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LOG K_i , ΔH_i° AND ΔS_i° VALUES FOR THE INTERACTION OF GLYCINATE ION
WITH Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} AND Cd^{2+}
AT 10, 25 AND 40°.

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SUMMARY

Values of $\log K_i$, ΔH_i° and ΔS_i° valid at zero ionic strength and at 10, 25 and 40° are reported for the reaction $M^{2+} + iG^- = MG_i^{2-i}$ where G = glycine and M = Mn(i=1), Fe(i=1), Co(i=1,2,3), Ni(i=1,2,3), Cu(i=1,2), Zn(i=1,2,3) and Cd(i=1,2,3). The ΔC_p° values calculated from the temperature dependence of ΔH_i° indicate that solvent effects for the various metal complexes are similar. The temperature dependence of the thermodynamic quantities for the formation of metal-glycinate complexes are similar for each of the metal glycinate systems studied. Values of pK , ΔH° and ΔS° valid at zero ionic strength and at 10, 25 and 40° are reported for proton ionization from glycine and a value of ΔC_p° is estimated from the variation of the ΔH° values with temperature.

INTRODUCTION

Glycine is known to be an important unit in protein structure. Since particular transition metal ions are also known to be indispensable in the proper functioning of many protein and enzyme systems, it is important to know the interaction energies of these metal ions both with the macromolecular compounds and with the individual amino acid units. The present study provides $\log K_i$, ΔH_i° and ΔS_i° values valid at zero ionic strength, μ , and at 10, 25 and 40° for reaction (1)

where G = glycine and M = Mn, Fe, Co, Ni, Cu, Zn and Cd. From the variation of ΔH_i° with temperature $\Delta C_p i$ values are calculated.

Numerous thermodynamic studies have been reported for the interaction of G with the metal ions studied here¹⁻²⁰ and the data from these studies are included in Table 2. However, no complete, consistent determination of the $\log K_i$ values valid at $\mu = 0$ for these metal ions has been made. Recently, ΔH_i values have been determined from calorimetric^{2,9,12,14,17} and $\log K_i$ vs. temperature¹¹ measurements. The ΔH_i values calculated from $\log K_i$ vs. $1/T$ data have some inherent inaccuracies since the $1/T$ method requires taking the derivative of $\Delta G_i^\circ/T$. Most of the previously reported calorimetric data have been determined at high ionic strength or where the stoichiometry of the reaction is uncertain. It, therefore, seemed desirable to study reaction (1) calorimetrically making the measurements in dilute solutions in order that the resulting ΔH_i° data might be combined with the $\log K_i$ data providing a consistent set of thermodynamic data for each M^{2+} -G system.

EXPERIMENTAL

Materials. The NaOH (Baker 'Analyzed') and HClO_4 (Baker and Adamson 'Reagent') solutions used in this study were standardized against potassium hydrogen phthalate (National Bureau of Standards) and tris (hydroxymethyl) aminoethane (THAM) (Fisher 'Certified Reagent'), respectively, and against each other. The sodium glycinate and glycine solutions were prepared from glycine (Calbiochem 'A grade') and NaOH solutions.

The $\text{M}(\text{ClO}_4)_2$ solutions were prepared as follows. $\text{Mn}(\text{ClO}_4)_2$: $\text{Mn}(\text{OH})_2$, precipitated from a MnCl_2 (Baker 'Analyzed') solution under oxygen free conditions with the supernatant having been removed by centrifugation, was dissolved in a known excess of HClO_4 and the solution was filtered to remove any MnO_2 . $\text{Fe}(\text{ClO}_4)_2$: Fe wire (Baker 'Analyzed') was dissolved in a known excess of HClO_4 . $\text{Co}(\text{ClO}_4)_2$ and $\text{Ni}(\text{ClO}_4)_2$: CoCO_3 (Baker 'Analyzed') and NiCO_3 (Baker 'Analyzed'), respectively, were refluxed with solutions containing known amounts of HClO_4 until the ^{values} pH of the solutions were greater than 6. The solutions were cooled, excess metal carbonate was filtered off, and a known amount of HClO_4 was added to suppress hydrolysis. $\text{Cu}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$ and $\text{Cd}(\text{ClO}_4)_2$: known amounts of CuO wire (Baker 'Analyzed'), ZnO (Merck Reagent) and CdO (Matheson, Coleman and Bell 'Reagent Powder'), respectively, were dissolved in known excesses of HClO_4 . The metal perchlorate solutions except $\text{Fe}(\text{ClO}_4)_2$ were standardized for metal ion concentration using EDTA (Baker 'Analyzed') with either Erichrome Black T or Xylenol Orange as indicator. The $\text{Fe}(\text{ClO}_4)_2$ solution was standardized by a thermometric titration of the Fe(II) solution with acidic dichromate.²¹ The results of the Fe(II) determinations gave reproducibility of 0.1% using

