[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Determination of the Cumulative Dissociation Constant of Tetracyanonickelate(II) Ion

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The ultraviolet absorption at 267.5 mμ provided a unique means of quantitatively determining $\text{Ni(CN)}_4^{=}$. Equilibration of nickel perchlorate and potassium cyanide systems, buffered at varying *p*H levels and ionic strengths, permitted evaluation of the cumulative dissociation constant of the complex. At 24.92° the cumulative constant was found to be $(1.0 \pm 0.2) \times 10^{-31}$.

Introduction

No satisfactory experimental value for the dissociation constant of the tetracyanonickelate(II) species has been determined. Hume and Kolthoff[1] reviewed the early investigations and indicated the values to be unreliable. Irreversibility precluded the use of thermodynamic calculations based on measured e.m.f. values. Polarographic studies on 0.1 *M* solutions of potassium tetracyanonickelate(II) in water failed to reveal an anodic wave due to cyanide. Assuming cyanide in the 10^{-5} molar range to be detectable, the dissociation constant of the complex would have a maximum value of 10^{-24}. This was taken as a confirmation of Latimer's[2] value of 10^{-22} at 25° which was calculated from thermodynamic data. Recently Duodoroff[3] on the basis of toxicity of nickel–cyanide systems to certain aquatic life, suggested a dissociation constant of approximately 10^{-30}.

It was the purpose of this research to determine accurately the cumulative dissociation constant of the tetracyanonickelate(II) species. If in a system containing low concentrations of nickel and cyanide, the principal species present in solution are Ni^{++}, $\text{Ni(CN)}_4^{=}$, CN^- and HCN, then the equations governing the relative amounts are

$$\text{Total cyanide} = 4(\text{Ni(CN}_4^{=}) + (\text{CN}^-) + (\text{HCN}) \quad (1)$$

$$\text{Total nickel} = (\text{Ni(CN)}_4^{=}) + (\text{Ni}^{++}) \quad (2)$$

$$K_a = (\text{H}^+)(\text{CN}^-)/(\text{HCN}) \quad (3)$$

$$K_D = (\text{Ni}^{++})(\text{CN}^-)^4/\text{Ni(CN)}_4^{=} \quad (4)$$

The ultraviolet absorption spectrum of the tetracyanonickelate(II) species has been reported[4,5] and used by several investigators for the determination of nickel.[6,7]

Stepwise formation of tetracyanonickelate(II) from aquonickel could result in the formation of several intermediate complexes, yet no such species have been reported. A structurally discontinuous change occurs in going from the tetrahedral aquo ion to the square planar tetracyano ion.[8] Intermediate species must conform to either the tetrahedral or square planar structures and would therefore be strained and not exist in significant quantities.

The hydrolysis of aquonickel ion is known to occur with the formation of monohydroxy and likely even more extensively hydrolyzed species including polymers.[9]

The need for *p*H control led to the use of acetate and phosphate buffers and the need for information on aceto and phosphato complexes of nickel. Evidence for orthophosphate complexation has not been reported.[10,11] Aceto complexes of nickel are well known[12,13] and corrections must be applied when acetate buffers are employed.

Experimental conditions were selected either to eliminate, minimize or provide data so that corrections could be made.

Experimental

Nickel perchlorate was prepared by fuming either nickel nitrate hexahydrate or nickel carbonate with perchloric acid. Stock solutions 0.05 and 0.0064 *M* in nickel perchlorate were standardized with dimethylglyoxime.[14]

Stock solutions 0.10 and 0.05 *M* in potassium cyanide were prepared by dissolving the salt in water. The Liebig titration as modified by Denigès was used for standardization.[15]

Stock potassium acetate, acetic acid buffers were 0.080 *M* in total acetate. Stock potassium hydrogen phosphate, potassium dihydrogen phosphate buffers were 0.1 or 0.5 *M* in total phosphate and contained sufficient potassium perchlorate to facilitate ionic strength adjustment.

Stock solutions 0.1 *M* in potassium perchlorate were prepared.

A Beckman Model DU Quartz spectrophotometer with matched 1 cm. silica cells was used.

A Beckman Model H-2 meter was used for *p*H determinations. The readings of the glass electrode–calomel pair were calibrated against standard *p*H buffer solutions, as described by Bates.[16]

A constant temperature bath operating at 24.92 ± 0.05° was used for equilibration.

