CCCXIX.—*Physico-chemical Studies of Complex Formation involving Weak Acids. Part I. The Hydrolysis of Complex Cyanides.*

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With the exception of mercuric cyanide, soluble normal cyanides are formed only by interaction of the acid with strong metallic bases, and in solution they suffer appreciable hydrolysis. This is in strict accordance with the extreme weakness of hydrocyanic acid, K being $4{\cdot}5 \times 10^{-10}$ (Britton and Robinson, this vol., p. 469). Moreover, the hydrogen-ion concentrations of solutions of hydrogen cyanide are too small to effect the dissolution of such weak bases as ferric hydroxide. For instance, in this case the acid is incapable of establishing a p_H value of 2, at which stage the base begins to be precipitated from ordinary solutions; yet in conjunction with alkali cyanides ferric hydroxide is able to combine with hydrocyanic acid in the form of well-defined and readily soluble salts. Such salts are usually regarded as those of complex acids, though hitherto there has been very little evidence concerning the precise nature of cyanide complexes in solution.

Electrical transference experiments have indicated that the weak base exists, at least in part, in the anion, but other physico-chemical measurements, *e.g.*, of conductivity and *E.M.F.*, have not generally led to anything that might be regarded as wholly satisfactory quantitative proof of the constitution of the complex ions themselves. Conductivity measurements lead to abnormally high mobilities for the supposed complex cyanide anions, which, except for those of complex metallic ammine kations (compare King, J., 1925, **127**, 2109), are without parallel. As a general rule, the heavier ions have the lower mobilities, as, for example, the anions of the higher fatty acids.

Coupled with this anomaly is the fact that the Ostwald–Walden basicity rule does not often supply unequivocal proof of the existence of the ions that had been assumed on the basis of the composition of the crystalline salts from which the solutions were prepared. Osmotic pressure and cryoscopic measurements have also led to unsatisfactory conclusions.

In view of the unsatisfactory state of the chemistry of solutions of complex cyanides, it was decided to make further investigations, particularly to see whether the acidic nature of hydrocyanic acid could be correlated with the formation of cyanide complexes, as it was felt that it must be involved even in complex reactions taking place in solutions.

This paper contains the results of some measurements of the hydrolysis of solutions containing the complexes, which are usually believed to exist, in presence of various proportions of potassium cyanide. For this purpose, the hydrogen electrode could not be used for obvious reasons, nor antimony and tungsten electrodes on account of their uncertain reproducibility in such solutions. A comparatively recent vapour-pressure method which gave promise was that of Worley and Brown (J., 1917, **111**, 1057), later used by Harman and Worley (*Trans. Faraday Soc.*, 1924, **20**, 502).

EXPERIMENTAL.

Air was drawn through a flask containing a solution of the cyanide undergoing test and was thereafter bubbled through 10 c.c. of a 0·2% solution of picric acid in 2% sodium carbonate, contained in a test-tube. This was connected in series with a similar flask, containing a volume (equal to that of the complex cyanide solution) of hydrocyanic acid solution of a suitable concentration, and a test-tube of sodium picrate solution. After air had been bubbled through the apparatus very slowly for about 30 minutes, the tubes containing the picrate solution were removed and placed in boiling water for 2—3 minutes. This caused brown colours to be developed, the intensities of which were dependent on the amounts of hydrocyanic acid absorbed, and consequently on the amounts of free hydrocyanic acid in the two cyanide solutions. Trials were performed with different known concentrations of hydrocyanic acid until a known and a test picrate solution produced colours of the same intensity when compared by means of the light emitted by a Mazda "daylight lamp." The apparatus was completely immersed in an electrically regulated thermostat at 25·0° and the air used was previously passed through a long tube packed with soda-lime.

(i) *Potassium Cyanide Solutions.*—Before this method of studying complex cyanide solutions was adopted, it was tested on a series of potassium cyanide solutions of the same concentrations reported by Harman and Worley (*loc. cit.*). The two sets of results are compared in Table I.

TABLE I.

Conc. KCN, *M.*	HCN hydrolysed, %.	$K_h \times 10_5$ (B. & D.).	$K_{HCN} \times 10^{10}$.	$K_h \times 10^5$. (H. & W.).
0·245	1·00	2·50	5·01	2·63
0·098	1·59	2·51	5·01	2·50
0·049	2·29	2·62	4·79	2·52
0·0245	3·18	2·56	4·90	2·51
		Mean 2·55	4·93	2·54

The values of the hydrolysis constant, K_h, given in columns 3 and 5 are in remarkably good agreement. Moreover, the calculated mean value of K_{HCN}, $4{\cdot}93 \times 10^{-10}$, ($p_{K_{\mathrm{HCN}}} = 9{\cdot}31$) agrees with that previously obtained by the present authors (this vol., p. 469), *viz.*, $4{\cdot}52 \times 10^{-10}$ ($p_{K_{\mathrm{HCN}}} = 9{\cdot}35$).

(ii) *Complex Cyanide Solutions.*—The complex solutions were prepared by adding various amounts of potassium cyanide to solutions of metallic salts—the nitrate was used in the case of silver, and the sulphate in the case of zinc, cadmium and nickel. The solutions of potassium ferrocyanide, ferricyanide and cobalticyanide were prepared directly from the complex salts. The purity of the potassium ferricyanide was confirmed by the titrimetric method of Müller and Diefenthaler (*Z. anorg. Chem.*, 1910, **67**, 448) and the cobalticyanide was purified by recrystallisation. The results obtained are in Table II. The figures given in the sixth column were calculated on the assumptions that the various complex cyanides did not hydrolyse to give free hydrocyanic acid, nor greatly affect the hydroxyl ion concentration of the solutions, and that the hydrocyanic acid originated solely from the excess of potassium cyanide. For this purpose, the mean value of the hydrolysis constant, $2{\cdot}55 \times 10^{-5}$, was used.