Fe(II) concentrations as low as $8 \times 10^{-3}M$.

Proton Ionization from H_2G^+ . Corrections at 10, 25 and 40° for the formation of H_2G^+ and HG were made using literature pK^{22} and ΔH°^{23} values for the reaction $H_2G^+ = HG + H^+$ and pK values²² for the reaction $HG = G^- + H^+$.

Values of ΔH° for the reaction $HG = H^+ + G^-$ were determined²⁴ at 10, 25 and 40° in the following manner using a thermometric titration procedure.²⁵ Glycine solutions were titrated with NaOH solutions, and the resulting heat changes Q , were corrected for heat losses from the calorimeter, heats of dilution and stirring. Appropriate equilibrium constants were used to evaluate the species present and the mmoles of reacted product. From the corrected Q values and mmoles of reacted product, ΔH values were calculated at each temperature, and combined with heat of ionization of water values, *i.e.*, 14.21²⁶, 13.34²⁷ and 12.61²⁶ kcal/mole at 10, 25 and 40°, respectively, to give heat of ionization values for HG at these temperatures. Values of ΔH° were calculated in each case by correcting the ΔH value for the effect of diluting the reactants from a finite concentration to $\mu = 0$. The correction used to extrapolate the ΔH values to $\mu = 0$ was the same as that used to correct the heat of ionization of water to $\mu = 0$.^{26,27}

The heats of dilution of the NaOH titrant were taken from the literature²⁸ at 25° and were measured²⁴ at 10 and 40°.

$M^{2+}-G^-$ Interaction

Equilibrium Constant Determinations. All equilibrium constant determinations were performed with the aid of a Beckman Research pH Meter (Model 1019) or an Orion Ionalyzer (Model 801). Both pH meters were fitted with

Corning Glass and Beckman saturated calomel reference electrodes. Each temperature at which the equilibrium constants were determined was controlled to $\pm 0.1^\circ$.

For experimental purposes, the metal ions were divided into two groups: (a) Mn^{2+} and Fe^{2+} and (b) Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} .

Equilibrium constants for the interaction of Mn^{2+} and Fe^{2+} with G^- were calculated from pH titration curves obtained by the titration in each case of a solution of appropriate HG and $\text{M}(\text{ClO}_4)_2$ concentrations with a NaOH solution. These titrations were performed at 10, 25 and 40° . A precipitate (presumably MnO_2) formed in the case of Mn^{2+} before sufficient of the MnG_2 species was formed to allow calculation of its formation constant. A precipitate also occurred in titrations involving the Fe^{2+} solutions because of the oxidation of Fe^{2+} with subsequent precipitation of $\text{Fe}(\text{OH})_3$. Attempted elimination of all oxygen from the system by using a pure nitrogen atmosphere made it possible to obtain $\bar{n}$ (average number of bound ligands per metal ion) values of approximately 1.2 before precipitation of $\text{Fe}(\text{OH})_3$ occurred, but this was not considered a large enough $\bar{n}$ value to calculate accurate constants for the formation of FeG_2 . Thus, K values for the formation of FeG^+ and MnG^+ , but not FeG_2 and MnG_2 are reported in this study.