Beer's law was found to hold at 267.5 and 285 mμ over the nickel perchlorate concentration range of 8.62×10^{-6} to 8.62×10^{-5} *M* in 0.02 *M* potassium cyanide. The molar absorptivities found were 11,680 ± 40 at 267.5 mμ and 4,590 ± 70 at 285 mμ. The precision measure is expressed as absolute standard deviation.

The molar absorptivity was checked by other workers during these investigations. The mean value at 267.5 mμ

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[15] H. F. Walton, "Principles and Methods of Chemical Analysis," Prentice–Hall, Inc., New York, N. Y., 1952, pp. 370–373.

[16] R. G. Bates, "Electrometric *p*H Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 118–121.

always agreed within the precision measure with that given above, although the absolute standard deviation was generally larger, about ±80.

Identical absorption spectra between 300 and 1200 mμ were obtained for aqueous 0.1 *M* nickel perchlorate and for 0.1 *M* nickel perchlorate in 1 *M* phosphoric acid. Further, the absorbance, 0.385, at 267.5 mμ of a solution 3.3×10^{-5} *M* in nickel perchlorate and 0.0149 *M* in potassium cyanide was not affected by addition of sufficient trisodium phosphate to give a total phosphate/total nickel molar ratio of 1000.

Near *p*H 7, the polarographic half-wave potential, −1.10 volt *vs.* S.C.E., of 0.001 *M* nickel perchlorate in 0.1 *M* nitrate was not affected by addition of phosphate up to 0.1 *M*.

The application of Job's method of continuous variations to systems involving three successive complexes has been developed by Katzin and Gebert.[17] Should cyano complexes other than $Ni(CN)_4^=$ be formed, which contribute to the absorption in the solution, this should be evidenced in distortion of the Net Absorbance *versus* mole ratio plot.

The test solutions were prepared by pipetting 25.00 ml. of the stock buffer (0.5 *M* in potassium dihydrogen phosphate, 5.7×10^{-3} *M* in sodium hydroxide) into a series of twelve 100.0-ml. volumetric flasks. The requisite amounts of dilute nickel nitrate and potassium cyanide were added to maintain the total millimoles of nickel plus cyanide at 47.7×10^{-3}. On dilution to the mark each solution was held at a *p*H of 6.1. The flasks were placed in a constant temperature bath maintained at 25.0°. Absorbance measurements at 267.6 mμ were made relative to blanks containing the same level of buffer and cyanide as the test solutions. At the concentration levels employed, none of the components of the mixture showed a measurable absorbance when measured alone against water. Absorbance readings were taken over a period of hours until equilibrium was attained, as judged by constancy of the absorbance values.

Series of solutions were prepared at ionic strengths 0.100, 0.048, 0.014 and 0.0028. Each series contained a number of pairs of solutions buffered to *p*H values covering part of the *p*H range of approximately 7.7 to 5.3. Acetate buffers were used between *p*H 5.3 and 6.6 while phosphate buffers were used between *p*H 5.7 and 7.7. A pair consisted of a "color" solution and a blank solution buffered to the same *p*H.

The "color" solution contained aliquots of dilute stock nickel perchlorate solution, dilute stock potassium cyanide, buffer and sufficient potassium perchlorate to adjust the ionic strength to the desired value. The blank solution contained everything except the nickel perchlorate. The solutions were equilibrated at 24.92° in a constant temperature bath. Periodically portions were removed and their absorbance measured relative to the corresponding blanks at 267.5 mμ and slit width 0.60 mm.

The time required for equilibration ranged from a few days for solutions of high *p*H to several weeks for those of lower *p*H.

Immediately after the final absorbance was determined, the *p*H was measured.

Discussion

The absorbance *versus* mole ratio of nickel to nickel plus cyanide in shown in Fig. 1. The maximum is precisely at a 1/4 mole ratio of nickel to cyanide. The existence of other cyano species would have flattened the maximum and shifted it toward a lower nickel to cyanide ratio. These data preclude the existence of the other cyano species that would influence the absorbance measurements at 267.5 mμ.

