365. *Physicochemical Studies of Complex Formation involving Weak Acids. Part VII. Hydroferrocyanic Acid, and the Precipitation of Ferrocyanides of Silver, Lead, Copper, Zinc, Cadmium, Cobalt, Nickel, and Manganese.*

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Malaprade (*Ann. Chim.*, 1929, **11**, 136) has shown by quinhydrone and hydrogen-electrode titrations that hydroferrocyanic acid is intermediate in strength between hydrochloric and sulphuric acids. As he admits, both electrodes are apt to give erroneous results; consequently we have used the glass electrode for the same purpose, and found the acid to be a little weaker than sulphuric acid, for in 0·00936*M*-solution it is but 33·7% ionised.

In view of the high strength of the acid, basic salts are not produced when potassium ferrocyanide reacts with solutions of heavy-metal salts. Only in a few instances are the normal ferrocyanides precipitated, however, the substances containing alkali ferrocyanides partly on account of chemical combination and partly as the result of adsorption by the highly colloidal precipitates. Treadwell and Chervet (*Helv. Chim. Acta*, 1922, **5**, 633; 1923, **6**, 550) have titrated various salt solutions with alkali ferrocyanides, using as indicator a platinum electrode in the presence of a little potassium ferrocyanide in the salt solution. This method was previously used by Knauth (Diss., Dresden, 1915), Hedrich and Müller (*Z. angew. Chem.*, 1919, **32**, 351), Treadwell and Weiss (*Helv. Chim. Acta*, 1919, **2**, 680), Bichowski (*Ind. Eng. Chem.*, 1917, **9**, 668), and Niemz (Diss., Dresden, 1920). Such electrometric titrations merely show when the ferrocyanide has finished reacting and give no idea of the manner in which the precipitations proceed. In a similar way, Kolthoff (*Z. anal. Chem.*, 1923, **62**, 209) used the conductometric titration method but, being concerned only with the positions of breaks, he neither determined the conductivities that were set up nor interpreted his titration graphs in detail.

Experimental.

Hydroferrocyanic acid, prepared by precipitation from a saturated solution of pure potassium ferrocyanide with concentrated hydrochloric acid, was separated, dissolved in alcohol, and reprecipitated with ether. 100 C.c. of 0·00936*M*-hydroferrocyanic acid were titrated at 18° with 0·198*N*-sodium hydroxide, the glass electrode–condenser–ballistic galvanometer system being used. The addition of exactly 4 equivalents of alkali was marked by a well-defined inflexion in the p_H curve. Sufficient of the data to construct the curve are given below :

NaOH, equivs.	0	0·5	1·0	1·5	2·0	2·5	3·0	3·5	3·75	4·0
p_H	1·90	1·94	2·03	2·14	2·33	2·62	3·09	3·74	4·40	11·30

The p_H values are consistently higher than those recorded by Malaprade, and indicate that, although hydroferrocyanic acid behaves as a strong acid in each of its four stages of ionisation, yet it is not quite as strong as sulphuric acid.

The precipitation of heavy-metal ferrocyanides was studied by means of conductivity measurements at 25° : first, in the form of direct conductometric titrations, and secondly, by means of several series of mixtures of the reactants which had been placed in stoppered bottles in a thermostat until equilibrium had been obtained, each bottle being given a thorough shaking daily. Fig. 1 gives the conductometric titration curves obtained for the titration of 100 c.c. of 0·025*M*-metal salt solution with 0·1*M*-potassium ferrocyanide. In the case of silver and lead, the nitrates were used, but in all other cases the sulphates were employed. The broken lines represent the specific conductivities due to the potassium sulphate formed in accordance with the equation

$$2MSO_4 + (1 + x)K_4Fe(CN)_6 \longrightarrow M_2Fe(CN)_6,xK_4Fe(CN)_6 + 2K_2SO_4.$$

FIG. 1.

