

**195.** *Studies of Ionisation in Non-aqueous Solvents. Part I.  
The Formation of Certain Complex Cyanides.*

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A series of reactions between metallic salts and potassium cyanide in solution in methyl and ethyl alcohols has been studied. The results indicate a close similarity between these reactions and those taking place in water.

THE reaction between solutions of sodium and potassium cyanide and salts of various metallic bases has been investigated in aqueous solutions by Moles and Izaguirre (*Anal. Fis. Quim.*, 1921, **19**, 33) and by Britton and Dodd (J., 1932, 1940) by conductivity titrations, and also by Glasstone (J., 1929, 690; 1930, 1237), who used potentiometric titrations. No attention seems to have been paid hitherto to analogous reactions in non-aqueous solvents. To this end reactions between potassium cyanide and salts of silver, cadmium, mercury, nickel, and copper have been studied in methyl and ethyl alcohols. The dielectric constants of these liquids are lower than that of water, and their dissociating power is thus less. Nevertheless, the reactions observed in these alcohols closely resemble those in aqueous solutions.

## EXPERIMENTAL.

The methyl alcohol (*ex* water gas) was found to contain 0.25% of acetone and about 5% of water. It was purified by the method of Hartley and Raikes (J., 1925, **127**, 524) and dehydrated with aluminium amalgam, since, as these authors point out, the use of quicklime causes considerable loss of solvent. The sample used for preparing the solutions had b. p. 64—65° and was stored in Pyrex flasks and protected from atmospheric moisture. The ethyl alcohol was purified by distilling it successively over dilute sulphuric acid, solid caustic potash, and silver nitrate according to Danner and Hildebrand (*J. Amer. Chem. Soc.*, 1922, **44**, 2824), and dehydrated by refluxing with freshly burnt lime. The fraction of b. p. 78—79° was collected. Water was present in these solvents only in minute traces, as shown by adding calcium carbide to a sample and testing for acetylene with ammoniacal cuprous chloride solution (see Weaver, *ibid.*, 1914, **36**, 2462).

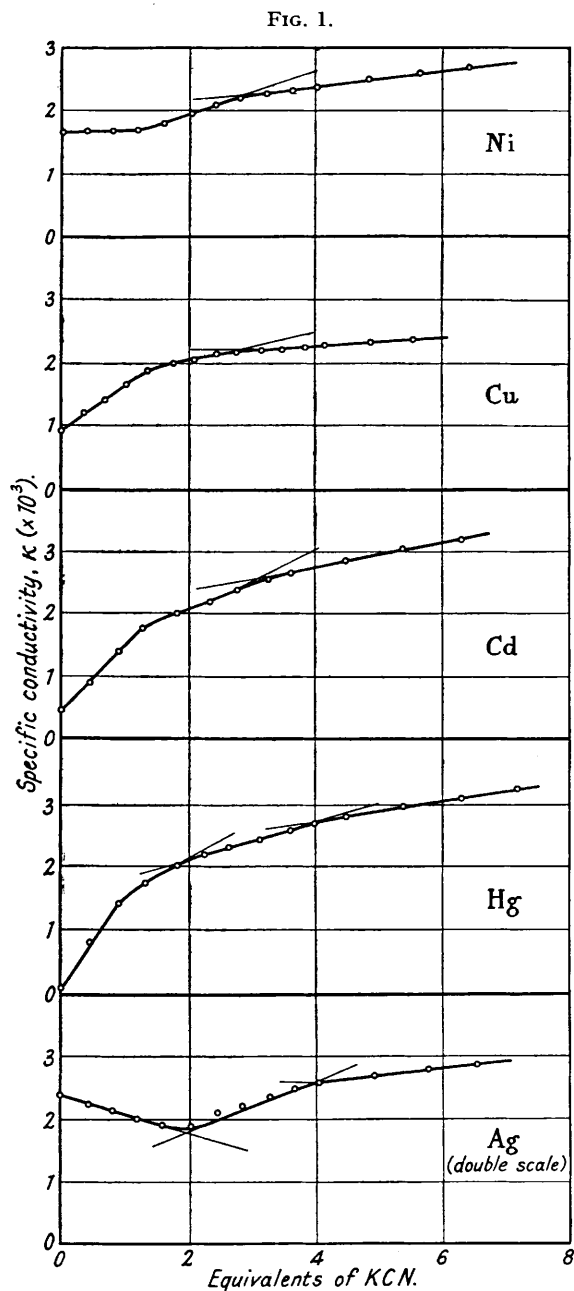
The salts used were of 'AnalaR' quality and were dehydrated where necessary and stored in vacuum desiccators over calcium chloride. Solutions of them were made by quickly weighing out the finely powdered anhydrous salt and dissolving it in the solvent. Where heating was necessary, precautions were taken to exclude atmospheric moisture. A good sample of potassium cyanide was dried at 120°, refluxed with the alcohol, cooled to room temperature, and standardised with silver nitrate by Liebig's method. Owing to the low solubility of potassium cyanide in the alcohols, it was only possible to prepare solutions of the order  $m/20$ . These were used within 2 or 3 days. If carefully stored out of contact with air in Pyrex bottles, such solutions maintained a constant conductivity over this interval, but on longer storage the solutions become yellow, recalling the behaviour of similar aqueous solutions, in which decomposition is known to take place.

