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THERMODYNAMICS OF METAL CYANIDE COORDINATION. IX. LOG K

ΔH°, AND ΔS° VALUES FOR THE Ni^{2+}-, Zn^{2+}-, Cd^{2+}-, AND

Hg^{2+}-CN^{-} SYSTEMS AT 10, 25, AND 40°.

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SUMMARY

Log K, ΔH^o, and ΔS^o 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°. From the values of ΔH^o as a function of temperature, average ΔCp° 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, equation (1), or overall, equation (2), log K, ΔH^o and ΔS^o

$$M(CN)_{i-1}^{3-i} + CN^- = M(CN)_i^{2-i} \qquad K_i, \ \Delta H^o_i, \ \Delta S^o_i \qquad (1)$$

$$M^{2+} + i \ CN^- = M(CN)_i^{2-i} \qquad K_{0-i}, \ \Delta H^o_{0-i}, \ \Delta S^o_{0-i} \qquad (2)$$
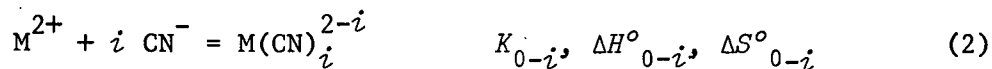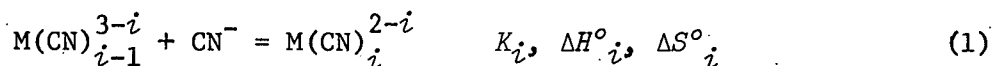
values valid at 25° and zero ionic strength, μ, for the interaction of CN^- with Ni^{2+},[3] Zn^{2+},[4] and Hg^{2+}.[5] Values of log K_i valid at $\mu = 0$ for the Hg^{2+}-CN^- system at 10 and 40° were also reported.[5] Several workers[6-9] have determined log K_i values for the Cd^{2+}-CN^- system 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 ΔH_i values valid at 25° and $\mu = 1.0$ for Cd^{2+}. Except for the K values in the case of the Hg^{2+}-CN^- system[5] no K, ΔG, ΔH^o or ΔS^o values have been reported previously at 10 or 40° for any of the systems studied.

In the present study log K, ΔG, ΔH^o and ΔS^o values for reaction (1) or (2) (M = Ni, Zn, Cd, Hg) at 10, 25, and 40° 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 ΔCp^o_i are estimated from the temperature dependence of the ΔH^o_i values.

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° 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°. 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 hours and the pH readings taken every 30 minutes 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° were determined by the same techniques as those previously used to study this system at 25°.[4]

<u>Heat Determinations</u>. The titration calorimetry procedure [13,14,15] 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 ΔH^{o}_{0-4} for the Ni^{2+}-CN^- system at 10 and 40° were determined by titration of $Ni(ClO_4)_2$ solutions with NaCN solutions.

Values of ΔH^{o}_{0-2}, ΔH^{o}_3 and ΔH^{o}_4 for the Zn^{2+}-CN^- system were calculated from calorimetric data obtained at 10, 25 and 40° by titrating $0.004M$ $Zn(ClO_4)_2$ solutions with NaCN solutions. The

dilute $Zn(ClO_4)_2$ solutions were used to avoid precipitation of $Zn(CN)_2$.

The ΔH_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°. First, a $M(ClO_4)_2$ solution was titrated with a NaCN solution to a CN^-:M^{2+} ratio of 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

$$\log \gamma = \frac{-Az^2\mu^{1/2}}{1 + Ba\mu^{1/2}} + Cz^2\mu \qquad (3)$$

was used to convert the ion product of water,[19] the dissociation constant of HCN[20,21] and pH to corresponding concentration quotients valid at a given μ value. Equation (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 a and C, respectively, were used since these values gave thermodynamic constants independent of μ.

The method used to calculate ΔH 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° and water[23] at 25°. Values for the heat of ionization of water at 10 and 40° and $\mu = 0$ were determined[24] to be 14.21 and 12.61 kcal./mole, respectively.