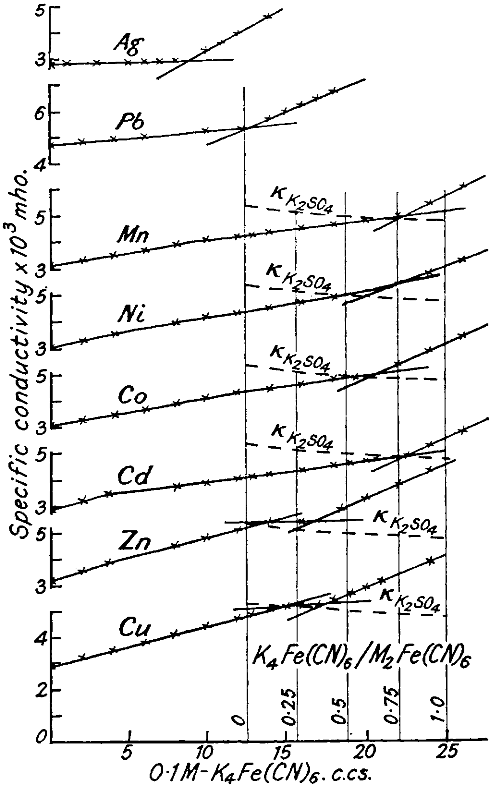

FIG. 2.

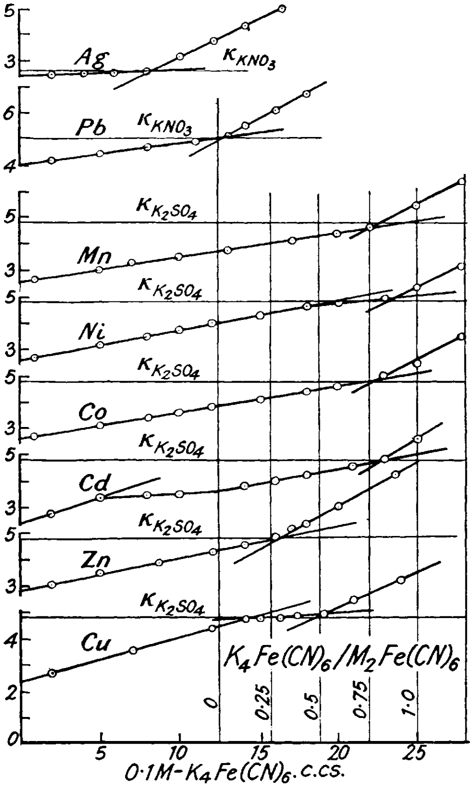

Fig. 2 gives the curves constructed from data corresponding to equilibrium conditions of 125 c.c. of 0·02*M*-salt solutions containing varying quantities of 0·1*M*-potassium ferrocyanide, and the horizontal lines represent the specific conductivity of the potassium sulphate formed as the result of the reactions indicated by the foregoing equation.

Only from the lead nitrate solution was the normal ferrocyanide precipitated. This was indicated both by the incidence of the break, *i.e.*, at $1K_4Fe(CN)_6 : 2Pb(NO_3)_2$, and also by the fact that the specific conductivity then obtained was such as would have been caused by the theoretical concentration of potassium nitrate. Gravimetric analysis of precipitates produced both with less and with more than the stoicheiometric amounts of potassium ferrocyanide gave Pb/Fe = 2·04 and 1·98 respectively. The reaction has also been confirmed by a potentiometric titration with a lead electrode. (In order to get an electrode that would give reproducible potentials, a long stick of pure lead was plated in 0·1*M*-lead nitrate solution for 3 hours at a very low current density.) There was no marked change in lead-ion concentration until the point representing the complete precipitation of lead ferrocyanide was reached. This was accompanied by a sudden diminution in the lead potential and a well-defined inflexion. Kolthoff (*loc. cit.*) obtained a "break" in his conductometric titration curve corresponding to the precipitation of the normal ferrocyanide, so also did Niemz (*loc. cit.*) in his potentiometric curve.

Speyer (*Z. anal. Chem.*, 1928, **74**, 108) observed that the potentiometric method gave results within 1% corresponding to the precipitation of normal silver ferrocyanide, $Ag_4Fe(CN)_6$, when potassium ferrocyanide was the precipitant, and Kolthoff in his conductometric curve claims to have detected a slight break at this stage, but it is scarcely perceptible. In the titration graph in Fig. 1 no such break appears, but there is one corresponding to the precipitation of $KAg_3Fe(CN)_6$, which was also obtained by Kolthoff. Moreover, the specific conductivity of the mother-liquor was then exactly that which would have existed in solution as suggested by the equation

