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# THERMODYNAMICS OF METAL CYANIDE COORDINATION

## PART IX. LOG $K$, $\Delta H^0$, AND $\Delta S^0$ VALUES FOR THE $Ni^{2+}$–, $Zn^{2+}$–, $Cd^{2+}$–, AND $Hg^{2+}$–$CN^-$ SYSTEMS AT 10, 25, AND 40 °C*

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## ABSTRACT

Log $K$, $\Delta H^0$, and $\Delta S^0$ values valid at zero ionic strength are reported or summarized from previous studies for cyanide ion interaction with bivalent nickel, zinc, cadmium, and mercury at 10, 25, and 40 °C. From the values of $\Delta H^0$ as a function of temperature, average $\Delta C_p{}^0$ values are calculated.

## INTRODUCTION

The general chemistry of metal–cyanide complexes has been discussed[1,2]. In previous papers in this series we reported stepwise, Eqn. (1), or overall, Eqn. (2), log $K$, $\Delta H^0$, and $\Delta S^0$

$$M(CN)_{i-1}^{3-i} + CN^- \rightleftarrows M(CN)_i^{2-i} \quad K_i, \Delta H^0{}_i, \Delta S^0{}_i \tag{1}$$

$$M^{2+} + i\,CN^- \rightleftarrows M(CN)_i^{2-i} \quad K_{0-i}, \Delta H^0{}_{0-i}, \Delta S^0{}_{0-i} \tag{2}$$

values valid at 25° and zero ionic strength, $\mu$, for the interaction of $CN^-$ with $Ni^{2+}$ (Ref. 3), $Zn^{2+}$ (Ref. 4), and $Hg^{2+}$ (Ref. 5). Values of log $K_i$ valid at $\mu = 0$ for the $Hg^{2+}$–$CN^-$ system at 10 and 40 °C were also reported[5]. Several workers[6–9] have determined log $K_i$ values for the $Cd^{2+}$–$CN^-$ system at $\mu > 0$. Values of log $K_{0-4}$ valid at $\mu = 0$ have been reported[10,11] but differ by two log $K$ units. Gerding[12] has published $\Delta H_i$ values valid at 25 °C and $\mu = 1.0$ for $Cd^{2+}$. Except for the $K$ values in the case of the $Hg^{2+}$–$CN^-$ system[5] no $K$, $\Delta G$, $\Delta H^0$, or $\Delta S^0$ values have been reported previously at 10 or 40 °C for any of the systems studied.

In the present study log $K$, $\Delta G$, $\Delta H^0$, and $\Delta S^0$ values for reaction (1) or (2) (M = Ni, Zn, Cd, Hg) at 10, 25, and 40 °C and $\mu = 0$ have been determined where these data are not presently available or where an independent check of existing data was desirable. Values of $\Delta C_p{}^0{}_i$ are estimated from the temperature dependence of the $\Delta H^0{}_i$ values.

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*Part VIII: R. M. Izatt, G. D. Watt, C. H. Bartholomew and J. J. Christensen, *Inorg. Chem.*, 7 (1968) 2236.

## EXPERIMENTAL

### *Materials*

Reagent grade $NiCO_3$ (Baker Analyzed), Zn (Baker Analyzed), CdO (Matheson, Coleman, and Bell), HgO (Baker and Adamson), $Hg(CN)_2$ (Mallinckrodt), $HClO_4$ (Baker and Adamson), and NaCN (Baker Analyzed) were used to prepare solutions for this study.

