \text{K}^+ + \text{Ag}(\text{CN})_2'$, we can calculate the $\text{Ag}(\text{CN})_2'$ concentration at any point in the second stage. As solid silver cyanide exists in equilibrium with the mother-liquor, it should be possible to calculate the solubility product $[\text{Ag}^+][\text{Ag}(\text{CN})_2']$ from the data available. The following table, which gives the result of typical calculations, justifies these assumptions.

Mols. of excess KCN.	<i>E.M.F.</i> of cell at 15°.	$-\log [\text{Ag}^+]$.	$[\text{Ag}(\text{CN})_2']$ $\times 10^3$.	$[\text{Ag}^+][\text{Ag}(\text{CN})_2]$ $\times 10^{12}$.
0.25	-0.429	8.63	2.21	5.17
0.50	-0.446	8.93	4.31	5.06
0.75	-0.456	9.10	6.32	5.02

The mean value of the solubility product, *viz.*, 5.1×10^{-12} , is in remarkable agreement with the value, 5×10^{-12} , obtained by Bodländer and Lucas (*Z. anorg. Chem.*, 1904, **41**, 192) from solubility determinations; Böttger (*Z. physikal. Chem.*, 1903, **46**, 602) found 2.25×10^{-12} by means of conductivity measurements.

Similar computations made to account for the zinc-ion concentrations prevailing during the second stage of the zinc reaction were not so successful. The equilibria involved were considered to be $2\text{Zn}(\text{CN})_2 \rightleftharpoons \text{Zn}^{++} + \text{Zn}(\text{CN})_4''$, and the values of the product $[\text{Zn}^{++}][\text{Zn}(\text{CN})_4''] \times 10^{11}$ obtaining when 0.5, 1.0, and 1.5 mols. of potassium cyanide had been added to 1 mol. of $\text{Zn}(\text{CN})_2$ were 14.0, 5.1, and 1.6 respectively.

The curve corresponding to the gradual formation of the cadmium complex is irregular, and, moreover, the upward inflexion occurs, as was the case in the glass-electrode curve, some time before the correct amount of potassium cyanide had been added to form $\text{K}_2\text{Cd}(\text{CN})_4$. As might be expected from the nature of both the glass-electrode and the cadmium amalgam curves, the ionic product, $[\text{Cd}^{++}][\text{Cd}(\text{CN})_4'']$, is not constant during the second stage of the

reactions. For 0.5, 1.0, and 1.5 mols. of potassium cyanide, the values were 410×10^{-10} , 29.8×10^{-10} , and 3.9×10^{-10} respectively.

With mercury, there appeared an inflexion when the amount of mercuric chloride was just sufficient to convert the potassium cyanide into $K_2Hg(CN)_4$. Thereafter, the mercuric chloride caused a gradual increase in mercuric-ion concentration until the amount had reached 0.5 mol., whereupon a sudden increase took place. This corresponds to the complete conversion of the complex cyanide into mercuric cyanide. The section of the curve, given as a broken line, does not represent the mercuric-ion concentrations of the solutions containing excess of mercuric chloride, for it was at this stage of the titration that the electrode became incapacitated on account of reduction of the mercuric chloride to calomel, which could be seen as a grey film on the electrode interface. It was for this reason that the direct titration of mercuric chloride with potassium cyanide proved unsuccessful, though it provided further evidence that reduction takes place, in that the incidence of the sharp inflexion was delayed until somewhat more than 2 mols. of reactant had been added. In mercuric cyanide and complex cyanide solutions, the mercury-electrode potential appears to depend only on the concentration of bivalent mercury ions. It is not possible to study the mercuric-ion concentrations ruling during the reaction involving the formation of the complex cyanide, for the existing knowledge of the very slight ionisation of mercuric cyanide is trivial.