The K values for the interaction of G^- with the metal ions of group (b) were determined by titration of each $\text{M}(\text{ClO}_4)_2$ solution with a sodium glycinate solution and measuring the resulting pH as a function of titrant added. In each case, except Cu^{2+} , three complexes, *i.e.*, MG^+ , $\text{MG}_2(\text{aq})$ and MG_3^- , were observed. In the case of Cu^{2+} , only CuG^+ and $\text{CuG}_2(\text{aq})$ were found for $\text{G}^-:\text{Cu}^{2+}$ ratios less than 4. Difficulty was encountered in the measurement of the equilibrium constant for the formation of the

ZnG_3^- species. This difficulty is reflected in the large deviations observed in the calculated K values which suggest either that the species was more complex than the simple stoichiometry predicted, or that some experimental parameter was in error. When $\text{Zn}(\text{ClO}_4)_2$ solutions were titrated with G^- solutions beyond a ratio of 2 G^- per Zn^{2+} , a poisoning effect of the glass electrode was observed which could be reversed by immersing the electrode in HCl solutions. It is, therefore, believed that the third species was formed and that the difficulty of determining K_3 was due to the poisoning of the glass electrode.

Heat Determinations. Heats of complexation for the $\text{Mn}^{2+}\text{-G}^-$ and $\text{Fe}^{2+}\text{-G}^-$ systems were determined by titration of metal perchlorate solutions containing an excess of glycine with NaOH solutions. The resulting heat changes were then corrected for heats of dilution and the heat effect resulting from the formation of water^{26,27} and proton ionization from H_2G^+ .²²⁻²⁵ The number of mmoles of MG_i^{2-i} formed was calculated using the appropriate K_i values, and the ΔH_i values were calculated.

The heats of $\text{M}^{2+}\text{-G}^-$ interaction for metal ions in group (b) were obtained from data measured by titrating the metal perchlorate solutions with sodium glycinate solutions. The measured heats were corrected for heat effects and ΔH values were calculated as was done in the Mn(II)- and Fe(II)-glycinate systems.

Calculations. The equilibrium constants were calculated by a procedure that has been previously described²⁹ and later improved.³⁰ Equation (2) was used to convert all concentrations to activities and pH values to concentrations.

$$\log \frac{-Az \mu^{1/2}}{1 + Ba \mu^{1/2}} + Cz^2 \mu \quad (2)$$

All activity coefficients were determined using an $\bar{a}$ value of 4.4 Å and a C value of 0.3 because thermodynamic constants independent of μ were calculated when these parameters were used. The ion product of water³¹ was taken from the literature.

The method used to calculate ΔH_i values from the thermometric titration data has been described,^{32,33} including modifications.²⁴ Since the μ values were low ($\mu < X.XX$) in all cases, the ΔH values were taken to be ΔH° values valid at $\mu = 0$.

RESULTS

The average values³⁴ for the thermodynamic functions for the second ionization of protonated glycine corrected to $\mu = 0$ are summarized in Table 1 along with comparative literature values.

Values for $\log K_i$, ΔH°_i , ΔS°_i and ΔC°_{pi} valid at $\mu = 0$ for all of the metal glycinate systems studied³⁴ are summarized in Table 2 together with comparative literature values.

DISCUSSION

The $\log K_i$ and ΔH_i° values determined in this study are generally in good agreement with previously reported values determined under similar conditions. The ionic strengths used in many studies^{6-11,13-20} varied so widely that no comparison of the data from studies at ionic strength other than zero or near zero is attempted.

The calorimetric data reported by Skinner and Stack¹² were determined under conditions where some question existed as to the final products of the reaction. In addition, large, somewhat uncertain corrections were made in their enthalpy values. These corrections were, in some cases, adjusted somewhat arbitrarily to allow for the presence of ML^+ and ML_3^- . If similar corrections are made using the constants determined in this study corrected to the ionic strength reported by Skinner and Stack, very good agreement is obtained between the values reported by them and those determined in this study.

