CCCCXXXI.—*A Phase-rule Study of the Zinci-, Cadmi-, Mercuri-, and Nickelo-cyanides of Potassium.*

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As several points of interest arose in a previous investigation on the cupro-, argento-, auro-, and thallo-cyanides of potassium (Bassett and Corbet, J., 1924, **125**, 1660) it appeared probable that other groups of complex cyanides would repay examination. The cyanides of zinc, cadmium, mercury, and nickel are closely allied; all form complex cyanides of the type $K_2M''(CN)_4$, whilst some give sodium salts $Na_2M''(CN)_4$ or $NaM''(CN)_3$ or both. Although previous investigations have been chiefly of a preparative or an analytical nature, the subject has also been studied from other aspects: thus, the electrical conductivities of aqueous solutions of the potassium salts under consideration have been determined at 25° by Walden (*Z. anorg. Chem.*, 1900, **23**, 373), and further electrolytic work has been carried out by Brochet and Petit (*Ann. Chim.*, 1904, **3**, 449) and by Kunschert (*Z. Elektrochem.*, 1905, **11**, 348). The chief interest in these compounds, however, lies in their use in qualitative and quantitative analysis, and a phase-rule study of the three-component systems, KCN–$Zn(CN)_2$–H_2O, etc., has afforded much information as to the conditions underlying their formation.

The System Potassium Cyanide–Zinc Cyanide–Water.

By crystallisation of a solution of zinc cyanide in aqueous potassium cyanide Rammelsberg (*Pogg. Ann.*, 1836, **38**, 364) obtained the salt $K_2Zn(CN)_4$ as colourless, octahedral crystals. This compound was investigated in more detail by Haidlen and Fresenius (*Annalen*, 1842, **43**, 129), Gmelin ("Handbook of Chemistry," 1852, VII, 424), Berthelot (*Compt. rend.*, 1899, **128**, 706), Loebe (Diss., Berlin, 1902), and Sharwood (*J. Amer. Chem. Soc.*, 1903, **25**, 570). A thermal investigation of the binary system KCN–$Zn(CN)_2$ by Truthe (Diss., Göttingen, 1912) gave no indication of complex cyanides other than the dipotassium salt.

Of the sodium zincicyanides, Rammelsberg (*Pogg. Ann.*, 1837, **42**, 114) prepared $NaZn(CN)_3,2\frac{1}{2}H_2O$ as glistening, white plates, and subsequently Loebe (*loc. cit.*) and Sharwood (*loc. cit.*) confirmed the existence of a monosodium salt, which was, however, decomposed by water with separation of a basic zinc cyanide. Although unable to obtain the monosodium salt, Herz (*J. Amer. Chem. Soc.*, 1914, **36**, 912) prepared a disodium compound, $Na_2Zn(CN)_4,3H_2O$, as efflorescent, orthorhombic crystals by crystallisation of a solution of zinc cyanide in aqueous sodium cyanide.

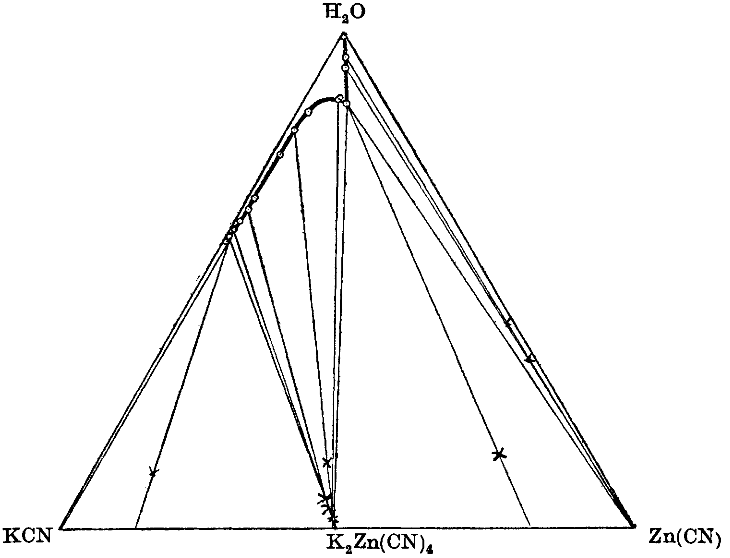
In the present investigation, the salt $K_2Zn(CN)_4$ was obtained readily as transparent, octahedral crystals by evaporation of an aqueous solution containing potassium and zinc cyanides in the molar ratio 2 : 1. By an analogous procedure the corresponding sodium compound was prepared admixed with a little sodium cyanide [Found : NaCN, 37·8; $Zn(CN)_2$, 41·1. $Na_2Zn(CN)_4,3H_2O$ requires NaCN, 36·4; $Zn(CN)_2$, 43·6%]. Thus prepared, the crystals were of indeterminate shape and stable in air. On application of pressure, however, they melted to a clear liquid from which transparent, hexagonal plates separated on evaporation. The transition point between this substance and a lower hydrate or the anhydrous salt was found to be *ca.* 52°.