In addition, a titration of a solution of nickel sulphate with potassium cyanide was performed, using rolled sheet nickel as the indicator electrode, any oxide that might tend to passivate the electrode having been removed by immersion in warm hydrochloric acid immediately before use. The electrode gave quite steady potentials. A small inflexion of 50 mv. occurred on complete precipitation of the simple cyanide, whilst a large diminution in $E.M.F.$ took place just after the addition of 4 mols. of potassium cyanide. The position of this inflexion was similar to that in the corresponding glass-electrode curve. Owing to the probable irreversibility of the nickel electrode, no attempt was made to calculate the nickel-ion concentrations. The apparent normal electrode potential, E_h , of the particular nickel used was -0.101 volt (Haring and Van den Bosche, *J. Physical Chem.*, 1929, **23**, 161, found -0.231 volt; see, however, Murata, *Bull. Chem. Soc. Japan*, 1928, **3**, 253; Newbery, *J. Amer. Chem. Soc.*, 1929, **51**, 1429).

Except in the case of the silver curve, the positions of the final inflexions in these metal-electrode curves were not produced when the theoretical quantities of alkali cyanide were added to form the complex ions that are generally supposed to exist, *viz.*, $Ag(CN)_2'$ and

those of the type $M(CN)_4''$. Nevertheless, calculations have been made to ascertain whether the metal-ion concentrations of those solutions containing the complexes in the presence of potassium cyanide could be explained on the basis of equilibria $Ag(CN)_2' \rightleftharpoons 2CN' + Ag^*$ and $M(CN)_4'' \rightleftharpoons 4CN' + M''$. Hence, if the mass law were applicable, computations of the expressions $[Ag^*][CN']^2/[Ag(CN)_2']$ and $[Zn''] [CN']^4/[Zn(CN)_4'']$, etc., should yield constant values. The values of these expressions for silver, zinc, cadmium, and mercury are given in the last column of Table III. For the silver complex ion, $Ag(CN)_2'$, the "instability" expression remains constant; the mean, 4.16×10^{-22} , agrees with the values obtained by Euler (*Ber.*, 1903, 36, 2878), viz., $8-20 \times 10^{-22}$, and by Bodländer and Eberlein (*loc. cit.*), viz., 8.8×10^{-22} . The values of \bar{K} for the other complexes increase with increasing proportion of potassium cyanide. Euler (*ibid.*, p. 3400) found \bar{K} to be $8-18 \times 10^{-18}$ for $Zn(CN)_4''$ and $7-18 \times 10^{-18}$ for $Cd(CN)_4''$. In both cases the ratio $[KCN]/[K_2M(CN)_4]$ was greater than 2. For the zinc complex ion in solutions containing more than 2 mols. of potassium cyanide, \bar{K} ranged from 1.4 to 3.7×10^{-19} , whereas the corresponding values for the cadmium complex ranged from 2.56 to 1.43×10^{-18} .

Similar variations will be observed in the case of the mercuric cyanide complex, $Hg(CN)_4''$. In the presence of amounts of potassium cyanide greater than 1 mol. the constant had increased to $1.3-2.1 \times 10^{-42}$. It is significant that *E.M.F.* measurements made by Sherrill (*Z. Elektrochem.*, 1903, 9, 549; *Z. physikal. Chem.*, 1903, 43, 705; 1904, 47, 103), in which he employed more than 2 mols. excess of potassium cyanide, led to a comparable value, viz., 4×10^{-42} .

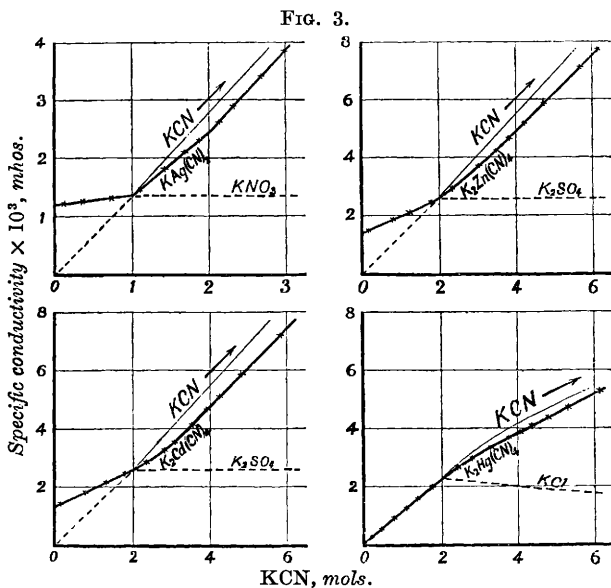
A method was devised in the previous section by which the cyanide-ion concentration could be calculated from the p_H value and the percentage hydrolysis. For the zinc, cadmium, and mercury curves both the p_H values and $-\log [M'']$ can be read off corresponding to the addition of 4 mols. of potassium cyanide to 1 mol. of salt, i.e., to the formation of $K_2M(CN)_4$, and these may be employed to calculate the respective instability constants, as shown below:

M.	$[M(CN)_4'']$ $\times 10^3$.	p_H .	p_M .	$\frac{[CN']}{[HCN]}$	$[HCN] \times 10^4$.	$[CN'] \times 10^4$.	% [CN'] from complex.	\bar{K} .
Zn	9.09	9.50	9.21	1.51	1.82	2.75	0.76	3.9×10^{-22}
Cd	9.13	10.27	10.08	8.91	1.94	17.25	4.72	8.1×10^{-20}
Hg	7.18	10.00	31.90	4.78	2.44	11.69	4.07	7.1×10^{-42}

These values of \bar{K} are of the same order as those in Table III: the lack of better agreement is probably to be ascribed to the errors inherent in the method by which $[CN']$ was calculated, very small errors in the p_H values sometimes leading to considerable differences

in $[\text{CN}^-]/[\text{HCN}]$. The foregoing table also shows that $[\text{CN}^-]$ liberated from the complex anion may be appreciable, reaching 4.7% from the cadmium complex. The effect of an increasing excess of potassium cyanide is to repress such secondary dissociation.

4. *Conductivity Measurements.*—Apart from some work by Rossi (*Gazzetta*, 1915, 45, i, 6) on the reaction of potassium cyanide with nickel and cobalt salts, the alterations in specific conductivity during the formation of complex cyanides in solution appear to have received no attention. Fig. 3 and Table IV give the specific conductivities at 25° of solutions of silver nitrate, zinc sulphate, cadmium sulphate, and mercuric chloride throughout their reactions with



potassium cyanide. The conductivities were measured with the apparatus described by Britton and German (*J.*, 1930, 1249). Dilution, v , is given in litres. The reaction between nickel sulphate and potassium cyanide was also studied, and its curve (not shown in Fig. 3) is almost identical at all points with that of zinc. On account of the precipitates involved in all these reactions, except that with mercuric chloride, the titrimetric procedure was not adopted. Instead, 10 c.c.-portions of 0.1*M*-salt solution were treated with definite volumes of 0.1*M*-potassium cyanide solution, each made up to 100 c.c., and, after thorough shaking at room temperature, were placed in the thermostat for some time before determinations were made. The mercury curve is that of a conductometric titration of 100 c.c. of 0.01*M*-mercuric chloride with 0.102*M*-potassium cyanide.

TABLE IV.

Conductivities of 100 c.c. of 0.01M-AgNO₃ and *x*M-KCN.

KCN, <i>x</i> × 10 ² .*	$\kappa_{obs.}$ × 10 ³ .	κ_{KCN} × 10 ³ .	$\kappa_{K_2M(CN)_4}^\dagger$ × 10 ³ .	<i>v.</i>	$\Lambda,$ $\frac{1}{2}K_2M(CN)_4, \ddagger$	Λ (Walden).
1.25	1.64	0	0.29	400	116.0	114.1
1.50	1.91	0	0.56	200	112.0	112.9
1.75	2.17	0	0.83	133	110.6	110.1
2.0	2.45	0	1.10	100	110.0	109.0
2.5	3.15	0.75	1.05	100	105.0	109.0
3.0	3.85	1.46	1.04	100	104.0	109.0
3.5	4.52	2.20	0.97	100	97.0	109.0

 κ_{KNO_3} at $v_{100} = 1.35 \times 10^{-3}$ mho.Conductivities of 100 c.c. of 0.01M-ZnSO₄ + *x* mols. of KCN.