The data in Table I were obtained from solutions containing nickel perchlorate and potassium cyanide, buffered to produce varying ratios of aquonickel to tetracyanonickelate(II). Before these data could be substituted into equations 1–4 several corrections were required. The measured *p*H values, which were essentially activity values, were converted to $-\log (m_H)$ using the method of Bates.[18] Thus all of the terms substituted in equations 1–4 were in concentration units. The dissociation constant thus calculated was a "concentration constant" and could then be extrapolated to infinite dilution to obtain the true cumulative constant.

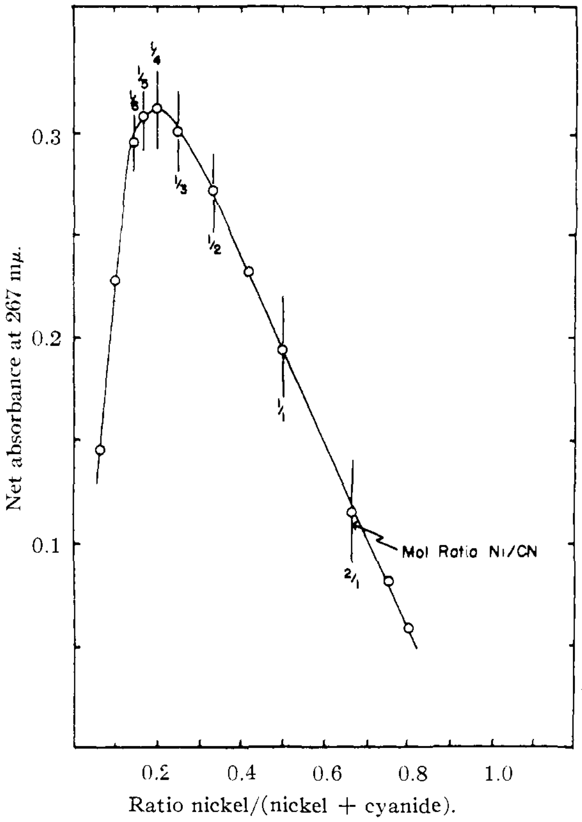

Fig. 1.—Job's method plot for tetracyanonickelate(II) ion.

The dissociation constant used for HCN was 4×10^{-10}, an average of the reported values.[19–25]

The formation of aceto complexes was evident and suitable corrections were made based on the stability constants of the complexes, total acetate and *p*H. In all cases, the correction applied to the apparent concentration of aquonickel ion represented only a small fraction of that term.

The solution conditions were so adjusted that at no time was the solubility product of $Ni(Ni(CN)_4)$ exceeded.

If significant decomposition of cyanide had occurred during equilibration, the calculated concentration of cyanide ion would be too high, leading to a positive error in the cumulative dissociation constant of the nickel complex. Aliquots of the color solution were treated with a slight excess of nickel ion; the *p*H was adjusted to about 10.

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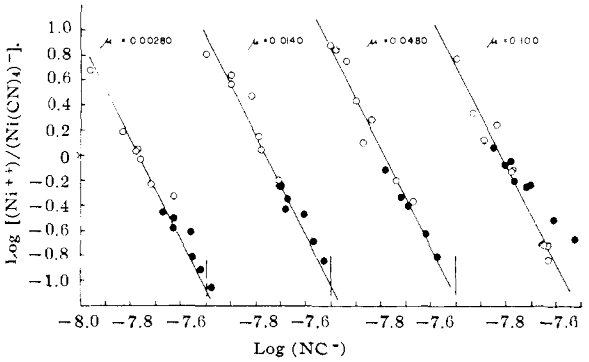

Fig. 2.—Log plot of nickel species *vs.* cyanide ion.

The conversion of excess cyanide to tetracyanonickelate(II) ion is essentially instantaneous, while the formation of hydrolytic species is relatively slow under these conditions. Hence, immediate measurement of the absorbance at 267.5 mμ gave a measure of the total cyanide. Although a small decrease was noted, it was not large enough to influence the results significantly.