In an endeavour to prepare the monosodium compound, excess of zinc cyanide was added to a 10% solution of sodium cyanide and maintained at a temperature just below the b. p. for an hour; the undissolved zinc cyanide was removed and the solution concentrated. The crystals which separated appeared to contain the mono- and di-sodium salts in the ratio 3 : 7 [Found : NaCN, 31·27;

$Zn(CN)_2$, 44·27%, corresponding to 1·67 NaCN, $Zn(CN)_2$, 3·57 H_2O], and gave a white turbidity on addition of water, confirming Sharwood's observations concerning the mono-salt. An attempt to prepare a monopotassium compound by a corresponding method yielded the salt $K_2Zn(CN)_4$.

The complex potassium zincicyanide was completely decomposed by 0·1*N*-sulphuric acid and hence it was possible to estimate the cyanogen group volumetrically: excess of acid was added to the solution and, after standing over-night, this excess was determined by titration with 0·1*N*-sodium hydroxide and methyl-orange.

FIG. 1.



An examination of the three-component system KCN–$Zn(CN)_2$ H_2O was carried out at 25° and the results are given in Table I and Fig. 1. No indication was obtained of a complex cyanide other than the well-known potassium salt. The diagram bears a striking resemblance to that representing the corresponding gold cyanide system (J., 1924, **125**, 1663), particularly in that solutions containing 20—41% of potassium cyanide contain less than 1% of zinc cyanide; the maximum solubility of the latter occurs in a solution in which the respective cyanides are present in approximately the ratio required to form the double salt. It may be seen from the figure that the solubility curve of zinc cyanide does not completely coincide with a line representing the ratio of potassium cyanide to zinc cyanide necessary to form the compound $K_2Zn(CN)_4$. This indicates that zinc cyanide is slightly soluble in a solution of potassium zincicyanide, a fact which is of importance in the cyanometric estimation of zinc (Treadwell, *Chem.-Ztg.*, 1914, **38**, 1230). By a volumetric method, depending on addition of a zinc solution to potassium cyanide until a permanent turbidity is produced, high values may be obtained, whilst low values may result if the reverse procedure is adopted. In both methods, however, the concentration of potassium cyanide is important, a 0·2*N*-solution being preferable to a 0·5*N*-solution, although Treadwell states that uncertain values may be obtained in very dilute solutions.

TABLE I.

The System $KCN–Zn(CN)_2–H_2O$ *at* 25°.

Liquid phase.		"Rest."		Comp. of solid phase.
% KCN.	% $Zn(CN)_2$.	% KCN.	% $Zn(CN)_2$.	
41·7	0·00	—	—	KCN.
41·15	Trace	77·79	10·13	KCN + $K_2Zn(CN)_4$.
39·04	Trace	51·59	44·24	$K_2Zn(CN)_4$.
37·15	0·12	—	—	
34·46	0·17	51·72	43·06	
32·65	0·20	—	—	
23·56	0·67	46·69	45·95	
18·22	0·47	47·60	39·48	
14·17	1·50	—	—	
7·65	5·75	—	—	
6·64	5·86	53·04	45·90	
6·77	6·97	16·09	68·19	$K_2Zn(CN)_4$ + $Zn(CN)_2$.
3·81	3·33	1·98	56·45	$Zn(CN)_2$.
2·50	2·30	1·52	63·93	
Trace	Trace	Trace	76·87	

The System Potassium Cyanide–Cadmium Cyanide–Water.