2.5	3.10	0	0.54	200	108.0	126.4
3.0	3.70	0	1.14	100	114.0	123.4
3.5	4.30	0	1.74	67	116.2	121.6
4.0	4.90	0	2.34	50	117.0	120.1
4.5	5.55	0.75	2.24	50	112.0	120.1
5.0	6.15	1.46	2.13	50	106.5	120.1
5.5	6.80	2.20	2.04	50	102.0	120.1
6.0	7.40	2.87	1.97	50	98.5	120.1

 $\kappa_{K_2SO_4}$ at $v_{100} = 2.56 \times 10^{-3}$ mho.Conductivities of 100 c.c. of 0.01M-CdSO₄ + *x* mols. of KCN.

2.5	3.00	0	0.44	200	88.0	117.8
3.0	3.52	0	0.96	100	96.0	116.0
3.5	4.15	0	1.59	67	106.0	114.3
4.0	4.80	0	2.24	50	112.0	112.7
4.5	5.44	0.75	2.13	50	106.5	112.7
5.0	6.10	1.46	2.08	50	104.0	112.7
5.5	6.73	2.20	1.97	50	98.5	112.7
6.0	7.32	2.87	1.89	50	94.5	112.7

 $\kappa_{K_2SO_4}$ at $v_{100} = 2.56 \times 10^{-3}$ mho.Conductivities of 100 c.c. of 0.01M-NiSO₄ + *x* mols. of KCN.

2.5	3.11	0	0.55	200	110.0	138.7
3.0	3.70	0	1.14	100	114.0	134.5
3.5	4.30	0	1.74	67	116.1	131.7
4.0	4.90	0	2.34	50	117.0	129.4
4.5	5.50	0.75	2.19	50	109.5	129.4
5.0	6.12	1.46	2.10	50	105.0	129.4
5.5	6.72	2.20	1.96	50	98.0	129.4
6.0	7.32	2.87	1.89	50	94.5	129.4

 $\kappa_{K_2SO_4}$ at $v_{100} = 2.56 \times 10^{-3}$ mho.* Since [AgNO₃] × 10² = 1.0, KCN × 10² also represents mols. of KCN per mol. of AgNO₃, and similarly for other salts except HgCl₂.† $\kappa_{KAg(CN)_2}$ for silver.‡ Λ , KAg(CN)₂ for silver.Conductometric titration of 100 c.c. of 0.01M-HgCl₂ with

0.102M-KCN at 25°.

Mols. KCN HgCl ₂ .	$\kappa_{obs.}$ × 10 ³ .	κ_{KCl} × 10 ³ .	κ_{KCN} × 10 ³ .	$\kappa_{K_2Hg(CN)_4}$ × 10 ³ .	<i>v.</i>	$\Lambda,$ $\frac{1}{2}K_2Hg(CN)_4,$	Λ (Walden).
2.5	2.69	2.22	0	0.47	248	116.9	124.8
3.0	3.06	2.15	0	0.91	130	118.0	121.3
3.5	3.42	2.08	0	1.34	89.6	120.0	119.2
4.0	3.80	2.00	0	1.80	69.5	125.3	117.7
4.5	4.15	1.95	0.54	1.66	72.0	119.6	118.0
5.0	4.49	1.91	1.00	1.58	74.5	117.7	118.1
5.5	4.79	1.84	1.43	1.52	76.9	116.9	118.2
6.0	5.06	1.78	1.86	1.42	79.4	112.7	118.4

The curves in Fig. 3 indicate by a "break" the point at which the double decompositions end, *viz.*, with 1 mol. of potassium cyanide in the silver reaction and with 2 mols. in the others. In the cadmium curve, the end-point is not definite. The curves also show a change in slope during the addition of the potassium cyanide required to form the complex cyanide, though it is only in the case of silver that the termination of complex formation is marked by a well-defined end-point. That potassium cyanide was being removed to form the different complexes is apparent from the divergence of the observed curves from the upper thin lines, marked KCN, which indicate the specific conductivities that would have been found had none of the potassium cyanide entered into a further reaction. The broken lines represent the contributions to the specific conductivities of the potassium nitrate, sulphate, or chloride, formed as the result of metathesis. The specific conductivities of these salts in the dilutions in which they were formed were calculated from the data published in the International Critical Tables. In the first stage of the mercury reaction practically the whole of the measured conductivity was due to the potassium chloride formed: according to Grotrian (*Wied. Ann.*, 1883, **18**, 177), the specific conductivity of a mercuric chloride solution at a dilution of 59.17 is 5.71×10^{-5} at 25°.