The conductivity titrations were performed in well-stoppered Pyrex cells in an electrically controlled thermostat at  $25^{\circ} \pm 0.01^{\circ}$ . Resistances were measured on an accurate helicoid bridge calibrated by the makers (Messrs. H. Tinsley and Co.). Alternating current at about 1000 cycles was supplied by a Cambridge reed hummer.

Owing to the slowness of some of the reactions, the conductivities only became constant after a considerable time. The precipitates for analysis were prepared by mixing the appropriate amounts of the solutions and leaving them overnight. In most cases they were gelatinous and often difficult to filter off and wash with the appropriate alcohol. They were dried by standing over calcium chloride for several weeks in vacuum desiccators, which were re-exhausted from time to time. The cyanide content in them was found either by dropping acid on the substance and distilling off the hydrogen cyanide (Schimpf, "Manual of Volumetric Analysis," 1926, p. 277) or, in the case of the more insoluble ones, by Kjeldahl's method. The metal contents were found gravimetrically by the usual procedures.

Results of the conductivity titrations for methyl alcohol are given in Fig. 1 and for ethyl

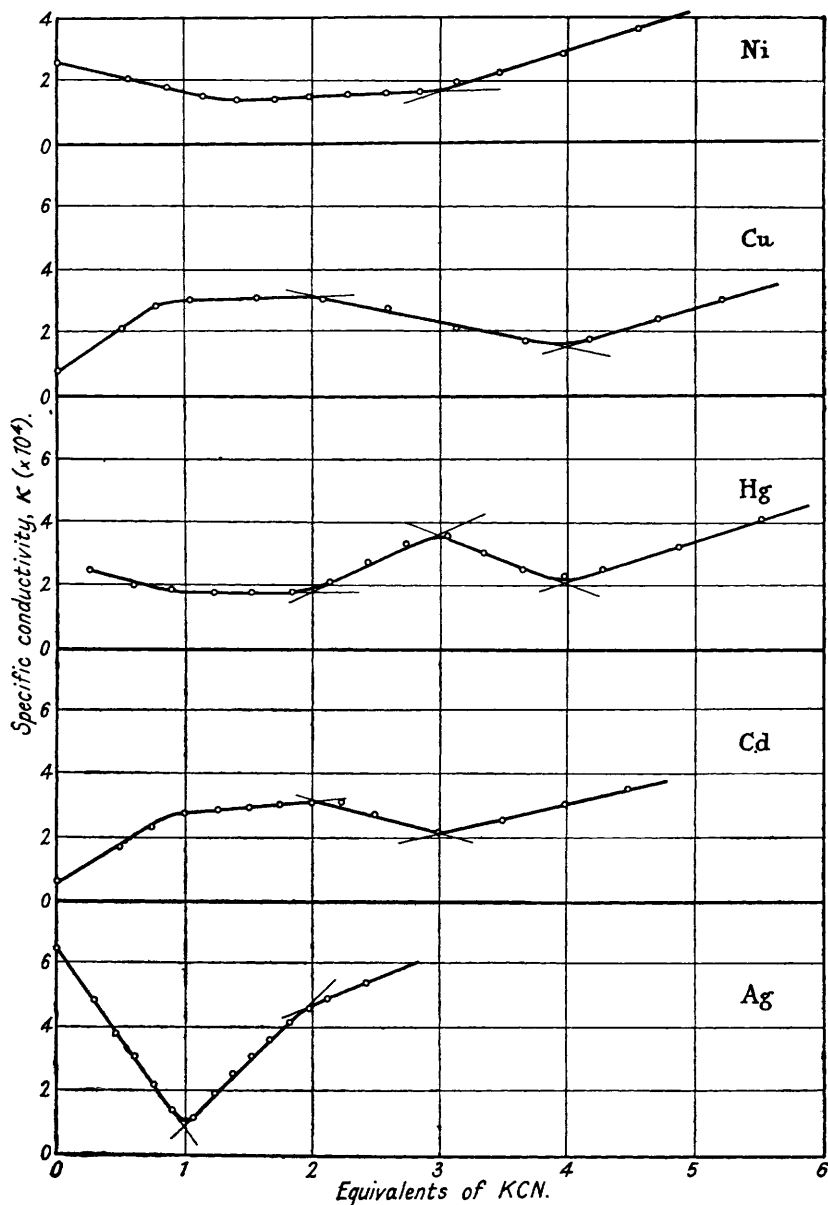
alcohol in Fig. 2. The abscissæ represent mols. of potassium cyanide per mol. of all titrates except silver nitrate, for which, in Fig. 1, 2 mols. are represented. The ordinates are conductivities.