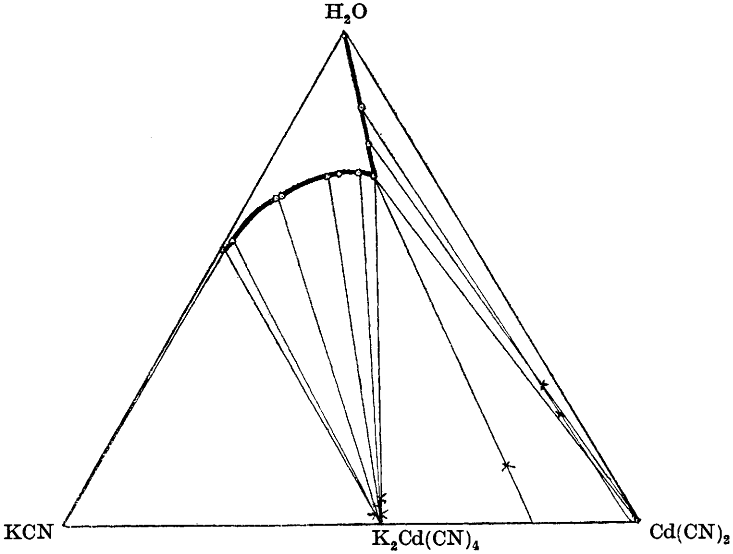
Rammelsberg (*Pogg. Ann.*, 1836, **38**, 364) described the preparation and properties of cadmium cyanide and of the dipotassium salt, $K_2Cd(CN)_4$, but later Joannis (*Compt. rend.*, 1881, **93**, 272; *Ann. Chim.*, 1882, **26**, 482) stated that the cyanide or a basic cyanide, $2Cd(CN)_2,CdO,5H_2O$, may be obtained according to the method of preparation. By mixing concentrated solutions of potassium cyanide and cadmium sulphate, and washing the adhering potassium sulphate from the precipitate, Joannis obtained the cyanide $Cd(CN)_2$ as a white, crystalline powder. Loebe (*loc. cit.*), whilst confirming the constitution of Joannis's basic compound, formulated a new substance as $3Cd(CN)_2,CdO,16H_2O$.

An unsuccessful attempt was made to prepare cadmium cyanide by Joannis's method. Very little precipitation occurred at room temperature and the product contained large and variable amounts of sulphate which could not be removed by washing. On boiling the freshly-precipitated solution a product richer in cadmium was precipitated but complete removal of sulphate was not accomplished. Employment of more dilute solutions did not yield very different results. That this behaviour may be attributed to some complex formation seems probable, for no immediate precipitation occurred on addition of cadmium sulphate to a solution of potassium cadmicyanide. On the other hand, by using cadmium nitrate, a white, amorphous powder, having the constitution

$$3Cd(CN)_2,CdO,4H_2O$$

and corresponding to Loebe's basic cyanide, was obtained.

FIG. 2.



Potassium cadmicyanide was readily prepared and its properties corresponded with those described by Haidlen and Fresenius, Gmelin, and Loebe. In addition to a sodium salt, $NaCd(CN)_3,1\frac{1}{2}H_2O$, Loebe prepared cadmicyanides of the alkaline-earth metals.

The results obtained in a phase-rule study of the system KCN–$Cd(CN)_2$–H_2O at 25° are given in Table II and plotted in Fig. 2. This system differs from any previously examined in that solutions of the double salt are capable of dissolving appreciable amounts of the cadmium cyanide. As in the zinc cyanide system the extended range of existence of the double salt indicates that it may be prepared readily, a solution of the simple cyanides in almost any ratio depositing pure crystals of the cadmicyanide on evaporation.

TABLE II.

The System $KCN\text{-}Cd(CN)_2\text{-}H_2O$ *at* 25°.

Liquid phase.		" Rest."		Comp. of solid phase.
% KCN.	% $Cd(CN)_2$.	% KCN.	% $Cd(CN)_2$.	
41·7	0·00	—	—	KCN.
40·67	0·82	44·18	53·63	$K_2Cd(CN)_4$.
28·62	4·65	43·23	55·61	
28·22	4·54	43·55	56·04	
17·79	10·70	43·11	54·56	
15·16	12·53	41·28	53·99	
11·65	16·15	43·35	49·81	
9·47	19·14	16·68	71·26	$K_2Cd(CN)_4 + Cd(CN)_2$.
* 7·82	15·73	2·07	69·48	$Cd(CN)_2$.
* 4·68	10·21	2·55	75·27	
* Trace	0·38	—	—	
* Trace	0·36	—	—	

* The solid phase in these cases was undoubtedly a basic cadmium cyanide, but the error introduced is not serious.