In the case of the $Cd^{2+}-CN^-$ and $Hg^{2+}-CN^-$ systems values of ΔH_3 and ΔH_4 were first approximated from the second set of runs and used to calculate ΔH_1 and ΔH_2 values from the first set of runs (see <u>Heat Determinations</u>). These ΔH_1 and ΔH_2 values were then used to calculate new ΔH_3 and ΔH_4 values from the second set of runs. The process was repeated until successively calculated values for the consecutive heats, ΔH_1 through ΔH_4, were obtained which agreed to within $\pm$ 0.005 kcal./mole.

The μ values of the solutions were low ($\mu \leq 0.02$) in all cases. Previous experience[3] with bivalent metal cyanide systems has shown that the dependence of ΔH on μ in dilute aqueous solutions is small compared to the error in measurement of the ΔH values, therefore the measured ΔH values were taken to be ΔH^o 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 ΔCp_i^o were obtained by fitting the ΔH_i^o 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° to give a ΔCp_i^o value. The uncertainty in each ΔCp_i^o value is expressed as twice the standard deviation reflecting the greater uncertainty of this value compared to the ΔH^o_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 μ values other than zero reported by earlier workers [6-9] are in qualitative agreement with those reported here. The ΔH_i values reported by Gerding[12] for the Cd^{2+} -CN^- system are valid in $1M$ $NaClO_4$ 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 ΔCp^o values calculated in the present study allow us to examine this behavior in greater detail and to propose reasons for it.

The effect of ΔCp on the free energy change of a reaction is non-linear. For example, assume that equation 4 accurately describes the variation of ΔCp with temperature. Equations 5 and 6 then follow from basic thermodynamics.

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$$\Delta Cp = a + bT \qquad (4)$$

$$\Delta H = aT + \frac{bT^2}{2} + c \qquad (5)$$

$$T\Delta S = aT\ln T + bT^2 + d \qquad (6)$$

Depending on the magnitude of the coefficients of T in equation (6), the effect of ΔCp on $T\Delta S$ may be larger than on ΔH. Therefore, ΔG may increase or decrease with temperature depending upon the relative magnitudes of the coefficients in equations (4)-(6).

The ΔCp_i^o values given in Table I vary both in sign and magnitude for the various metal cyanide complexes. Such variations in the ΔCp_i^o 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 ΔG_i^o values for the $Cd^{2+}-CN^-$ system is shown in Figure 1 which was constructed by first assuming that equation 4 correctly describes the variation of ΔCp with temperature and then calculating values for a and b from the experimental ΔH values. Values for ΔH and ΔS as a function of temperature were calculated from equations 5 and 6 using the experimental data at 25° to evaluate the integration constants. Free energy changes were then calculated from the relationship: $\Delta G = \Delta H - T\Delta S$. Figure 1 is admittedly hypothetical and may be a gross simplification of the actual temperature variance of ΔG, but it does indicate that the stable species in solution may vary significantly with temperature. For example, at temperatures below −75°, only the $Cd(CN)_2$ and $Cd(CN)_4^{2-}$ species would be predicted to exist in solution. This is similar to the behavior actually observed[4]

for the Zn^{2+}-CN^- system at 25°. Although ΔG, ΔH, and ΔS 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. At 200°C the trend is reversed and only the $CdCN^+$ and $Cd(CN)_3^-$ species would be expected. 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 ΔCp 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 ΔCp values could be more accurately described and these ideas be more rigorously tested.

The effect of temperature on the ΔH°_{0-4} values for the several M^{2+}-CN^- systems is shown in Figure 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.