Standard $Ni(ClO_4)_2$ solutions were prepared by refluxing excess $NiCO_3$ in $HClO_4$ until the carbonate was removed as $CO_2(g)$, removing any excess $NiCO_3$ by filtration, and adding sufficient $HClO_4$ to suppress hydrolysis of the $Ni^{2+}$. The resulting solutions gave a negative test for carbonate ion. The solutions were standardized for $Ni^{2+}$ by titration with a standard EDTA solution and for $H^+$ by pH titration. The $Zn(ClO_4)_2$ solutions were prepared by dissolving a weighed sample of zinc metal in excess $HClO_4$. The solutions were then standardized for $Zn^{2+}$ with standard EDTA solutions and for $H^+$ by pH titration. Solutions of $Cd(ClO_4)_2$ and $Hg(ClO_4)_2$ were prepared by dissolving the corresponding metal oxides in a known excess of perchloric acid. In both cases the metal ion concentration was determined by conventional techniques and the acid concentration was determined by taking the difference between the total $ClO_4^-$ and metal ion concentrations. Solutions of $Hg(CN)_2$ were prepared by dissolving a weighed quantity of solid $Hg(CN)_2$ in water. Sodium cyanide solutions were prepared fresh at least every two to three days and were stored at 4°C to minimize decomposition. All NaCN solutions were standardized daily against standard $AgNO_3$ solutions in order to insure their reliability.

All solutions used in this study were prepared under a pure nitrogen atmosphere using freshly boiled, doubly distilled water of pH 6.5 to 6.8.

### *Equilibrium constant determinations*

The $\log K_i$ values ($i = 1, 2, 3, 4$) for the $Cd^{2+}$–$CN^-$ and $\log K_{0-4}$ for the $Ni^{2+}$–$CN^-$ systems were calculated from pH titration data obtained by titrating dilute metal perchlorate solutions with NaCN at 10, 25, and 40°C. Using this method equilibrium was attained rapidly in the $Cd^{2+}$–$CN^-$ system but slowly in the $Ni^{2+}$–$CN^-$ system in which portions of the NaCN titrant were added every 4–6 h and the pH readings taken every 30 min to check the attainment of equilibrium. The pH measurements were made using a Model 1019 Beckman Research pH meter or a Model 801 Orion Ionalyzer both fitted with Corning Glass and Beckman saturated calomel electrodes. The pH meters were standardized against National Bureau of Standards pH standard (potassium hydrogen phthalate, borax, and phosphate) buffers.

The $\log K_{0-2}$, $\log K_3$ and $\log K_4$ values for the $Zn^{2+}$–$CN^-$ system at 10 and 40°C were determined by the same techniques as those previously used to study this system at 25°C[4].

### *Heat determinations*

The titration calorimetry procedure[13-15] and the equipment used[16], including modifications, have been described.

Heats of dilution were measured by titrating the standard NaCN titrant into boiled, doubly distilled water and into NaCN solutions and measuring the heat change under the same ionic strength conditions as those used to study the metal cyanide systems.

The amount of HCN volatilized during the equilibrium constant and heat determinations was minimized by titrating all solutions in a closed vessel under a standing nitrogen atmosphere. The volume of gas ($<30$ ml for pH titrations, $<10$ ml for heat determinations) above the solution was kept small to minimize HCN volatilization.

Values of $\Delta H^0_{0-4}$ for the $Ni^{2+}$–$CN^-$ system at 10 and 40°C were determined by titration of $Ni(ClO_4)_2$ solutions with NaCN solutions.

Values of $\Delta H^0_{0-2}$, $\Delta H^0_3$ and $\Delta H^0_4$ for the $Zn^{2+}$–$CN^-$ system were calculated from calorimetric data obtained at 10, 25 and 40°C by titrating 0.004 M $Zn(ClO_4)_2$ solutions with NaCN solutions. The dilute $Zn(ClO_4)_2$ solutions were used to avoid precipitation of $Zn(CN)_2$.

The $\Delta H^0_i$ ($i = 1, 2, 3, 4$) values for the $Cd^{2+}$–$CN^-$ and $Hg^{2+}$–$CN^-$ systems were obtained in each case from two sets of heat determinations at 10, 25, and 40°C. First, a $M(ClO_4)_2$ solution was titrated with a NaCN solution to a $CN^-:M^{2+}$ ratio 2:1. Then a second solution with an initial $CN^-:M^{2+}$ ratio of 2:1 was titrated with a NaCN solution to a $CN^-:M^{2+}$ ratio greater than 4:2.

In all cases sufficient $HClO_4$ was added to the $M(ClO_4)_2$ solutions to prevent hydrolysis of the $M^{2+}$ species.