The System Potassium Cyanide–Mercuric Cyanide–Water.

The solubility of mercuric cyanide in water and the density of aqueous solutions of the salt have been the subject of numerous investigations. When plotted, however, the results obtained for the solubility determinations at various temperatures do not fall on a smooth curve. Mercuric cyanide readily forms double crystalline compounds with many metallic salts and, of these, a large number have been described. By crystallisation of a solution of mercuric cyanide in aqueous potassium cyanide, Rammelsberg (*Pogg. Ann.*, 1836, **38**, 364) obtained potassium mercuricyanide as transparent, octahedral crystals and showed its constitution to be $K_2Hg(CN)_4$. In addition to the sodium compound, $NaHg(CN)_3$, other mercuricyanides of various types have been prepared by Grossmann and Forst (*Ber.*, 1904, **37**, 4141).

The results of a phase-rule examination of the system $KCN\text{–}Hg(CN)_2\text{–}H_2O$ at 25° are given in Table III and plotted in Fig. 3. As in the two previous systems, the range of existence of solid potassium cyanide in contact with solutions containing the double salt is very limited. The increased solubility of potassium mercuricyanide in presence of mercuric cyanide and *vice versa* is, however, the most striking feature of the diagram.

The System Potassium Cyanide–Nickel Cyanide–Water.

Potassium nickelocyanide, $K_2Ni(CN)_4,H_2O$, was obtained as reddish-yellow, rhombic prisms by Rammelsberg (*loc. cit.*) by crystallisation of an aqueous solution of potassium cyanide containing nickel cyanide. The compound was examined further by

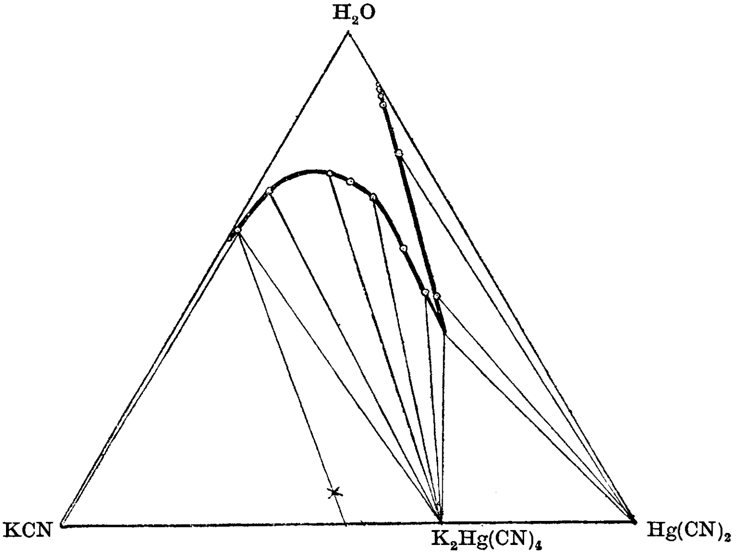
TABLE III.

The System KCN–$Hg(CN)_2$–H_2O *at* 25°.

Liquid phase.		"Rest."		
% KCN.	% $Hg(CN)_2$.	% KCN.	% $Hg(CN)_2$.	Comp. of solid phase.
41·7	0·00	—	—	KCN.
39·71	0·49	49·17	44·82	KCN + $K_2Hg(CN)_4$.
29·47	2·34	34·59	63·07	$K_2Hg(CN)_4$.
17·34	11·09	32·79	63·54	
14·54	15·54	31·42	64·01	
12·54	20·65	32·81	62·97	
12·51	31·19	33·62	64·16	
12·81	39·96	33·87	65·86	
11·37	41·85	0·81	98·02	$Hg(CN)_2$.
3·97	20·34	0·48	98·00	
* 1·09	13·53	—	—	
* 0·56	11·83	—	—	
* 0·28	10·89	—	—	
* 0·00	10·00	—	—	
0·00	10·00	0·00	81·33	

* Sherrill, *Z. physikal. Chem.*, 1903, **43**, 719.