The only figures available for the conductivity of potassium cyanide are two determinations, *viz.*, of 0.5*M*- and 1*M*-solutions, by Kohlrausch (*ibid.*, 1879, **6**, 1, 145) at 18°. A determination of the conductivity of this salt at 25° was therefore carried out at a number of dilutions, some of the measured values being quoted below. The salt used was a recrystallised "A.R." product.

Conductivities of potassium cyanide at 25°.

<i>v</i>	20	40	60	80	100	120
$\kappa \times 10^3$	6.85	3.53	2.42	1.84	1.47	1.22
Λ	137.0	141.2	145.2	147.2	147.0	146.4
<i>v</i>	140	160	180	200	220	240
$\kappa \times 10^3$	1.05	0.931	0.834	0.756	0.695	0.639
Λ	147.0	148.9	150.1	151.2	152.9	153.3

The analysis of the conductivity measurements given in Table IV postulates the formation of complexes of the type $K_2M(CN)_4$ in the cases of zinc, cadmium, mercury, and nickel, and $KAg(CN)_2$ for silver. At various points on the curves the specific conductivity of the complex is found by subtraction of the specific conductivities of the potassium salt formed by metathesis, and of the excess potassium cyanide, from the observed specific conductivity. The equivalent conductivities of the complexes are then obtained at the respective dilutions, and are compared with the values obtained by Walden (*loc. cit.*) for solutions prepared directly from the crystalline bodies. It will be noticed that, except for mercury, the figures in the last

column are consistently higher than those in the preceding column, and that the equivalent conductivities of the complexes decrease with increasing concentration of free potassium cyanide. It has already been shown that there is a very appreciable concentration of cyanide ions in solutions of the complexes, due both to hydrolytic action and to the ionisation of the complex anion, and hence the conductivity of such solutions would tend to be higher than if the complex merely ionised normally. Presence of free potassium cyanide would repress this dissociation and so give a truer value of the conductivity of the complex salt. The values obtained by Walden were made with solutions in which the simple cyanides, as will be understood from the reactions here investigated, are only just held in solution, and further dissociation of the complex anion is at a maximum. It is noteworthy that, in the case of silver, where hydrolytic action is negligible, the values obtained by the authors are in closest agreement with those of Walden.

Summary.

(1) The progressive formation in dilute solution of the complex cyanides of silver, zinc, cadmium, mercury, and nickel has been investigated by means of (a) the glass electrode, (b) metal-electrode potentials, (c) conductivity measurements.

(2) The amounts of free cyanide ions in the complex cyanide solutions have been calculated from the p_H values and extents of hydrolysis, and evidence has been secured for $Ag(CN)_2'$ and $M(CN)_4''$, where $M = Zn, Cd, Hg, Ni$. With cadmium, there also exists an anion having a lower cyanogen content.

(3) The metal-potential curves usually comprise a distinct section corresponding to complex formation. In the case of silver, satisfactory values of the solubility product $[Ag^+][Ag(CN)_2']$ have been calculated. The "instability constants" of the complex ions, except in the case of $Ag(CN)_2'$, are shown to increase with increasing proportion of cyanide.

(4) A determination of the hydrolysis of the mercury complex cyanide in the presence of varying amounts of free potassium cyanide has been carried out.

(5) The conductivity of potassium cyanide has been measured at 25° for a number of dilutions.

The authors wish to acknowledge a grant made by the Government Grants Committee of the Royal Society, and one of us (E. N. D.) thanks the Department of Scientific and Industrial Research for a grant which made this collaboration possible.