*Calculations*

Values for $K$ (M = Ni, Zn, Cd) were calculated by procedures which have been described[17,18].

A Debye–Hückel expression of the form

$$\log \gamma = \frac{-Az^2\mu^{1/2}}{1 + B\mathring{a}\mu^{1/2}} + Cz^2\mu \tag{3}$$

was used to convert the ion product of water[19], the dissociation constant of HCN[20,21] and pH to corresponding concentration quantities valid at a given $\mu$ value. Eqn. (3) was also used to calculate the activity coefficients necessary to correct equilibrium constants to thermodynamic constants valid at $\mu = 0$. In the calculation of all activity coefficients the values 4.0 Å and 0.3 for å and C, respectively, were used since these values gave thermodynamic constants independent of $\mu$.

The method used to calculate $\Delta H$ values from the calorimetric titration data has been described[22]. For calculation purposes a typical run was divided into eighteen one-minute intervals. The measured heat was then corrected for nonchemical heat effects and heats of dilution. Literature values were used to make corrections for the heat of ionization of HCN[21] at 10, 25, and 40°C and water[23] at 25°C. Values for the heat of ionization of water at 10 and 40°C and $\mu = 0$ were determined[24] to be 14.21 and 12.61 kcal.mole$^{-1}$, respectively.

In the case of the $Cd^{2+}$–$CN^-$ and $Hg^{2+}$–$CN^-$ systems values of $\Delta H_3$ and $\Delta H_4$ were first approximated from the second set of runs and used to calculate $\Delta H_1$ and $\Delta H_2$ values from the first set of runs (see *Heat determinations*). These $\Delta H_1$ and $\Delta H_2$ values were then used to calculate new $\Delta H_3$ and $\Delta H_4$ values from the second set of runs. The process was repeated until successively calculated values for the consecutive heats, $\Delta H_1$ through $\Delta H_4$, were obtained which agreed to within $\pm 0.005$ kcal.mole$^{-1}$.

The $\mu$ values of the solutions were low ($\mu < 0.02$) in all cases. Previous experience[3] with bivalent metal cyanide systems has shown that the dependence of $\Delta H$ on $\mu$ in dilute aqueous solutions is small compared to the error in measurement of the $\Delta H$ values, therefore the measured $\Delta H$ values were taken to be $\Delta H^0$ values valid at $\mu = 0$.

The calculations were aided by IBM 7040 and 360 computers.

## RESULTS

Thermodynamic quantities for the $M^{2+}$–$CN^-$ systems studied are summarized in Table I together with literature data. Values of $\Delta C_p{}^0{}_i$ were obtained by fitting the $\Delta H^0{}_i$ values for each system by a least squares process to a quadratic function in $T$. The function was then differentiated and the derivative evaluated at 25°C to give a $\Delta C_p{}^0{}_i$ value. The uncertainty in each $\Delta C_p{}^0{}_i$ value is expressed as twice the standard deviation reflecting the greater uncertainty of this value compared to the $\Delta H^0{}_i$ value from which it is derived.

The calorimetric and potentiometric titration data for these systems are given elsewhere[13,14].

## DISCUSSION

The $K$ values valid at $\mu$ values other than zero reported by earlier workers[6-9] are in qualitative agreement with those reported here. The $\Delta H_i$ values reported by Gerding[12] for the $Cd^{2+}$–$CN^-$ system are valid in 1 M $NaClO_4$ and, hence, are not comparable with those given here.

A general discussion of the $Ni^{2+}$–, $Zn^{2+}$–, and $Hg^{2+}$–$CN^-$ systems has appeared in previous papers in this series[3-5] and is not repeated here. The $M^{2+}$–$CN^-$ systems studied here are characterized by the variety of species formed in aqueous solution. The data in Table I show that only the $Cd^{2+}$–$CN^-$ system shows the behavior usually observed in the consecutive addition of ligands to a metal ion, *i.e.*, for the interaction of four $CN^-$ with $M^{2+}$ the four log $K$ values decrease in a regular manner only in the case of $Cd^{2+}$. In contrast, the $ZnCN^+$ species is missing, $NiCN^+$, $Ni(CN)_2$ (aq) and $Ni(CN)_3^-$ are missing and there is a very large difference between the log $K$ values for the consecutive formation of $Hg(CN)_2$ (aq) and $Hg(CN)_3^-$, respectively. These aspects of $M^{2+}$–$CN^-$ behavior have been discussed with respect to the individual systems in previous papers[3-5]. The $\Delta C_p{}^0$ values calculated in the present study allow us to examine this behavior in greater detail and to propose reasons for it.