The values reported by Brannan, Dunsmore and Nancollas³ agree well with the $\log K$ determinations given here, but their enthalpy values are in general considered less accurate since the ΔH values reported by them were determined from a plot of $1/T$ vs. $\log K$. The calorimetric ΔH values reported by Boyd, *et al.*,⁹ are generally in good agreement with those reported in this study except in the case of the copper glycinate system. Their ΔH values for this system are much larger than the ΔH values reported by any of the authors cited in Table 2.

The $\log K$ values in Table 2 which were reported by Anderson, *et al.*,^{1,14} are generally in agreement with those reported in this study, but their enthalpy results are considered to be less reliable than the $\log K$ values. The ΔH values for the protonation of the glycinate ion as well as the ΔH

values for the ionization of water at 10 and 40° reported by Anderson, *et. al.*, do not agree well with the calorimetric determination reported here or elsewhere. The pK vs. $1/T$ data for glycine ionization^{22,35} indicate that the changes in ΔH should follow a smooth, regular trend as reported in this study, and not an irregular trend like that reported by Anderson, *et. al.*^{1,14}

The ΔH° values for the consecutive reactions in the $M^{2+}-G^-$ systems become more negative with each step. For the same consecutive reactions the ΔG° values become more positive paralleling the change in ΔS° . This observation of ΔG° paralleling changes in ΔS° , but not in ΔH° is also generally true for the cyanide complexes³⁶ and other metal ligand systems.

Comparisons of ΔCp values have the advantage over ΔS comparisons that there is no cratic or statistical term contributing to the magnitude of ΔCp . This means that ΔCp provides a more direct measure of the solute-solvent interaction. In the case of the ligand glycine, the $M^{2+}-G^-$ systems studied have very similar ΔCp values which indicates that for the metal glycinate systems, the metal and metal complex interaction with the solvent is quite similar for each of the metal ions. Thus direct comparison of ΔH values should correlate relative bond strengths of metal-ligand bonds, provided that ligand field effects have been previously removed from the system.

Because of the lack of reliable ΔH data for metal complexation reactions, the assumption that ΔG is proportional to ΔH is usually invoked to make comparisons of the ligand field effects on the various metal ions. Since this study contains reliable, measured ΔH values, a comparison was made between these values and the predicted stabilization energies using ΔG as a reference state calculated by George and McClure.³⁷

The ligand field stabilization energy added by the ligand was estimated by plotting the ΔH_L value from Equation 2 vs. atomic number. Values for the heats of hydration of the various metal ions were taken from HBS Circular 500³⁸ and Brewer, *et al.*³⁹

$$M^{2+} (g) + G^- (aq) = MG^+ (aq) \quad \Delta H_L = \Delta H_{\text{hydration}} + \Delta H_{\text{complexation}} \quad (2)$$

The values reported by George have been adjusted to correspond to the same ΔH_L values for Mn^{2+} as those reported in this study (*i.e.*, George and McClure reported relative values only) and are also plotted in Figure 1. The values reported by George and McClure are in agreement with ± 1.5 kcal/mole in each case.

Values for the stabilization energies were computed by taking the difference in the ΔH_L values reported for Zn^{2+} and Mn^{2+} which have no stabilization energies associated with their ground states, and assuming that the increase in ΔH_L with atomic number between Mn^{2+} and Zn^{2+} would be linear in the absence of ligand field effects.³⁷ The difference between the ΔH value computed from the consideration that the increase in ΔH is linear and the ΔH_L value experimentally determined was taken to be the ligand field stabilization energy. The stabilization energies calculated were 19.5, 25.7, 36.7, and 28.8 kcal/mole for the FeG^+ , CoG^+ , NiG^+ and CuG^+ , respectively. When all of the ligand field effects are considered to be directed in a symmetrical octahedral field, values for the splitting parameter, Δ , for the Fe^{2+} - Cu^{2+} glycinate systems were calculated to be 58, 32, 30, and 48 kcal/mole, respectively.