TABLE I

EQUILIBRATION OF NICKEL PERCHLORATE AND POTASSIUM CYANIDE AT VARIOUS IONIC STRENGTHS

Ionic strength	Buffer	*p*H	Absorbance	Total Ni, mole/l. × 10⁻⁵	Total CN, mole/l. × 10⁻⁵
0.100	Phosphate	7.65[a]	0.437	4.05	16.34
		7.65[a]	.431		
		7.30[a]	.379		
		6.88[a]	.414		
		6.68	.409		
		6.66	.404		
		6.50	.387		
		6.50	.391		
		6.31	.364		
		6.31	.364		
		6.03	.301		
		6.02	.306		
		5.94	.292		
		5.93	.291		
		5.84	.260		
		5.74	.244		
.100	Acetate	6.52	.408	4.05	16.25
		6.42	.391		
		6.33	.375		
		6.33	.373		
		5.87	.262		
		5.64	.190		
		5.64	.163		
		5.53	.139		
		5.35	.062		
.048	Phosphate	7.34[a]	.449	3.97	16.11
		6.93[a]	.431		
		6.72[a]	.418		
		6.53	.401		
		6.35	.376		
		6.12	.335		
		6.04	.318		
		5.95	.292		
		5.85	.265		
.048	Acetate	6.10	.322	3.99	16.10
		5.93	.281		
		5.65	.204		
		5.50	.124		
		5.28	.054		
		5.58	.133	3.97	16.06
		5.40	.068		
		5.33	.058		
.014	Phosphate	7.38[a]	.450	3.97	16.08
		7.02[a]	.433		
		6.81[a]	.421		
		6.62	.407		
		6.42	.386		
		6.21	.348		
		6.12	.399		
		6.07	.320		
		5.98	.297		
.014	Acetate	6.27	.349	3.99	16.10
		5.94	.285		
		5.74	.223		
		5.50	.143		
		5.30	.063		
		5.69	.193	3.97	16.06
		5.50	.193		
		5.44	.103		
.0028	Phosphate	7.32[a]	.444	3.97	16.03
		6.98[a]	.436		
		6.80	.427		
		6.65	.414		
		6.54	.402		
		6.36	.373		
		6.26	.366		
		6.21	.355		
		6.13	.344		
.0028	Acetate	6.66	.404	3.99	16.10
		6.57	.400		
		6.08	.318		
		5.73	.222		
		5.61	.185		
		5.34	.081		
		5.93	.293	3.97	16.06
		5.78	.242		
		5.72	.244		

[a] Not used in plot.

Expressing the equation for the over-all dissociation of tetracyanonickelate(II) in logarithmic form results in

$$\log [(\mathrm{Ni}^{++})/(\mathrm{Ni(CN)_4}^{=})] = -4 \log (\mathrm{CN}^-) + \log K_\mathrm{D} \quad (5)$$

A plot of the logarithm of the nickel ratio *versus* the logarithm of the cyanide ion concentration should yield a straight line with a slope of −4 and an intercept of $^1/_4 \times \log K_\mathrm{D}$. The corrected data are plotted in Fig. 2.

Data taken above *p*H 6.8 were not included in Fig. 2. These data showed marked deviation from the simple relations suggested in equations 1–4. These deviations probably are attributable to hydrolyzed nickel species which formed slowly during equilibration.

The phosphate to nickel ratios in some of the final equilibration solutions, especially at the higher *p*H values at ionic strength 0.100, were considerably greater than those employed in the preliminary studies on phosphate complexation. Consequently, the deviations of some of the phosphate points in

TABLE II

PRECISION BASED ON THE CALCULATED VALUE OF DISSOCIATION CONSTANT FOR EACH EQUILIBRATION SOLUTION

Ionic strength	Mean value $K_D \times 10^{31}$	Absolute stand dev.	No. of equilibration soln.
0.100	0.5	±0.11	15
.048	0.7	± .18	14
.014	1.0	± .28	14
.0028	0.9	± .20	14

Mean value K_D extrapolated to infinite dilution is $1.0 \pm 0.2 \times 10^{-31}$.

Fig. 2 might still be attributable to weak nickel phosphate complexes undetected by the preliminary experiments. Unfortunately, the lack of analytical sensitivity in the preliminary systems made complete duplication of phosphate to nickel ratios impossible.

The dissociation constants obtained from the intercepts of Fig. 2 are extrapolated to infinite dilution in Fig. 3, yielding a dissociation constant for the tetracyanonickelate(II) species of 1×10^{-31}.

A summary of the experimental values for the cumulative dissociation constant of tetracyanonickelate(II) is given in Table II.