The effect of $\Delta C_p$ on the free energy change of a reaction is nonlinear. For example, assume that Eqn. (4) accurately describes the variation of $\Delta C_p$ with temperature. Eqns. (5) and (6) then follow from basic thermodynamics.

$$\Delta C_p = a+bT \tag{4}$$

$$\Delta H = aT+\frac{bT^2}{2}+c \tag{5}$$

$$T\Delta S = aT\ln T+bT^2+d \tag{6}$$

Depending on the magnitude of the coefficients of $T$ in eqn. (6), the effect of $\Delta C_p$ on $T\Delta S$ may be larger than on $\Delta H$. Therefore, $\Delta G$ may increase or decrease with temperature depending upon the relative magnitudes of the coefficients in Eqns. (4)–(6).

The $\Delta C_p{}^0{}_i$ values given in Table I vary both in sign and magnitude for the various metal cyanide complexes. Such variations in the $\Delta C_p{}^0{}_i$ values point out a possible pitfall in comparing the thermodynamic quantities for metal ion–ligand reactions at a single temperature. Species which are stable at room temperature may not form if the temperature is raised or lowered significantly and, furthermore, species absent at room temperature may be stable at other temperatures.

The effect of temperature on the $\Delta G^0{}_i$ values for the $Cd^{2+}$–$CN^-$ system is shown in Fig. 1 which was constructed by first assuming that Eqn. (4) correctly describes the variation of $\Delta C_p$ with temperature and then calculating values for $a$ and $b$ from the experimental $\Delta H$ values. Values for $\Delta H$ and $\Delta S$ as a function of temperature were calculated from Eqns. (5) and (6) using the experimental data at 25 °C to evaluate the integration constants. Free energy changes were then calculated from the relationship: $\Delta G = \Delta H - T\Delta S$. Fig. 1 is admittedly hypothetical and may be a gross simplification of the actual temperature variance of $\Delta G$, but it does indicate that the stable species in solution may vary significantly with temperature. For example, at temperatures below −175°, the $Cd(CN)_2$ and $Cd(CN)_4{}^{2-}$ species would be predicted to predominate

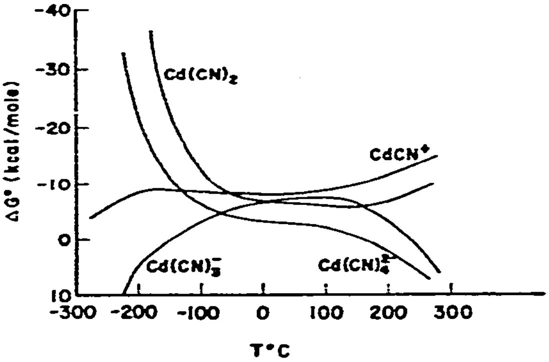

Fig. 1. Plot of $\Delta G^0$ values for the consecutive formation of the indicated species *vs.* temperature for the $Cd^{2+}$–$CN^-$ system.

