In fact, it might be said that if this were the first comparison of theory and experiment, agreement would be considered very satisfactory.

As for the entropy results, they do not confirm the notion that local order exists in these solutions. From Table III it is apparent that the best accounting for the entropies is in terms of a random distribution, including the observed number of Schottky defects. It should be realized, however, that the awkward way of evaluating the entropies of formation makes it difficult to assess their reliability so that conclusions based upon them must be viewed with caution. This is especially true since the vibrational contribution, which may be appreciable, is unknown. Wasastjerna follows the usual practice of factoring the partition function into vibrational and configuration parts, which assumes the vibrational modes to be independent of configuration and implies that the vibrational specific heat of the solution and the equivalent mixture are identical and ΔS(vib.) is zero. To explain the discrepancy of the observed and calculated entropy as vibrational in origin means that one of the basic theoretical tenets is in need of revision (which is undoubtedly true) and leaves questions of the internal consistency of Wasastjerna's theory to be answered.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Mechanism of the Reduction of Potassium Tetracyanonickelate(II) and Potassium Hexacyanocobaltate(III) with Potassium in Liquid Ammonia[1]

BY GEORGE W. WATT, JAMES L. HALL, GREGORY R. CHOPPIN AND PHILIP S. GENTILE

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Uncertainties remaining from earlier work on the reduction of potassium tetracyanonickelate(II) with potassium in liquid ammonia at $-33.5°$ have been clarified by means of potentiometric titrations. Two one-electron steps are involved when the salt is in excess, and one two-electron reaction when potassium is in excess. Potassium tetracyanocobaltate(I) has been shown to be an intermediate in the reduction of potassium hexacyanocobaltate(III) to potassium tetracyanocobaltate(0).

Eastes and Burgess[2] reported that addition of potassium to potassium tetracyanonickelate(II) in liquid ammonia at $-33.5°$ resulted in reduction to potassium tetracyanonickelate(I) but they were unable to reduce the latter to potassium tetracyanonickelate(0) upon addition of excess potassium. Burbage and Fernelius,[3] however, demonstrated both of these one-electron reductions in liquid ammonia at 0° but their efforts to effect both of these reactions at $-33.5°$ were successful in some cases but not in others. More recently, the reduction of another cyanide complex to a product in which the central metal atom is apparently in the zero oxidation state has been reported by Hieber and Bartenstein[4] who have demonstrated the reduction of potassium hexacyanocobaltate(III) to potassium tetracyanocobaltate(0). Particularly in view of the fact that Hume and Kolthoff[5] have provided evidence in support of the view that the reduction of the $[Ni(CN)_4]^=$ ion in aqueous media does not involve a one-electron step, it seemed worthwhile to attempt to bring another kind of evidence to bear upon the mechanism of these interesting reduction reactions. Accordingly, these reactions have been studied by means of potentiometric titration techniques developed in these laboratories[6]; the results of these experiments are described below.

Experimental

Materials.—Potassium tetracyanonickelate(II) was prepared by the method of Fernelius and Burbage.[7] *Anal.* Calcd. for $K_2Ni(CN)_4$: Ni, 24.4. Found: Ni, 24.1. In preliminary experiments, it was found that this salt is soluble in liquid ammonia at its boiling point to the extent of approximately 45 g./100 ml. of solution.

Potassium hexacyanocobaltate(III) was prepared as described by Bigelow.[8] *Anal.* Calcd. for $K_3Co(CN)_6$: Co, 17.7. Found: Co, 17.4. The solubility of this salt was found to be <0.2 g./100 ml. of solution.

Potassium samples were purified and prepared for use in the manner described previously.[6]

Potentiometric Titrations.[6]—In a typical experiment, a solution of 0.1068 g. of potassium tetracyanonickelate(II) in 40 ml. of liquid ammonia was titrated with 0.0821 *N* potassium solution. An orange-red precipitate began to form upon the first addition of potassium and the first significant change in potential was observed after addition of 5.6 ml. of potassium solution as compared with 5.4 ml. calculated on the assumption of a one-electron change. During addition of the next 3.0 ml. of potassium solution, the potential increased as shown in Fig. 1, the rate of reaction of the added potassium decreased progressively, and the color of the precipitate became increasingly intense. This titration was not carried to the tetracyanonickelate(0) stage owing to the extreme slowness with which equilibrium was reestablished after about 8.5 ml. of titrant had been added.

In a related case, 0.0659 g. of potassium dissolved in 40 ml. of liquid ammonia was titrated with 0.1401 *N* potassium tetracyanonickelate(II) solution. A brown precipitate formed immediately. As is evident from the data of Fig. 2, the end-point corresponding to the change in potential that occurred upon addition of 12.0 ml. of the cyanonickelate(II) solution is in agreement with the value of 12.0 ml. calculated on the basis of a two-electron change.