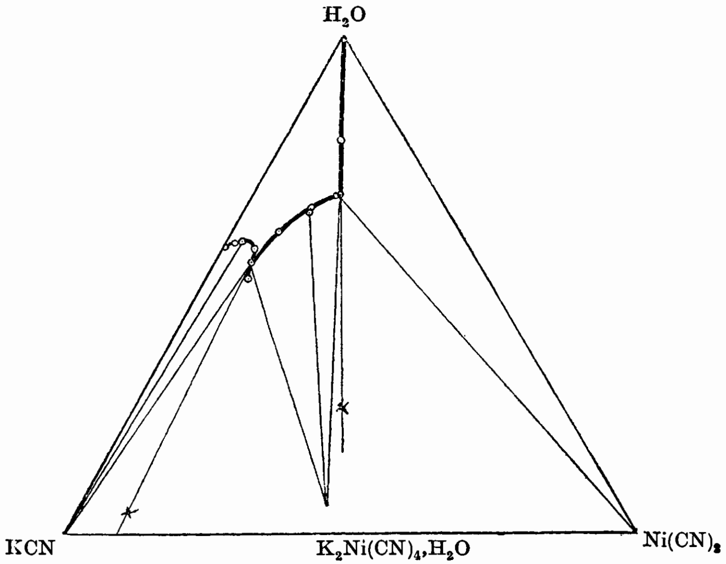
FIG. 3.



Haidlen and Fresenius (*loc. cit.*), Balard (*Compt. rend.*, 1844, **19**, 909), Gmelin (*loc. cit.*), and Clarke (*Jahresb.*, 1877, 43). Rammelsberg (*Pogg. Ann.*, 1837, **42**, 114) also prepared the sodium salt, $Na_2Ni(CN)_4,3H_2O$, and all other nickelocyanides described in the literature are of this type.

The equilibrium in the system KCN–$Ni(CN)_2$–H_2O was investigated at 25° and the results are given in Table IV and Fig. 4. The solubility curve of potassium cyanide, which can be followed into metastable regions, has a wider range of existence than in any other system in this investigation. In solutions in equilibrium with solid nickel cyanide, the simple cyanides are present in the stoicheiometrical ratio required for the double salt, a fact of interest in connexion with the cyanometric estimation of nickel (Treadwell, "Analytical Chemistry," II, 5th ed., 721). Essentially this method comprises addition of excess of potassium cyanide to a nickel solution and estimation of the excess above that required to form the salt, $K_2Ni(CN)_4$, by titration with silver nitrate. From a study of the diagram it would be anticipated that accurate results should also be obtained by the reverse process of adding nickel solution to a standard solution of potassium cyanide. The objection to such a procedure, however, lies in the difficulty of determining the exact end-point of the titration.

FIG. 4.



That potassium nickelocyanide is hydrated is a matter of interest in connexion with the Langmuir–Lewis electronic theory of valency. According to this theory, the substance $K_2Ni(CN)_4,H_2O$ has 18 electrons in the outer shell, thus representing a condition of maximum stability, such as obtains with the anhydrous compounds, $K_2Zn(CN)_4$

and $K_2Cd(CN)_4$. A similar condition is found in the salt $K_2Hg(CN)_4$, which has an outer shell of 32 electrons.

TABLE IV.

The System $KCN–Ni(CN)_2–H_2O$ *at* 25°.

Liquid phase.		"Rest."		Comp. of solid phase.
% KCN.	% $Ni(CN)_2$.	% KCN.	% $Ni(CN)_2$.	
41·7	0·0	—	—	KCN.
39·85	1·00	93·70	Trace	
38·79	1·88	93·73	Trace	
37·64	4·69	89·80	Trace	
* 41·11	6·56	91·33	0·77	
39·09	5·95	86·23	9·02	KCN + $K_2Ni(CN)_4,H_2O$.
30·94	7·46	—	—	$K_2Ni(CN)_4,H_2O$.
23·97	10·82	48·94	41·31	
23·14	10·34	47·15	39·96	
16·82	14·29	50·04	42·53	
16·82	13·94	38·15	35·92	$K_2Ni(CN)_4,H_2O$ + $Ni(CN)_2$.
10·58	9·13	—	—	$Ni(CN)_2$.
0·28	0·23	Trace	38·89	

* Metastable.