A simple electrostatic model⁴⁰ has been used to attempt to explain metal ligand behavior. The model predicts that ΔG would decrease in a regular fashion to $\Delta Cp = 0$ for the reaction $MG_2 + G^- = MG_3^-$. The proportionality for ΔG vs. ΔS is not observed for the metal glycinate nor was it observed for the metal cyanide complexes of Zn^{2+} , Ni^{2+} , Cd^{2+} and

Hg^{2+} .³⁶ Also, ΔC_p does not decrease in a predicted regular fashion for the third glycinate ion is near zero in all cases reported in this study. These observations suggest that the electrostatic model does not generally predict metal glycinate behavior.

The ΔC_p values reported in this study are in good agreement with those published previously. The ΔC_p values were calculated by fitting the experimental ΔH values to a quadratic function of T and differentiating with respect to T . Ackermann⁴¹ has made calorimetric measurements for ΔC_p for the reaction $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ and has found ΔC_p to be a nonlinear function (probably quadratic) of temperature and by inference has indicated that ΔC_p for other systems have large non-linear temperature dependence. The data given in Table 2 were not of sufficient accuracy to allow a calculation of ΔC_p temperature dependence and therefore uncertainties of twice the standard deviation were assigned to the reported values.

To consider the effect of temperature on the free energy, ΔC_p values were fitted to equation 3 using the ΔH and ΔS functions could be calculated and using the relationship $\Delta G = \Delta H - T\Delta S$, a temperature dependent function for ΔG was derived. The ΔG values for the stepwise formation of MG_3^- as a function of temperature are plotted in Figures 2 and 3 for the Ni^{2+} - and Zn^{2+} - G^- systems, respectively.

These two plots show many dissimilarities presumably due to the uncertainties in the experimental data, but they both illustrate a definite trend toward more stable second and third species at low temperature and less stability of the third species at high temperature. The ΔS values for the reaction $\text{MG}_2^+ - \text{G}^- = \text{MG}_3^-$ becomes negative enough that the MG_3^- species becomes metastable or nonexistent.

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TABLE 1

THERMODYNAMICS OF THE IONIZATION OF GLYCINE IN AQUEOUS SOLUTION

T°C	pK	ΔG° (kcal/mole)	ΔH° (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
10	(10.193±0.001) ^a	(13.205) ^a	10.85±0.03 (10.73) ^a (11.57) ^b	-8.25±0.11	
		(13.205) ^c	(10.72) ^c		
25	(9.780±0.001) ^a	(13.341) ^a	10.55±0.03 (10.55) ^a (10.76) ^b	-9.36±0.10	17±2
		(13.339) ^c	(10.56) ^c (10.57) ^d (10.6) ^e (10.60) ^f		
40	(9.412±0.001) ^a	(13.485) ^a	10.38±0.03 (10.37) ^a (10.22) ^b	-10.01±0.13	
		(13.484) ^c	(10.40) ^c		

^aRef. 22. ^bRef. 14. ^cRef. 35. ^dJ. A. Partridge, J. J. Christensen and R. M. Izatt, *J. Amer. Chem. Soc.*, 88, 1649 (1966). ^eJ. Sturtevant, *J. Amer. Chem. Soc.*, 72, 1804 (1950). ^fRef. 31, corrected using data from Ref. 27.

TABLE 2
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
$Mn^{2+} + G^- = MnG^+$	10	0	3.23 $\pm$.02	4.18	0.40 $\pm$ 0.20	13.3 $\pm$ 0.2	
		0	(3.18) ^a		(0.50)*, ^a		
	20	0.01	(3.2) ^b				
	25	0	3.21 $\pm$.02	4.38	0.30 $\pm$ 0.10	13.7 $\pm$ 0.2	12 $\pm$ 10
		0	(3.17) ^c		(0.29)*, ^c	(13.5) ^c	(16) ^c
		0	(3.44) ^d				
		0.01	(3.66) ^e				
	30	0.09	(3.12)		(5) ^f	(-3) ^f	
	40	0	3.15 $\pm$.02	4.52	0.04 $\pm$ 0.13	14.3 $\pm$ 0.1	
		0	(3.16) ^a		(0.03)*, ^a		
$Fe^{2+} + G^- = FeG^+$	10	0	4.36 $\pm$.03	5.65	3.72 $\pm$ 0.20	6.8 $\pm$ 0.2	
	20	0.01	(4.3) ^b				
	25	0	4.31 $\pm$.02	5.88	3.64 $\pm$ 0.15	7.5 $\pm$ 0.2	7 $\pm$ 10
		1.0	(3.83) ^g				
	40	0	4.28 $\pm$.02	6.13	3.55 $\pm$ 0.16	8.2 $\pm$ 0.2	