In a manner analogous to the first of the two runs described above, 0.0427 g. of potassium hexacyanocobaltate(III) and 0.168 g. of potassium iodide (as a supporting electrolyte) dissolved in 50 ml. of liquid ammonia was titrated with 0.0397 *N* potassium solution (Fig. 3). Upon addition

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[1] This work was supported in part by the Office of Naval Research, Contract N6onr-26610.

[2] J. W. Eastes and W. M. Burgess, THIS JOURNAL, **64**, 1187 (1942).

[3] J. J. Burbage and W. C. Fernelius, *ibid.*, **65**, 1484 (1943).

[4] W. Hieber and C. Bartenstein, *Naturwissenschaften*, **13**, 300 (1952).

[5] D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **72**, 4423 (1950).

[6] G. W. Watt and J. B. Otto, Jr., *J. Electrochem. Soc.*, **98**, 1 (1951).

[7] W. C. Fernelius and J. J. Burbage, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 227.

[8] J. H. Bigelow, *ibid.*, p. 225.

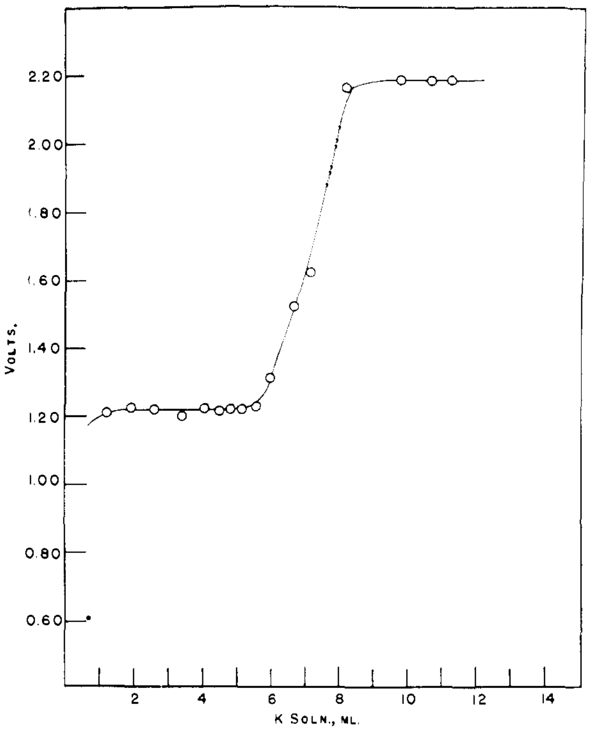

Fig. 1.—Potentiometric titration: potassium tetracyanonickelate(II) with potassium.

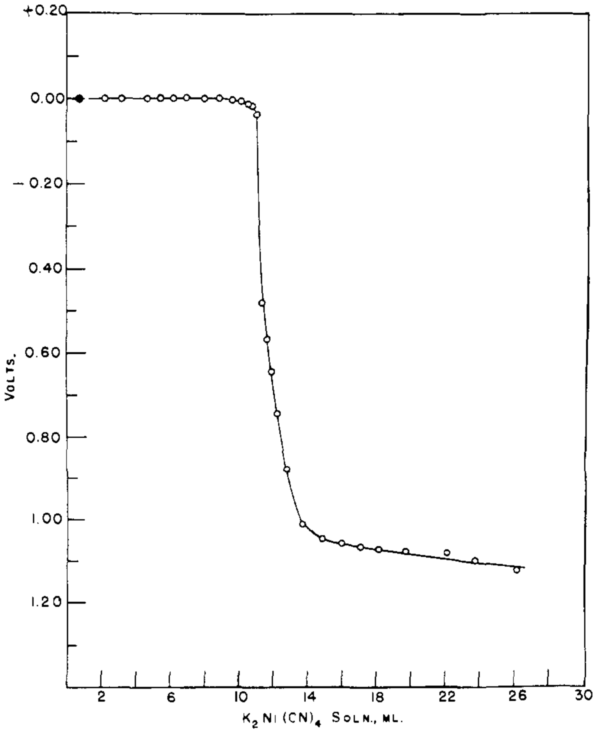

Fig. 2.—Potentiometric titration: potassium with potassium tetracyanonickelate(II).