$$3AgNO_3 + K_4Fe(CN)_6 \longrightarrow KAg_3Fe(CN)_6\downarrow + 3KNO_3$$

the precipitate being sufficiently insoluble to have a negligible effect on the conductivity. The change in conductivity throughout the titration, however, was not sufficiently great to show with certainty whether any normal salt was not previously precipitated. The behaviour of the precipitate during the titration seems to indicate the formation of at least some normal salt which was subsequently converted into the double salt, for at first it was white and flocculent, and settled quickly, but on adding the potassium ferrocyanide in excess of 1 mol. to 4 mols. of silver nitrate the precipitate suddenly became pale bluish, very fine in texture, and much remained in a turbid suspension. Analysis of the precipitate formed when 0·5 mol. of potassium ferrocyanide had been added gave $Ag/Fe = 3{\cdot}96$, showing that the normal salt alone was originally precipitated. Analysis of the precipitate formed with a slight excess confirmed its complete conversion into the double salt.

The precipitation was again followed by means of the variation in silver-ion concentration using a silver electrode. By carrying out the titration as rapidly as possible (the potential being quickly reached), the curve became inflected when 2% more potassium ferrocyanide had been added than was necessary to form $Ag_4Fe(CN)_6$, evidently owing to formation of a little double salt. It thus appears that two successive reactions, *viz.*, (1) precipitation of normal ferrocyanide, (2) its transformation into $KAg_3Fe(CN)_6$, took place. As the latter reaction is heterogeneous, time will be required, and consequently the more rapid potentiometric methods will give end-points with less precipitant than in the slower conductometric method.

With the exception of the cadmium graphs in both Figs. 1 and 2, the change in specific conductivity, as shown by the manganese, nickel, cobalt, zinc, and copper graphs, is almost rectilinear, ending at the intersection of the theoretical " salt line " when rather more than the stoicheiometrical amounts of reactant had been added. These uniform changes point to the precipitation of double ferrocyanides, $M_2Fe(CN)_6,xK_4Fe(CN)_6$. The values of x, calculated from the quantity of potassium ferrocyanide then added, are given in the following table. In several instances, *e.g.*, with copper, the addition of more potassium ferrocyanide causes but little change in conductivity from that corresponding to the theoretical amount of potassium sulphate, until points are reached when the final sections of the graphs begin, indicating the passage of free potassium ferrocyanide into the mother-liquors. These pauses are evidently caused by the absorption by the precipitates, either chemically or physically, of potassium ferrocyanide, the total amounts being given by the values of x corresponding to the second breaks.

	Titration.				Equilibrium.				
	1st Break.		2nd Break.		1st Break.		2nd Break.		Value of x
	C.c.	x.	C.c.	x.	C.c.	x.	C.c.	x.	in ppts.
Cu	14·5	0·16	17·5	0·40	14·0	0·12	18·7	0·52	0·52—0·71
Zn	13·7	0·10	16·6	0·33	—	—	16·4	0·31	0·71—0·78
Cd	—	—	22·5	0·80	—	—	23·0	0·84	0·59—0·90
Co	—	—	20·4	0·63	—	—	22·3	0·78	0·50—0·74
Ni	18·7	0·50	22·2	0·78	19·7	0·58	23·4	0·87	0·56—1·22
Mn	—	—	22·25	0·78	—	—	23·0	0·84	0·83—0·92

Analysis of the various precipitates was of little use in determining their exact composition, since they were all very colloidal and became peptised before they could be washed entirely free from entrained substances. However, the ratios of metal to iron in precipitates obtained (i) with about half the quantity of potassium ferrocyanide required for complete precipitation and (ii) with a small excess were determined. For instance, from copper sulphate solution the first precipitate was the normal ferrocyanide containing a little entrained copper sulphate, whereas with excess of potassium ferrocyanide the precipitate was $Cu_2Fe(CN)_6,0{\cdot}71K_4Fe(CN)_6$. As the final break in the conductometric graph indicated $Cu_2Fe(CN)_6,0{\cdot}52K_4Fe(CN)_6$, it appears that the increase in the potassium ferrocyanide content must have been due to entrainment. All the other precipitates contained the normal ferrocyanide and varying amounts of the potassium salt which were slightly higher than those indicated by the graphs, as shown in the last column of the above table.

Numerous double ferrocyanides have been reported which, in general, do not contain more than 1 mol. of potassium ferrocyanide per mol. of normal heavy-metal ferrocyanide. The conductometric curves here described show, not only that double salts are formed, but that they are sparingly soluble. On the present evidence, however, it does not seem justifiable to discriminate between the double salts as to which are definite compounds. Such information can only be satisfactorily obtained from an extended phase-rule study.

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