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
$Co^{2+} + G^- = CoG^+$	10	0	5.16 $\pm$ 0.01	6.68	3.00	13.0 $\pm$ 0.2	
		0	(5.18) ^a		(3.09)*, ^a		
	15	0.2	(4.76) ^h		(2.0)*, ^h	(14.9) ^h	
	20	0.01	(5.1) ^b				
		0.5	(4.61) ⁱ				
	25	0	5.07 $\pm$ 0.01	6.91	2.86 $\pm$ 0.06	13.6 $\pm$ 0.2	28 $\pm$ 3
		0	(5.072) ^c		(2.82)*, ^c	(13.7) ^c	(22) ^c
		0	(5.23) ^d				
		0.01	(4.95) ^e				
		0.1			(2.83) ^j		
		0.15	(4.65) ^k				
	40	0	4.98 $\pm$ 0.01	7.14	2.15 $\pm$ 0.03	15.9 $\pm$ 0.1	
		0	(4.98) ^a		(2.44)*, ^a		
$CoG^+ + G^- = CoG_2$	10	0	4.07 $\pm$ 0.01	5.27	4.00 $\pm$ 0.02	4.49 $\pm$ 0.08	
		0	(4.12) ^a		(3.85)*, ^a		
	15	0.2	(3.56) ^h		(3.6) ^h	(3.7) ^h	

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
$\text{CoG}_2 + \text{G}^- = \text{CoG}_3^-$	20	0.01	(3.8) ^b				
		0.5	(3.75) ⁱ				
	25	0	4.02±0.01	5.48	3.54±0.03	6.52±0.11	20±2
		0	(3.97) ^c		(3.55)* ^c	(6.3) ^c	(24) ^c
		0	(4.02) ^d				
		0.01	(3.99) ^e				
		0.1			(2.72) ^j		
		0.15	(3.78) ^k				
	40	0	3.91±0.01	5.60	3.41±0.02	7.00±0.07	
		0	(3.86) ^a		(3.13)* ^a		
	10	0	2.67±0.06	3.46	3.63±0.02	-0.6±0.2	
	20	0.5	(2.56) ⁱ				
	25	0	2.54±0.04	3.47	3.41±0.06	0.2±0.2	21±3
		0.15	(2.38) ^k				
	40	0	2.45±0.05	3.51	3.01±0.04	1.6±0.2	

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC°_p (cal/deg-mole)
$Co^{2+} + 2G^- = CoG_2$	10	0	9.23	11.95	7.00	17.5	
	15	0.2			(5.6) ^h	(19) ^h	
	23	0.1			(6.6) ^l		
	25	0	9.09	12.39	6.40	20.1	48
	40	0	8.89	12.74	5.56	22.9	
$Co^{2+} + 3G^- = CoG_3^-$	10	0	11.90	15.41	10.63	16.9	
	23	0.1			(9.8) ^m		
	25	0	11.62	15.86	9.81	20.3	69
	40	0	11.34	16.25	8.57	24.5	
$Ni^{2+} + G^- = NiG^+$	10	0	6.28±0.01	8.14	4.63±0.11	12.4±0.4	
		0	(6.34) ^a		(4.27)*, ^a		
		0	(6.36) ⁿ		(5.2) ⁿ		
	15	0.2	(6.04) ^h		(4.3)*, ^h	(12.7) ^h	
	20	0.01	(6.1) ^b				
		0.5	(5.77) ⁱ				