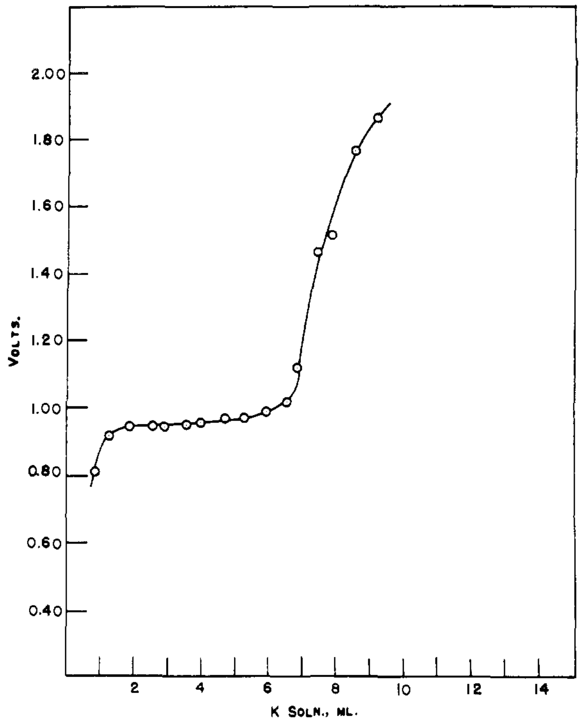

Fig. 3.—Potentiometric titration: potassium hexacyanocobaltate(III) wtih potassium.

of the first portion of titrant, the intensity of the yellow color of the initial solution increased; thereafter a yellow-brown precipitate formed upon addition of each increment of potassium solution. Coincident with the marked increase in potential upon addition of 6.9 ml. of titrant, the rate of reaction of the added potassium decreased sharply; the corresponding value calculated for a two-electron change is 7.3 ml. The titration was discontinued after addition of 9.2 ml. of potassium solution since the reaction became impractically slow. In related experiments, however, the ultimate formation of an end-product having the characteristics attributed to potassium tetracyanocobaltate(0)[4] was demonstrated. Owing to the very limited solubility of potassium hexacyanocobaltate(III) in liquid ammonia, attempts to carry out titrations involving the reverse order of addition of reactants were not conclusive.

Discussion

The data of Fig. 1 show that, in liquid ammonia at or near its boiling point, the first step in the reduction of potassium tetracyanonickelate(II) with potassium is the one-electron change

$$[\mathrm{Ni(CN)_4}]^{=} + e^- \longrightarrow [\mathrm{Ni(CN)_4}]^-$$

and the qualitative observations made during the course of the potentiometric titrations indicate that this reaction is followed by

$$[\mathrm{Ni(CN)_4}]^- + e^- \longrightarrow [\mathrm{Ni(CN)_4}]^0$$

even though this reaction is too slow at −33.5° to follow conveniently by this method. Our experience with this reduction confirms the conclusions reached by Burbage and Fernelius[3] with respect to the reactions that occur and the reasons for the relatively low rate of the second one-electron reaction. On the other hand, the data of Fig. 2 show that, when potassium is in excess, potassium tetracyanonickelate(II) is reduced directly to tetracyanonickelate(0) without intermediation of the complex corresponding to the +1 oxidation state of nickel. Information relative to the latter point was not provided by earlier workers.

With reference to the titrations involving potassium hexacyanocobaltate(III), the data of Fig. 3

show that the reduction of this salt to potassium tetracyanocobaltate(0) involves the formation of a complex of Co^{+1} as an intermediate. Hence, the first reaction that occurs is most probably the two-electron change

$$K_3Co(CN)_6 + 2K^+ + 2e^- \longrightarrow 2KCN + K_3Co(CN)_4$$

which is followed by the reduction of potassium tetracyanocobaltate(I) to the product reported by Hieber and Bartenstein,[4] *i.e.*, potassium tetracyanocobaltate(0). Attention should be called to the fact that Grube and Schächterle[9] have reported evidence for the existence of cobalt(I) from their studies on the reduction of potassium hexacyanocobaltate(III) in alkaline aqueous media at a cobalt cathode by means of potassium amalgam. Similarly, Hume and Kolthoff[10] have shown that the aquopentacyanocobaltate(III) ion is reduced to a cobalt(I) complex at the dropping mercury electrode.

[9] G. Grube and P. Schächterle, *Z. Elektrochem.*, **32**, 565 (1926).

[10] D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **71**, 867 (1949).

AUSTIN, TEXAS

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Studies on Coördination Compounds. IX. The Solution Stabilities of the Chelate Compounds of a Number of Organic Ligands

BY LEGRAND G. VAN UITERT[1] AND W. CONARD FERNELIUS

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The chelate compound species formed in solution by a number of chelating agents which coördinate through oxygen, nitrogen and combinations of the two are discussed and their stability constants in 75 vol. % dioxane–25 vol. % water solution are given. Compounds formed by chelating agents bonding through nitrogen show a greater dependency upon metal ion electronegativity than those bonding through oxygen. The following types of chelate species of divalent metal ions are found to exist in solution—for Ch, MCh^{++} and MCh_2^{++}: for HCh, MCh^+, MCh_2 and MCh_3^-; for H_2Ch, MCh and $MCh_2^{=}$; for H_3CH, MHCh and MCh^-.