Table II shows that no hydrolysis occurred in solutions of $KAg(CN)_2$, $K_2Ni(CN)_4$ and $K_4Fe(CN)_6$. The first set of data refers to a solution prepared from the crystalline complex potassium silver cyanide. The absence of hydrolysis in the silver complex solution was confirmed by the fact that no colour change was produced when the picric acid indicator was warmed in a solution of the salt.

No trace of hydrogen cyanide could be liberated from potassium ferrocyanide solutions, even by bubbling air for very considerable periods. Potassium zinc cyanide and potassium cadmium cyanide are slightly hydrolysed, though it appears from Table II that the effect of excess of potassium cyanide is to repress the hydrolysis rather than to make it greater as might have been expected. The hydrogen cyanide present in the silver and ferrocyanide solutions that contained an excess of potassium cyanide appears to be adequately accounted for as having been hydrolysed from the simple cyanide, leaving the complexes intact. No explanation can be given for the slight excess of hydrocyanic acid found in potassium nickel cyanide solutions containing small proportions of potassium cyanide.

No trace of hydrolysis was found in freshly prepared solutions of potassium ferricyanide and cobalticyanide, but when solutions containing free potassium cyanide were made up, hydrocyanic

Table II.

		Conc., *M*.		Conc. HCN × 10^4.		%
		Complex cyanide.	KCN.	Obs.	Calc.	Hydrolysis of complex.
$KAg(CN)_2$	—	0·0933	0	0	0	0
,,	—	0·0320	0	0	0	0
,,	—	0·0082	0	0	0	0
,,	+ 2·00 KCN	0·0197	0·0393	9·9	9·9	0
,,	+ 3·98 ,,	0·0141	0·0562	11·9	11·8	+ 0·02
,,	+ 8·00 ,,	0·0089	0·0714	13·2	13·3	– 0·06
,,	+ 11·98 ,,	0·0066	0·0785	13·8	14·0	– 0·16
$K_2Zn(CN)_4$	—	0·0198	0	3·8	0	0·50
,,	+ 1·00 KCN	0·0165	0·0165	9·0	6·4	0·40
,,	+ 1·99 ,,	0·0149	0·0297	10·5	8·6	0·33
,,	+ 3·90 ,,	0·0116	0·0451	10·8	10·6	0·04
,,	+ 5·99 ,,	0·0095	0·0567	11·9	11·9	0·00
$K_2Cd(CN)_4$	—	0·0245	0	5·0	0	0·53
,,	+ 1·00 KCN	0·0196	0·0196	9·1	6·9	0·28
,,	+ 2·00 ,,	0·0167	0·0347	11·0	9·3	0·26
,,	+ 4·00 ,,	0·0115	0·0460	11·2	10·7	0·11
,,	+ 6·00 ,,	0·0094	0·0565	11·8	11·8	0·00
$K_2Ni(CN)_4$	—	0·0201	0	0	0	0
,,	+ 1·00 KCN	0·0167	0·0168	7·8	6·4	0·21
,,	+ 2·01 ,,	0·0143	0·0288	9·8	8·4	0·24
,,	+ 4·00 ,,	0·0114	0·0456	10·6	10·6	0·00
,,	+ 6·00 ,,	0·0094	0·0565	11·8	11·9	– 0·02
$K_4Fe(CN)_6$	—	0·1000	0	0	0	0
,,	+ 1·00 KCN	0·0253	0·0253	7·8	7·9	– 0·01
,,	+ 2·00 ,,	0·0170	0·0339	9·2	9·2	0
,,	+ 4·00 ,,	0·0102	0·0409	10·0	10·1	– 0·01
,,	+ 6·00 ,,	0·0073	0·0438	10·5	10·4	+ 0·01

acid was liberated far in excess of that due to hydrolysis of the potassium cyanide. Moreover, these amounts of hydrocyanic acid were much too large to be measured by the method here employed, even after dilution of the solutions. In order to eliminate any possible photochemical decomposition, the determinations were repeated in the absence of light, but with the same result. The solution of ferricyanide was stable for several days in the absence of light, but the cobalticyanide solution became hydrolysed to the extent of 0·1% on standing for a week. When the ferricyanide solution was refluxed for 30 minutes, decomposition ensued with liberation of hydrocyanic acid and deposition of a trace of ferric hydroxide. The amount of free hydrocyanic acid was estimated by distillation into silver nitrate solution and subsequent weighing of the precipitated silver cyanide : this indicated hydrolysis of the ferricyanide to the extent of 0·5%.

It would appear from the foregoing measurements that the complex cyanides enumerated in Table II are exceptionally stable, despite the fact that alkaline solutions are produced when an excess of potassium cyanide is added. It happens, however, that the metallic bases involved are moderately strong, especially when considered from the standpoint of the p_H values at which they become precipitable and the extent of hydrolysis of their salts with strong acids. Although potassium ferricyanide and potassium cobalticyanide solutions do not hydrolyse, it is significant that appreciable hydrolysis ensues on addition of an excess of potassium cyanide, when it is remembered that ferric and cobaltic hydroxides are the only very weak bases considered.

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