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	$\Delta C^\circ p$ (cal/deg-mole)
	25	0	6.13±0.01	8.36	4.38±0.05	13.4±0.4	28±6
		0	(6.18) ^c		(4.09)* ^c	(14.5) ^c	(18) ^c
		0	(6.18) ⁿ		(4.9) ⁿ		
		0	(6.18) ^d				
		0.01	(6.12) ^e				
		0.1			(4.34) ^j		
	40	0	6.00±0.01	8.60	3.77±0.12	15.4±0.4	
		0	(6.04) ^a		(3.73)* ^a		
		0	(6.09) ⁿ		(4.3) ⁿ		
NiG ⁺ + G ⁻ = NiG ₂	10	0	5.14±0.01	6.66	5.30±0.04	4.8±.2	
		0	(5.14) ^a		(5.03)* ^a		
		0	(5.29) ⁿ		(5.8) ⁿ		
	15	0.2	(4.98) ^h		(4.4)* ^h	(6.0) ^h	
	20	0.01	(4.9) ^b				
		0.5	(4.80) ⁱ				
	25	0	4.92±0.01	6.71	4.97±0.05	5.8±0.2	23±3

TABLE 2 (cont.)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
		0	(4.95) ^c		(4.69)* ^c	(6.9) ^c	(28) ^c
		0	(5.07) ⁿ		(4.7) ⁿ		
		0	(4.96) ^d				
		0.01	(5.03) ^e				
	40	0	4.76±0.01	6.82	4.60±0.06	7.1±0.2	
		0	(4.79) ^a		(4.19)* ^a		
		0	(4.92) ⁿ		(4.7) ⁿ		
$NiG_2 + G^- = NiG_3^-$	10	0	3.51±0.03	4.55	5.64±0.05	-3.9±0.3	
	20	0.5	(3.61) ⁱ				
	25	0	3.18±0.03	4.34	5.55±0.03	-4.1±0.3	5±5
	40	0	3.00±0.03	4.30	5.50±0.07	-3.8±0.2	
$Ni^{2+} + 2G^- = NiG_2$	10	0	11.42	14.80	9.92	17.2	
	15	0.2			(8.8) ^h	(20) ^h	
	23	0.1			(8.8) ^l		
	25	0	11.05	15.07	9.35	-19.2	51

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	$\Delta C^\circ p$ (cal/deg-mole)
$Ni^{2+} + 3G^- = NiG_3^-$		0.15	(10.92) ^a		(14.0) ^o	(2.5) ^o	
	40	0	10.76	15.42	8.37	22.5	
	10	0	14.93	19.35	15.56	13.3	
	23	0.1			(14.80) ^m		
	25	0	14.23	19.41	14.90	15.1	56
	40	0	13.76	19.72	13.87	18.7	
$Cu^{2+} + G^- = CuG^+$	10	0	8.85 $\pm$ 0.02	11.01	6.23 $\pm$ 0.06	16.9 $\pm$ 0.2	
		0	(8.85) ^p		(7.28) ^p		
	15	0.2	(8.54) ^h		(4.8) ^{*h}	(22.4) ^h	
	20	0.01	(8.5) ^b				
		0.0001	(8.6) ^q				
		0.5	(8.22) ⁱ				
	25	0	8.57 $\pm$ 0.02	11.69	5.82 $\pm$ 0.09	19.7 $\pm$ 0.3	25 $\pm$ 4
		0	(8.58) ^p		(6.22) ^p		
		0	(8.62) ^d				

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
$CuG^+ + G^- = CuG_2$		0	(8.29) ^r				
		0	(8.53) ^s		(6.0) ^s		
		0.01	(8.51) ^e				
		0.1			(7.11) ^j		
	30	0.09	(8.00) ^f		(7.00) ^f	(14) ^f	
	40	0	8.33±0.02	11.94	5.47±0.08	20.6±0.3	
		0	(8.42) ^p		(5.75) ^p		
	10	0	7.52±0.02	9.74	7.20±0.11	9.0±0.4	
		0	(7.36) ^p		(6.92) ^p		
	15	0.2	(7.00) ^h		(6.8)*, ^h	(11.4) ^h	
	20	0.01	(6.9) ^b				
		0.0001	(7.14) ^q				
		0.5	(6.97) ⁱ				
	25	0	7.26±0.02	9.90	6.93±0.07	10.0±0.2	20±5
		0	(7.09) ^p		(6.96) ^p		