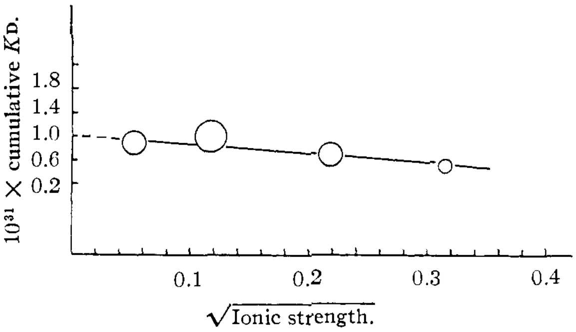

Fig. 3.—Plot of cumulative dissociation constant of tetracyanonickelate(II) *vs.* square root of ionic strength.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CONNECTICUT]

Cation Substitution in Perovskite-like Phases[1,2]

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Several phases with a face-centered cubic structure representing an ordered perovskite-like arrangement of cations have been prepared having the general formula $A(B_{0.5}^{II}W_{0.5}^{VI})O_3$ where A = Ba or Sr and B^{II} = Zn, Fe, Co, Ni. The strontium compounds show a tetragonal distortion at room temperatures but become cubic at elevated temperatures. Phases of the type $Sr_xBa_{(1-x)}(Zn_{0.5}W_{0.5})O_3$ are cubic at room temperatures over the range $0 < x < 0.4$. $Sr_{0.5}Ba_{0.5}(Zn_{0.5}W_{0.5})O_3$ becomes cubic above 300° whereas $Sr(Zn_{0.5}W_{0.5})O_3$ becomes cubic at 570°. The cubic structure appears when the Goldschmidt tolerance factor, calculated from the weighted averages of the A and B cations, is 0.89 or greater.

Introduction

Compounds with the type formula A_3WO_6 (where A = an alkaline earth cation) have been shown by Steward and Rooksby[3] to have structures related to that of perovskite and may be written $A(A_{0.5}W_{0.5})O_3$ to indicate that half of the octahedral B-cation sites are occupied by A cations. Moreover the cations in the B-sites are ordered in such a manner that the unit cell edge must be doubled giving a large face-centered cubic structure with lattice constant about 8 Å. A similar structure and ordering of the cations in B-sites has been observed in $A(La_{0.5}Ta_{0.5})O_3$[4] and in the oxygen-deficient phases $A(A_{0.5}Ta_{0.5})O_{2.75}$[4] and $A(A_{0.5}Nb_{0.5})O_{2.75}$.[5] It is not surprising, therefore, to find that other ions may be introduced into the B-positions to yield similar structures. This paper is concerned with the compounds $A(B_{0.5}^{II}W_{0.5})O_3$ where A = Sr or Ba and B^{II} = Zn, Fe, Co, Ni.

Experimental

Reagents.—Barium oxide was prepared from the peroxide at 950° *in vacuo*, strontium oxide by heating the carbonate in hydrogen at 1150° for 48 hr., cobaltous oxide by heating the carbonate in an argon atmosphere. Iron(II) was introduced by using equimolar proportions of metallic iron and Fe_2O_3. The other reactants were C.P. or reagent grade chemicals. X-Ray diffraction data were obtained using a Philips X-ray camera of radius 57.3 mm. Ten hour exposures were made using copper K_α radiation. A Central Research Laboratories high temperature camera model H(10), radius 57.3 mm., was used for following crystallographic transformations.

Intimate mixtures of the reactants in proportion to give $A(M_{1/2}W_{1/2})O_3$ (A = Sr, Ba; M = Fe, Co, Ni, Zn) were heated for 24 hr. at 1100 to 1250°. The nickel and zinc compounds were prepared by heating in air using zirconium silicate boats as containers, whereas the iron and cobalt compounds were made in evacuated silica capsules. The mixtures were reground several times during the heating period. Some preparations were obtained by first preparing zinc tungstate and then heating this compound with the alkaline earth oxide. In all cases small amounts of the alkaline earth tungstate could be detected in the final product. No procedure was found to prevent its formation or to remove it from the principal phase. It seemed clear from X-ray data,

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(1) Taken in part from the Masters Thesis submitted by E. J. Fresia to The University of Connecticut, 1958.

(2) Part of this work was supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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