EXPERIMENTAL.

Zincicyanides.

Potassium cyanide. The best samples which could be procured commercially contained 2—3% of hydroxide. The presence of this impurity introduced a slight error in the solubility determinations when potassium cyanide was present in large amount. This difficulty was overcome by preparing the mixtures from weighed quantities of the constituents and deducting the known amount of potassium hydroxide present from the total potassium found in the liquid phase by analysis. This procedure seems justified, since James (*J. Soc. Chem. Ind.*, 1897, **16**, 120) showed that the solid deposited on evaporating a solution containing equivalent weights of potassium hydroxide and zincicyanide was practically pure $K_2Zn(CN)_4$. The figures given in the table have been thus corrected.

Zinc cyanide. The precipitate obtained by addition of a zinc salt to a solution of potassium cyanide contains a variable amount of basic cyanide. The zinc cyanide used was obtained as a microcrystalline powder by addition of excess of zinc sulphate to a warm solution of potassium zincicyanide. After standing over-night, the white precipitate of zinc cyanide was removed by filtration, washed with cold water, and dried in air.

Potassium zincicyanide. This was prepared in the manner described on p. 3191 [Found: KCN, 52·0; $Zn(CN)_2$, 47·2. $K_2Zn(CN)_4$ requires KCN, 52·5; $Zn(CN)_2$, 47·5%].

Water. All water used for the solubility determinations was boiled to remove carbon dioxide.

Solubility Determinations.—Mixtures of the double salt and potassium or zinc cyanide were made up in presence of water in wax bottles so that liquid and solid phases were present. After rotation in a thermostat at 25° for 1 or 2 days, the bottles were opened and the solid thoroughly ground. The bottles were then replaced in the thermostat for a further 4 or 5 days. On attainment of equilibrium, the liquid and solid phases were separated and analysed. This procedure was adopted in investigating the three remaining systems.

Analysis.—After decomposition of any complex present by warming with dilute hydrochloric acid, the zinc was separated as sulphide and weighed as pyrophosphate. The potassium remaining in the filtrate was estimated as sulphate. A microscopic examination of the solid phases confirmed the analyses, the double salt being obtained as crystals of indeterminate shape or, less frequently, as transparent octahedra.

Cadmicyanides.

Cadmium cyanide. Pure cadmium cyanide could not be prepared and the basic cyanide, $3Cd(CN)_2,CdO,4H_2O$, was used; by addition of a slight excess of strong cadmium nitrate solution to a concentrated solution of potassium cyanide, this substance was obtained as a white precipitate which increased in bulk on warming. After being washed with cold water and dried in air at 110°, it was analysed. The cadmium was precipitated as sulphide and weighed as sulphate. In two separate samples the cyanide was estimated (*a*) by warming with silver nitrate solution, removing the precipitated silver cyanide, igniting, and weighing the silver obtained; (*b*) by distillation with $0{\cdot}1N$-sulphuric acid, the hydrocyanic acid evolved being collected in dilute potassium hydroxide and titrated with silver nitrate. The second method can only be regarded as confirmatory, for, on distillation with dilute sulphuric acid, cyanides of the heavy metals frequently do not give a theoretical yield of hydrocyanic acid. That a theoretical yield would result in the present case seemed probable in view of the fact that cadmium cyanide is somewhat soluble in water and that potassium zincicyanide liberates 4 mols. of hydrocyanic acid under similar conditions [Found: Cd, 64·6; CN, (*a*) 22·4, (*b*) 22·4%, corresponding to $3Cd(CN)_2,CdO,4{\cdot}12\,H_2O$].

This basic cadmium cyanide was slightly soluble in water, giving a solution alkaline to methyl-orange. A distinct tendency towards formation of colloidal solutions was noted and this rendered solubility determinations of questionable value. The solid and liquid phases could not be separated by filtration, but the solution was removed in a pipette fitted with a cotton-wool filter. The results give values between 0·36 and 1·25 g. of "cadmium cyanide" per 100 g. of solution, but the most probable figure appears to be in the neighbourhood of 0·37. Joannis gives the solubility of $Cd(CN)_2$ in water as 17 g. per litre at 15°.