TABLE I

THERMODYNAMIC QUANTITIES[a] FOR THE $Ni^{2+}$–, $Zn^{2+}$–, $Cd^{2+}$– AND $Hg^{2+}$–$CN^-$ SYSTEMS

| *Reaction* | *T* (°C) | *μ* | *Log K* | $-\Delta G^0$ (*kcal·mole⁻¹*) | $-\Delta H^0$ (*kcal·mole⁻¹*) | $\Delta S^0$ (*cal·deg⁻¹·mole⁻¹*) | $\Delta C_p^0$ (*cal·deg⁻¹·mole⁻¹*) |
|---|---|---|---|---|---|---|---|
| $Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$ | 10 | 0 | 32.2 ±0.2 | 43.0 | 45.2 ±0.3 | − 7.8 ±0.9 | |
| | 25 | 0 | 30.22 ±0.05 | 41.22 | | − 6.6 ±0.6 | 36 ±10 |
| | | 0 | (30.1)[c] | | (43.2)[c] | (− 7)[c] | |
| | | 0 | (30.3)[d] | | | | |
| | 40 | 0 | 27.43 ±0.09 | 39.30 | 43.9 ±0.2 | −14.7 ±0.8 | |
| $Zn^{2+} + 2CN^- \rightleftharpoons Zn(CN)_2$ | 10 | 0 | 11.47 ± .04 | 14.86 | 11.6 ±0.2 | 11.5 ±0.2 | |
| | 25 | 0 | (11.07)[e] | | 11.0 ±0.1 | 13.7 ±0.2 | 36 ±8 |
| | | | | | (10.8)[e] | (14.4)[e] | |
| | 40 | 0 | 10.70 ±0.02 | 15.33 | 10.5 ±0.1 | 15.4 ±0.2 | |
| $Zn(CN)_2 + CN^- \rightleftharpoons Zn(CN)_3^-$ | 10 | 0 | 5.17 ±0.02 | 6.70 | 9.5 ±0.2 | − 9.9 ±0.2 | |
| | 25 | 0 | (4.98)[e] | | 9.2 ±0.2 | − 8.0 ±0.3 | 5 ±10 |
| | | | | | (8.4)[e] | (− 5.3)[e] | |
| | 40 | 0 | 4.50 ±0.02 | 6.45 | 9.3 ±0.1 | − 9.1 ±0.2 | |
| $Zn(CN)_3^- + CN^- \rightleftharpoons Zn(CN)_4^{2-}$ | 10 | 0 | 3.79 ±0.02 | 4.91 | 7.4 ±0.3 | − 8.8 ±0.2 | |
| | 25 | 0 | (3.57)[e] | | 7.7 ±0.1 | − 9.5 ±0.3 | −17 ±12 |
| | | | | | (8.6)[e] | (−12)[e] | |
| | 40 | 0 | 3.10 ±0.03 | 4.44 | 7.9 ±0.1 | −14.2 ±0.2 | |
| $Zn^{2+} + 4CN^- \rightleftharpoons Zn(CN)_4^{2-}$ | 10 | 0 | 20.43 | 26.47 | 28.5 | − 7.2 | |
| | 25 | 0 | (19.62)[e] | | 27.9 | − 3.8 | 24 |
| | | | | | (27.8)[e] | (− 3.4)[e] | |
| | 40 | 0 | 18.30 | 26.22 | 27.7 | − 4.7 | |
| $Cd^{2+} + CN^- \rightleftharpoons CdCN^+$ | 2 | — | (5.39)[g] | | | | |
| | 10 | 0 | 6.22 ±0.02 | 8.06 | 7.9 ±0.2 | 0.6 ±0.2 | |
| | 25 | 0 | 6.01 ±0.01 | 8.20 | 7.3 ±0.1 | 3.0 ±0.1 | 42 ±5 |
| | | 1.0 | | (7.47)[i] | (7.39)[i] | (0.3)[i] | |
| | | 3.0 | (5.48)[f] | | | | |
| | | — | (5.18)[h] | | | | |
| | 40 | 0 | 5.73 ±0.02 | 8.21 | 6.65 ±0.08 | 5.0 ±0.1 | |
| $CdCN^+ + CN^- \rightleftharpoons Cd(CN)_2$ | 2 | — | (4.73)[g] | | | | |
| | 10 | 0 | 5.38 ±0.02 | 6.97 | 6.89 ±0.10 | − 0.3 ±0.3 | |
| | 25 | 0 | 5.11 ±0.02 | 6.97 | 5.7 ±0.2 | 4.3 ±0.2 | 56 ±5 |
| | | 1.0 | | (6.99)[i] | (7.73)[i] | (− 2.5)[i] | |
| | | 3.0 | (5.12)[f] | | | | |