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
		0	(6.97) ^d				
		0	(7.61) ^r				
		0	(7.14) ^s		(6.4) ^s		
		0.01	(6.91) ^e				
		0.1			(7.06) ^j		
	30	0.09	(6.39) ^f				
	40	0	7.00±0.02	10.03	6.59±0.05	11.0±0.2	
		0	(6.85) ^p		(7.33) ^p		
$Cu^{2+} + 2G^- = CuG_2$	10	0	16.36	20.75	13.43	25.9	
	15	0.2			(10.7)* ^h	(34) ^h	
	23	0.1	(15.10) ^p		(12.8) ^p		
	25	0	15.83	21.59	12.75	29.7	45
		0.15	(15.10) ^o		(21.0)* ^o	(-1.2) ^o	
	40	0	15.33	21.97	12.06	31.6	
$Zn^{2+} + G^- = ZnG^+$	10	0	5.50±0.02	7.16	3.14±0.07	14.2±0.3	

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
$ZnG^+ + G^- = ZnG_2$	15	0.2	(5.27) ^h		(3.3)* ^h	(12.7) ^h	
	20	0.01	(5.2) ^b				
		0.5	(4.80) ⁱ				
	25	0	5.38±0.02	7.34	2.76±0.05	15.4±0.2	31±4
		0	(5.52) ^d				
		0.01	(5.33) ^e				
		0.1			3.39		
	40	0	5.29±0.02	7.58	2.22±0.07	17.1±0.2	
	10	0	4.57±0.02	5.92	3.73±0.03	7.7±0.1	
	15	0.2	(4.31) ^h		(4.0)* ^h	(6.0) ^h	
	20	0.01	(4.1) ^b				
		0.5	(4.14) ^a				
	25	0	4.43±0.02	6.04	3.22±0.04	9.5±0.2	28±2
		0	(4.44) ^d				
		0.01	(4.39) ^e				
	40	0	4.29±0.01	6.14	2.90±0.03	10.4±0.1	

TABLE 2 (con't)
THERMODYNAMICS OF M^{2+} -GLYCINATE ION INTERACTION

Reaction	T°C	μ	Log K	$-\Delta G^\circ$ (kcal/mole)	$-\Delta H^\circ$ (kcal/mole)	ΔS° (cal/deg-mole)	ΔC_p° (cal/deg-mole)
$Cd^{2+} + 2G^- = CdG_2$	10	0	8.46	11.00	6.00	17.7	
	25	0	8.41	11.46	5.36	20.5	36
	40	0	8.20	11.75	4.90	21.8	
$Cd^{2+} + 3G^- = CdG_3^-$	10	0	10.99	14.28	8.84	19.2	
	25	0	10.60	14.57	8.57	20.2	18
	40	0	10.20	14.61	8.29	20.1	

* ΔH Values determined from $1/T$ data. ^aData calculated from results in Ref. 3. ^bRef. 2. ^cRef. 3.
^dRef. 4. ^eRef. 6. ^fRef. 18. ^gRef. 7. ^hRef. 11. ⁱRef. 8. ^jRef. 9. ^kRef. 10. ^lRef. 12. ^mData
calculated from results in Ref. 12. ⁿRef. 1. ^oRef. 13. ^pRef. 14. ^qRef. 15. ^rRef. 16. ^sRef. 17.
^tRef. 19. ^uRef. 20.

FIGURE CAPTIONS

Figure 1. Plot of ΔH_L vs. atomic number (Mn-Zn) for the reaction

Figure 2. Plot of ΔG_i^o vs. temperature for the Ni^{2+} - G^- system.

Figure 3. Plot of ΔG_i^o vs. temperature for the Zn^{2+} - G^- system.

FIGURE 1

FIGURE 2

FIGURE 3