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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TABLE I

THERMODYNAMIC QUANTITIES[a] FOR THE

Ni^{2+}-, Zn^{2+}-, Cd^{2+}- AND Hg^{2+}-CN^- SYSTEMS

Reaction	T (°C)	μ	Log K	$-\Delta G^o$ (kcal/mole)	$-\Delta H^o$ (kcal/mole)	ΔS^o (cal/deg-mole)	ΔCp^{o}[b] (cal/deg-mole)
Ni^{2+} + 4CN^- = $Ni(CN)_4^{2-}$	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^- = $Zn(CN)_2$	10	0	11.47±0.04	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^- = $Zn(CN)_3$	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	

Reaction	T (°C)	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	$\Delta C_p^{\circ b}$ (cal/deg-mole)
$Zn(CN)_3^- + CN^- = Zn(CN)_4^{2-}$	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	
$Zn^{2+} + 4CN^- = Zn(CN)_4^{2-}$	10	0	20.43	26.47	28.5	-7.2	
	25	0	$(19.62)^e$		27.9	-3.8	24
					(27.8)	$(-3.4)^e$	
	40	0	18.30	26.22	27.7	-4.7	
$Cd^{2+} + CN^- = CdCN^+$	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	
$CdCN^+ + CN^- = Cd(CN)_2$	2	-	$(4.73)^g$				

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Reaction	T (°C)	μ	Log K	$-\Delta G^o$ (kcal/mole)	$-\Delta H^o$ (kcal/mole)	ΔS^o (cal/deg-mole)	$\Delta Cp^{o b}$ (cal/deg-mole)
	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	
$Cd(CN)_2 + CN^- = Cd(CN)_3^-$	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	
$Cd(CN)_3^- + CN^- = Cd(CN)_4^{2-}$	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	

Reaction	T (°C)	μ	Log K	$-\Delta G°$ (kcal/mole)	$-\Delta H°$ (kcal/mole)	$\Delta S°$ (cal/deg-mole)	$\Delta Cp°^b$ (cal/deg-mole)
		3.0	$(3.55)^f$				
		–	$(3.19)^h$				
	40	0	$2.12\underline{+}0.08$	3.04	$5.42\underline{+}0.09$	$-7.6\underline{+}0.1$	
$Cd^{2+} + 4CN^- = Cd(CN)_4^{2-}$	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	
$Hg^{2+} + CN^- = HgCN^+$	10	0	$(17.97)^l$		$23.92\underline{+}0.04$	$-2.3\underline{+}0.1$	
	25	0	$(17.00)^l$		$23.2\underline{+}0.2$	$0.0\underline{+}0.3$	$43\underline{+}8$
					$(23.0)^l$	$(0.7)^l$	
	40	0	$(16.26)^l$		$22.6\underline{+}0.1$	$2.2\underline{+}0.1$	
$HgCN^+ + CN^- = Hg(CN)_2$	10	0	$(16.74)^l$		$24.04\underline{+}0.05$	$-8.3\underline{+}0.1$	
	25	0	$(15.75)^l$		$23.4\underline{+}0.2$	$-6.4\underline{+}0.5$	$37\underline{+}11$
					$(25.5)^l$	$(-13.4)^l$	

Reaction	T (°C)	μ	Log K	$-\Delta G^o$ (kcal/mole)	$-\Delta H^o$ (kcal/mole)	ΔS^o (cal/deg-mole)	$\Delta Cp^{o[b]}$ (cal/deg-mole)
	40	0	$(15.02)^{[l]}$		22.9 ± 0.2	-4.4 ± 0.2	
$Hg(CN)_2 + CN^- = Hg(CN)_3^-$	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
					$(7.6\pm0.2)^{[l]}$	$(-9.0)^{[l]}$	
	40	0	$(3.37)^{[l]}$		6.71 ± 0.03	-6.0 ± 0.1	
$Hg(CN)_3^- + CN^- = Hg(CN)_4^{2-}$	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
					$(7.2)^{[l]}$	$(-12.1)^{[l]}$	
	40	0	$(2.46)^{[l]}$		7.10 ± 0.03	-11.4 ± 0.1	
$Hg^{2+} + 4CN^- = Hg(CN)_4^{2-}$	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	

[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*, 4780 (1959). [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.

FIGURE CAPTIONS

Figure 1.   Plot of ΔG^o values for the consecutive formation

of the indicated species $vs.$ temperature for the

Cd^{2+}-CN^- system.

Figure 2.   Plot of ΔH^o values for the reaction $M^{2+} + 4\ CN^- =$

$M\ (CN)_4^{2-}$ $vs.$ temperature for M = Ni, Zn, Cd, Hg.

FIGURE 1

FIGURE 2