| | | — | (4.42)[h] | | | | |
| | 40 | 0 | 4.90 ±0.02 | 7.02 | 5.15 ±0.15 | 6.0 ±0.2 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Cd(CN)_2 + CN^- \rightleftharpoons Cd(CN)_3^-$ | 2 | — | (4.91)[g] | | | | |
| | 10 | 0 | 4.77±0.05 | 6.18 | 8.3±0.1 | −7.6±0.1 | |
| | 25 | 0 | 4.53±0.03 | 6.18 | 8.56±0.09 | −8.0±0.2 | −7±4 |
| | | 1.0 | | (6.20)[i] | (7.12)[i] | (−3.1)[i] | |
| | | 3.0 | (4.63)[f] | | | | |
| | | — | (4.32)[h] | | | | |
| | 40 | 0 | 4.12±0.02 | 5.90 | 8.6±0.2 | −8.5±0.2 | |
| $Cd(CN)_3^- + CN^- \rightleftharpoons Cd(CN)_4^{2-}$ | 2 | — | (2.71)[g] | | | | |
| | 10 | 0 | 2.52±0.08 | 3.26 | 5.2±0.1 | −7.0±0.2 | |
| | 25 | 0 | 2.27±0.05 | 3.10 | 5.1±0.2 | −6.9±0.5 | −7±4 |
| | | 1.0 | | (4.31)[i] | (7.03)[i] | (−9.1)[i] | |
| | | 3.0 | (3.55)[f] | | | | |
| | | — | (3.19)[h] | | | | |
| | 40 | 0 | 2.12±0.08 | 3.04 | 5.42±0.09 | −7.6±0.1 | |
| $Cd^{2+} + 4CN^- \rightleftharpoons Cd(CN)_4^{2-}$ | 10 | 0 | 18.89 | 24.47 | 28.37 | −13.8 | |
| | 25 | 0 | 17.92 | 24.44 | 26.76 | −8.0 | 84 |
| | | 0 | (18.24)[j] | | | | |
| | | 0 | (16.04)[k] | | | | |
| | 40 | 0 | 16.87 | 24.17 | 25.77 | −5.1 | |
| $Hg^{2+} + CN^- \rightleftharpoons HgCN^+$ | 10 | 0 | (17.97)[l] | | 23.92±0.04 | −2.3±0.1 | |
| | 25 | 0 | (17.00)[l] | | 23.2±0.2 | 0.0±0.3 | 43±8 |
| | | | | | (23.0)[i] | (0.7)[i] | |
| | 40 | 0 | (16.26)[l] | | 22.6±0.1 | 2.2±0.1 | |
| $HgCN^+ + CN^- \rightleftharpoons Hg(CN)_2$ | 10 | 0 | (16.74)[l] | | 24.04±0.05 | −8.3±0.1 | |
| | 25 | 0 | (15.75)[l] | | 23.4±0.2 | −6.4±0.5 | 37±11 |
| | | | | | (25.5)[i] | (−13.4)[i] | |
| | 40 | 0 | (15.02)[l] | | 22.9±0.2 | −4.4±0.2 | |
| $Hg(CN)_2 + CN^- \rightleftharpoons Hg(CN)_3^-$ | 10 | 0 | (3.81)[l] | | 7.36±0.06 | −8.5±0.1 | |
| | 25 | 0 | (3.56)[l] | | 6.84±0.08 | −6.6±0.1 | 21±6 |
| | | | | | (7.6±0.2)[i] | (−9.0)[i] | |
| | 40 | 0 | (3.37)[l] | | 6.71±0.03 | −6.0±0.1 | |
| $Hg(CN)_3^- + CN^- \rightleftharpoons Hg(CN)_4^{2-}$ | 10 | 0 | (2.81)[l] | | 5.26±0.08 | −5.7±0.1 | |
| | 25 | 0 | (2.66)[l] | | 6.3±0.2 | −9.0±0.2 | −61±10 |
| | | | | | (7.2)[i] | (−12.1)[i] | |
| | 40 | 0 | (2.46)[l] | | 7.10±0.03 | −11.4±0.1 | |
| $Hg^{2+} + 4CN^- \rightleftharpoons Hg(CN)_4^{2-}$ | 10 | 0 | (41.33)[l] | 53.54 | 60.59 | −24.9 | |
| | 25 | 0 | (38.97)[l] | 53.16 | 59.8 | −22.0 | 41 |
| | 40 | 0 | (37.11)[l] | 53.17 | 59.3 | −19.6 | |