*Potassium Cyanide and Silver Nitrate.*—In dilute aqueous solution the first reaction is the formation of silver cyanide, which then dissolves in excess cyanide forming a complex compound  $\text{KAg}(\text{CN})_2$ , which gives rise to an  $\text{Ag}(\text{CN})_2'$  ion (see Euler, *Ber.*, 1903, **36**, 2878; Bodlander and Eberlein, *Z. anorg. Chem.*, 1904, **39**, 197; Glasstone, *loc. cit.*; Britton and Dodd, *loc. cit.*; Bassett and Corbet, *J.*, 1924, **125**, 1660). There are indications that in more concentrated solutions other ions such as  $\text{Ag}(\text{CN})_3''$  and  $\text{Ag}(\text{CN})_4'''$  are formed. In the dilute

alcoholic solutions used the behaviour seems to be analogous: in both alcohols on addition of potassium cyanide there is immediate precipitation of the normal cyanide (Found, for ppt. in ethyl alcohol: Ag, 42.20; CN, 9.98%; Ag:CN = 1.02:1. Found, for ppt. in methyl alcohol: Ag, 44.51; CN, 10.70%; Ag:CN = 1:0.99).

FIG. 2.



The specific conductivity decreases until 1 equiv. of cyanide has been added, and thereafter increases as the precipitate dissolves in the excess alkali cyanide. Dissolution is complete after the addition of 2 equivs., and thereafter there is little change in conductivity. The solution of silver cyanide in excess potassium cyanide in methyl and ethyl alcohols therefore contains the ion  $\text{Ag}(\text{CN})_2'$  at these dilutions.

*Potassium Cyanide and Copper Chloride.*—In aqueous solution the compounds formed between copper salts and excess of potassium cyanide solution seem again to depend on the

concentration. Bassett and Corbet (*loc. cit.*) concluded from a phase-rule study of the system KCN—CuCN—H<sub>2</sub>O that compounds KCu<sub>2</sub>(CN)<sub>3</sub>, KCu(CN)<sub>3</sub>, and K<sub>2</sub>Cu(CN)<sub>4</sub> are formed in concentrated solutions. Kunschert (*Z. anorg. Chem.*, 1904, **4**, 359) concluded from *E.M.F.* measurements on solutions of copper salts in excess potassium cyanide that the complex ions Cu(CN)<sub>4</sub>''' and to a less extent Cu(CN)<sub>3</sub>'' were formed. Moles and Izaguirre (*loc. cit.*), from conductivity titrations, deduced the formation of a Cu(CN)<sub>4</sub>''' ion at ordinary temperatures: other compounds were formed at 0° but were not very stable. Glasstone's electrometric titration of copper cyanide with sodium cyanide solution (*loc. cit.*) points to the formation at the dilution used of Cu(CN)<sub>2</sub>' and Cu(CN)<sub>3</sub>'' ions.

In ethyl alcohol, addition of potassium cyanide to the solution of cupric chloride results in the formation of a brown gelatinous precipitate of indefinite composition; *e.g.*, that prepared by the addition of a little more than 1 equiv. of cyanide had copper and cyanide in the ratio 1 : 0.80 (Found : Cu, 28.50; CN, 9.25%). Precipitation of the copper at this point was incomplete, the solution remaining green. After the addition of 2 equivs. of cyanide precipitation was complete, and the conductivity fell as the cyanide was used to dissolve the precipitate and rose again after the addition of 4 equivs. Actually, the precipitate had dissolved to a clear solution after the addition of 3 equivs. of cyanide, pointing to the formation of a Cu(CN)<sub>3</sub>' ion, but as there is no rise in conductivity till after the addition of 4 equivs. of cyanide, it appears that this ion is not very stable and that the ultimate product is a Cu(CN)<sub>4</sub>'' ion.