Introduction

The potentiometric study of chelate compound formation not only enables one to calculate the solution stability constants for many chelate compounds, but also yields considerable interesting information concerning the chelate compound species that exist in solution. The stability constants for a number of chelate compounds of structurally different ligands have been determined in the course of investigating these relationships. Soluble coördination complexes having charges ranging from +2 to −2 are described and their solution stability constants tabulated. The constants are only applicable in the 75 vol. % dioxane–25 vol. % water solution in which they were determined.

Experimental

The apparatus and procedures that have been employed, except as noted, are as described in a previous paper.[2] The following typical solution was titrated with 0.100 *N* $(CH_3)_4NOH$: 1×10^{-4} mole of metal salt and 4×10^{-4} mole of chelating agent in 75 ml. of dioxane and 25 ml. of water.

The chelating agents were titrated alone in determining their dissociation constants (pK_D values). In the cases of 8-hydroxyquinoline and glycine, 5.8×10^{-4} mole of $HClO_4$ was also present. The solutions were titrated with 0.37 *N* $(CH_3)_4NOH$ in the latter cases. A 0.100 *M* solution of NH_4NO_3 was employed in place of the chelating agent, above, in determining the coördination constant for ammonia. In the case of ethylenediamine, 5.00×10^{-4} mole of $HClO_4$ was added to the solutions. The acid or the acid plus the metal salt was then titrated with 0.100 *N* ethylenediamine solution.

C.P. or reagent grade copper(II), nickel(II), manganese(II), zinc(II) and magnesium(II) perchlorates and ammonium and calcium nitrates were employed. Catechol, 2-acetyl-1-naphthol, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, 8-hydroxyquinoline, glycine, ethylenediamine, ethyl benzoylacetate, *d*-tartaric acid, ethyl *d*-tartrate, salicylic acid and salicylaldehyde were obtained from the Eastman Kodak Co. Benzoylpyruvic acid and ethyl benzoylpyruvate were student preparations.

The calculation procedures for the compounds involving chelating agents which lose one proton have previously been reported.[3] Briefly

$$pK_D = B + \log U_H + \log 1/\gamma^2$$

where pK_D is the negative logarithm of the dissociation constant of the chelating agent, B the *p*H meter scale reading, $\log U_H = B - \log C_{H^+}$ = a constant for a fixed solvent and mean electrolyte molality and γ is the mean stoichiometric activity coefficient for HCl of the same mean molality.[4]

For example, in a two millimolal solution containing 75 vol. % dioxane–25 vol. % water, $\log U_H = 0.75$ and $\log 1/\gamma^2 = 0.6$. Also

$$\log K_{f_1} \approx pK_D - B_{n=1/2} - \log U_H - \log C_{HCh_{n=1/2}}$$

where n is the average number of chelating agent ions associated with the metal ions per metal ion.

Hence for the above typical conditions in the case of 2-acetyl-1-naphthol with magnesium (see Fig. 1 and Table I).

$$\log K_{f_1} = 13.4 - 8.0 - 0.75 + 2.5 = 7.1 \text{ approximately.}$$

For the chelating agents which lose two protons at a time the relationship $pK_{D_{1,2}} - \log K_{f_{\alpha,\beta}} = -\log [H^+]^2/[H_2Ch]$ when $[MCh] = [M^{++}]$ is employed ($pK_{D_{1,2}} = pK_{D_1} + pK_{D_2}$; $K_{f_{\alpha,\beta}} = [MCh]/[M^{++}][Ch^{=}]$).

In the case of *d*-tartaric acid where a total of three protons is given up by the chelating agent, the first two at the same time and the third at a higher *B*-value (*p*H meter reading[3]), the above relationship is employed to find $\log K_{f_{\alpha,\beta}}$ and the relationship $pK_{D_3} - \log K_{f\gamma} = \log 1/[H^+]$ where $[MCh^-] = [MHCh]$ is employed to find $\log K_{f\gamma}$. Then (for MCh^-) $\log K_{f_{\alpha,\beta,\gamma}} = \log K_{f_{\alpha,\beta}} + \log K_{f\gamma}$. The pK_D values and the formation constants obtained are assembled in Table I.

Discussion

It has been shown in a previous paper[5] that the logarithms of the first formation constants for the

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[1] Union Carbide and Carbon Corporation Fellow 1951–1952.

[2] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 457 (1953).

[3] L. G. Van Uitert and C. G. Haas, *ibid.*, **75**, 451 (1953).

[4] H. S. Harned and J. O. Morrison, *ibid.*, **58**, 1908 (1936).

[5] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 2736 (1953).