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[a] Uncertainties are expressed as standard deviations among runs. [b] Uncertainties are expressed as twice the standard deviations among runs. [c] Ref. 3. [d] H. Freund and C. R. Schneider, *J. Amer. Chem. Soc.*, 81 (1959) 4780. [e] Ref. 4. [f] Ref. 6. [g] Ref. 7, μ unspecified. [h] Ref. 9, μ variable. [i] Ref. 12. [j] Ref. 10. [k] Ref. 11. [l] Ref. 5.

in solution. This is similar to the behavior actually observed[4] for the $Zn^{2+}$–$CN^-$ system at 25°C. Although $\Delta G$, $\Delta H$, and $\Delta S$ values are not known for the formation of the $ZnCN^+$ species at or near room temperature, the $ZnCN^+$ species could be present in the system at higher or lower temperatures. Above 200°C the $CdCN^+$ and $Cd(CN)_2$ species would be expected to predominate. These observations suggest that the apparent differences in the behavior of the $Ni^{2+}$–, $Zn^{2+}$–, $Cd^{2+}$–, and $Hg^{2+}$– $CN^-$ systems are a consequence of the fact that these systems have been studied over a very limited temperature range. Obviously, the extrapolation of $\Delta C_p$ data measured over a 30° temperature range to a wide temperature range could lead to gross uncertainties in the plotted data. However, it is consistent with the data reported in this study to say that stepwise behavior appears to be strongly temperature dependent in these systems. It would be desirable to extend the data over a wider temperature range so that the $\Delta C_p$ values could be more accurately described and these ideas be more rigorously tested.

The effect of temperature on the $\Delta H^0{}_{0-4}$ values for the several $M^{2+}$–$CN^-$ systems is shown in Fig. 2. The temperature variation is comparable for all four metal ions and particularly so for $Ni^{2+}$, $Zn^{2+}$, and $Cd^{2+}$. This similarity in the several $M^{2+}$–$CN^-$ systems suggests there are no unusual solvent interactions in these systems, which is expected since the three $d^{10}$ metal ions should be similar in this respect. Furthermore, the energy due to the ligand field stabilization present in the $Ni^{2+}$–$CN^-$ system should be largely independent of temperature. These results suggest that the unusually high stability of $Hg(CN)_4{}^{2-}$ relative to the remaining $M(CN)_4{}^{2-}$ species largely disappears at very high and very low temperatures.

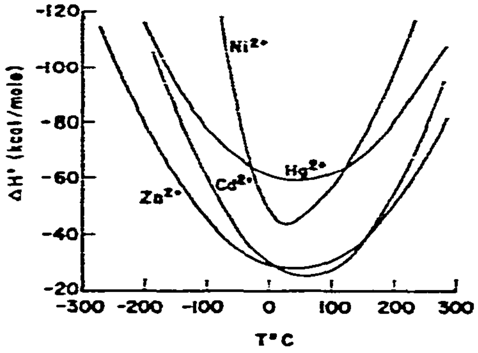

Fig. 2. Plot of $\Delta H^0$ values for the reaction $M^{2+} + 4\, CN^- \rightarrow M(CN)_4{}^{2-}$ *vs.* temperature for M = Ni, Zn, Cd, Hg.

It thus appears that whether a particular species is stable in any one of these $M^{2+}$–$CN^-$ systems, and perhaps in other systems as well, is a result of the balance of the relative magnitudes of the energies involved in complex formation rather than an inherent property of the element itself.

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