In methyl alcohol, precipitation of the copper as a brown gelatinous substance which turns green later occurs immediately, and on addition of 1 equiv. of cyanide a powder was formed in which the ratio Cu : CN was 1.0 : 0.98 (Found : Cu, 56.01; CN, 21.80%). It seems therefore that, on standing, cupric cyanide decomposes into the cuprous compound in methyl alcohol as it does in water. After the addition of 2 equivs. of cyanide precipitation was complete: there was little further conductivity change and the precipitate dissolved completely to a colourless solution after the addition of 3 equivs. of cyanide. There is thus formed a Cu(CN)<sub>3</sub>' ion, though the conductivity curve does not show this as clearly as in some of the other curves.

It appears therefore that the behaviour of copper salts towards potassium cyanide is very similar in methyl and ethyl alcohols to that in water.

*Potassium Cyanide and Mercuric Chloride.*—Sherill (*Z. physikal. Chem.*, 1903, **43**, 705) concluded from his observations on the physicochemical properties of solutions of mercuric cyanide in potassium cyanide that ions Hg(CN)<sub>4</sub>'' and Hg(CN)<sub>3</sub>' could be formed in aqueous solution, and Glasstone (*loc. cit.*) confirmed this. Bassett and Corbet (*loc. cit.*) showed that a compound K<sub>2</sub>Hg(CN)<sub>4</sub> was formed in concentrated solutions, and Britton and Dodd (*loc. cit.*) concluded that this was the ultimate product.

In ethyl alcohol the addition of a small amount of potassium cyanide to mercuric chloride causes a rapid rise in conductivity. This is to be expected, since it is well known that even in water mercuric chloride behaves as a non-electrolyte. Thereafter, there is little conductivity change till 2 equivs. of cyanide have been added, the opalescence which appears at first (insufficient separates for analysis) having cleared before this stage. This probably corresponds to the formation of an indefinite compound, which is continually changing as more cyanide is added until mercuric cyanide forms. Thereafter there are breaks in the conductivity curve at 3 and 4 equivs., corresponding to the formation of Hg(CN)<sub>3</sub>' and Hg(CN)<sub>4</sub>'' ions. After the addition of 4 equivs. there is a rise in conductivity due to excess potassium cyanide.

With methyl alcohol as the solvent there is a similar behaviour, but no break corresponding to the formation of an Hg(CN)<sub>3</sub>' ion. The final product is an Hg(CN)<sub>4</sub>'' ion. There is thus again a close similarity between the reactions in water and in these alcohols.

*Potassium Cyanide and Cadmium Chloride.*—Euler (*loc. cit.*) and Bassett and Corbet (*loc. cit.*) obtained evidence for the existence of a Cd(CN)<sub>4</sub>'' ion, but Glasstone (*loc. cit.*) considered that a Cd(CN)<sub>3</sub>' ion may also be formed in aqueous solutions. Britton and Dodd (*loc. cit.*) concluded that the compound formed was K<sub>2</sub>Cd(CN)<sub>4</sub>.

In ethyl alcohol, the white gelatinous precipitate first obtained was of indefinite composition and it was difficult to obtain sufficient for an analysis. The precipitate formed on addition of 1 equiv. of cyanide contained Cd : CN = 2.13 : 1 (Cd, 36.6; CN, 3.93%). After the addition of 2 equivs. of cyanide the conductivity falls, and solution of the precipitate is complete after the addition of 3 equivs. Thereafter the conductivity rises. The complex ion formed is thus Cd(CN)<sub>3</sub>'.

In methyl alcohol there is an almost similar behaviour, but insufficient precipitate settled

for an analysis. The solution became clear after the addition of 3 equivs. of cyanide and there is a break in the conductivity curve at this point. The complex ion formed is thus similar to that formed in ethyl alcohol.

*Potassium Cyanide and Nickel Chloride.*—Rossi (*Gazzetta*, 1915, 45, i, 6) concluded from his conductivity titration of an aqueous solution of nickel chloride with potassium cyanide that a complex ion  $\text{Ni}(\text{CN})_4''$  was formed. Both Britton and Dodd's titration (*loc. cit.*) and Bassett and Corbet's phase-rule study (*loc. cit.*) support this view.

In methyl and ethyl alcohols the first gelatinous pale green precipitates are of indefinite composition (Found, for ppt. in ethyl alcohol: Ni, 20.6; CN, 16.51%; Ni:CN = 1:1.80. Found for ppt. in methyl alcohol: Ni, 27.4; CN, 21.51%; Ni:CN = 1:1.76). After the addition of 3 equivs. of cyanide solution the precipitate had dissolved in each case, and the conductivity curve showed a break. In both cases therefore the complex ion is  $\text{Ni}(\text{CN})_3'$ .

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