Potassium cadmicyanide. This was readily obtained by dissolving cadmium hydroxide in aqueous potassium cyanide and slowly evaporating the solution. The colourless, hexagonal plates which separated were crystallised from water and air-dried [Found : KCN, 44·8; $Cd(CN)_2$, 55·5. $K_2Cd(CN)_4$ requires KCN, 44·2; $Cd(CN)_2$, 55·8%].

Analysis.—Cadmium was precipitated from the cold solution by hydrogen sulphide in presence of sulphuric acid. The precipitated sulphide was removed, dissolved in hydrochloric acid, and weighed after conversion into sulphate. The potassium remaining in the filtrate was estimated as sulphate, a correction being applied as before.

Microscopic examination of the solid phases showed that the double salt occurred as colourless crystals of indeterminate shape or as transparent, hexagonal plates.

Mercuricyanides.

Potassium cyanide. Recrystallisation of potassium cyanide from 60% alcohol gave a product in which the potassium present as cyanide agreed closely with the total potassium found. The potassium cyanide thus prepared did not develop a yellow colour in aqueous solution after several days, whereas the untreated substance did so.

Mercuric cyanide. "B.D.H. pure" mercuric cyanide was twice recrystallised from hot water, colourless, anhydrous crystals being obtained. The solubilities given by Sherrill (*loc. cit.*) and Herz and Anders (*Z. anorg. Chem.*, 1907, **52**, 164) for mercuric cyanide in water at 25°, when recalculated, are respectively 10·00 and 10·13 g. of salt per 100 g. of solution, in agreement with that now found.

Potassium mercuricyanide. This was obtained as large, transparent, colourless crystals of indeterminate shape by slow evaporation of a solution containing the simple cyanides in the theoretical proportions.

Analysis.—After slight acidification with hydrochloric acid, the mercury was separated and estimated as sulphide, and the potassium remaining in the filtrate was determined as sulphate.

Under the microscope, the large, transparent crystals of the double salt were readily distinguished from those of mercuric cyanide, which showed a distinct tendency to form needles.

Nickelocyanides.

Nickel cyanide. Addition of excess of nickel sulphate to an aqueous solution of potassium cyanide yielded the nickel cyanide as a bluish-green, gelatinous precipitate. After standing overnight, it was filtered off and washed with water until free from sulphate. The colour changed to pale blue on drying at 110°.

Potassium nickelocyanide. This was readily obtained by slow evaporation of an aqueous solution of potassium cyanide saturated with nickel cyanide, the potassium cyanide having been purified by alcohol as before.

Solubility Determinations.—All the solutions were orange-yellow. When nickel cyanide was present as a solid phase, filtration was slow. More difficulty in attaining equilibrium was experienced than hitherto. An attempt to obtain the isothermal invariant point [solid KCN + $K_2Ni(CN)_4,H_2O$], by addition of solid potassium cyanide to a saturated solution of the double salt in presence of excess of solid, gave a solution containing no excess of potassium cyanide, even if the mixture was maintained at 25° for 3 weeks. The results are in Table V.

TABLE V.

Liquid phase.		" Rest."		Comp. of solid phase.
% KCN.	% $Ni(CN)_2$.	% KCN.	% $Ni(CN)_2$.	
17·08	14·24	62·66	28·43	KCN + $K_2Ni(CN)_4,H_2O$.
16·98	13·92	51·23	40·46	

The invariant point given in Table IV was readily obtained by addition of excess of potassium nickelocyanide to a saturated solution of potassium cyanide.

Analysis.—Nickel was estimated by means of dimethylglyoxime. In a further portion of the solution, slightly acidified with acetic acid, the nickel was separated by means of hydrogen sulphide, and the potassium remaining in the filtrate determined as sulphate.

Under the microscope, the double salt obtained as the solid phase was seen to consist of large, orange-yellow crystals of indeterminate shape.

Summary.

A phase-rule investigation of the systems KCN–$M(CN)_2$–H_2O (where M = Zn, Cd, Hg, or Ni) has been carried out at 25°. The conditions of concentration underlying the formation of the double salts at this temperature have thus been determined. A gradual increase occurs in the solubility of the heavy-metal cyanides in aqueous solutions of their respective double salts on passing from

zinc to mercury. A similar increase is shown in the solubilities of the complex cyanides in water.

The cyanometric estimation of zinc and nickel is discussed in the light of the results obtained.

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