Log K_i, ΔH°_i, and ΔS°_i Values for the Interaction of Glycinate Ion with H^+, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} at 10, 25, and 40°

By **Reed M. Izatt**, **H. Dee Johnson**, and **James J. Christensen**,* Departments of Chemistry and Chemical Engineering and No. 11 from the Center for Thermochemical Studies, Brigham Young University, Provo, Utah 84601

Values of log K_i, ΔH°_i, and ΔS°_i valid at zero ionic strength in aqueous solution are reported for the reaction $MG_i^{2-i} + G^- = MG_{i+1}^{1-i}$ where G = glycine and M = Mn(i = 0), Fe(i = 0), Co(i = 0,1,2), Ni(i = 0,1,2), Cu(i = 0,1), Zn(i = 0,1,2), and Cd(i = 0,1,2) at 10, 25, and 40°. The ΔC°_{pi} values calculated from the temperature dependence of ΔH°_i indicate that solvent effects for the various metal complexes are similar. Values of pK, ΔH°, and ΔS° valid at zero ionic strength are determined or summarized from the literature for proton ionization from glycine at 10, 25, and 40° and a value of ΔC°_p is calculated from the temperature variation of the ΔH° values.

GLYCINE is an integral unit of protein structure. Since particular transition-metal ions are 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 macro-molecular compounds and with the individual amino-acid units. In the present study K_i, ΔH°_i, and ΔS°_i values valid at zero ionic strength, μ, have been determined for reactions (1) and (2) at 10, 25, and 40° where G = glycine and

$$HG = H^+ + G^- \qquad (1)$$

$$MG_i^{2-i} + G^- = MG_{i+1}^{1-i} \qquad (2)$$

M = Mn, Fe, Co, Ni, Cu, Zn, and Cd. Values of ΔC°_{pi} are calculated from the variation of corresponding ΔH°_i values with temperature.

Numerous thermodynamic studies, mainly involving the determination of K_i values, have been reported for the interaction of G^- with H^+ and with the metal ions at the same conditions as studied here and the results from these studies are summarized together with the results reported here in Tables 1 and 2.* Recently, ΔH_i values have been determined for reactions (1) and (2) both from calorimetric and variation of K_i with temperature data. Calculation of ΔH_i values from K_i *vs.* $1/T$ data usually involves the assumption that ΔH_i is constant over the temperature range involved. The recent determination of ΔH_i values as a function of temperature has shown that this assumption is often unfounded, *i.e.* ΔC_p values for proton ionization and metal-complex formation reactions are frequently large.[1-5] Furthermore, errors in ΔH_i values cannot be estimated from the corresponding log K_i values alone. Most of the previously reported calorimetric data have been determined at high ionic strengths or where the stoicheiometry of the reactions was uncertain. It seemed desirable, therefore, to study reactions (1) and (2) calorimetrically making the measurements in dilute solutions in order that the resulting ΔH°_i values might be combined with the corresponding K_i values to provide a consistent set of thermodynamic data for each system.

EXPERIMENTAL

Materials.—The NaOH (Baker Analysed) 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)-aminomethane (Fisher Certified Reagent), respectively, and against each other. The sodium glycinate and glycine solutions were prepared from glycine (Calibiochem A grade) and NaOH solutions.

The $M(ClO_4)_2$ solutions were prepared as follows.

$Mn(ClO_4)_2$. $Mn(OH)_2$ was precipitated from a $MnCl_2$ (Baker Analysed) solution under oxygen-free conditions and the supernatant liquid was removed by centrifugation. The $Mn(OH)_2$ was then dissolved in a known excess of $HClO_4$ and the solution was filtered to remove any MnO_2.

$Fe(ClO_4)_2$. Fe wire (Baker Analysed) was dissolved in a known excess of $HClO_4$.

$Co(ClO_4)_2$ and $Ni(ClO_4)_2$. $CoCO_3$ (Baker Analysed) and $NiCO_3$ (Baker Analysed), respectively, were refluxed with solutions containing known amounts of $HClO_4$ until the pH values of the solutions were greater than 6. The solutions were cooled, excess of metal carbonate was filtered off, and a known amount of $HClO_4$ was added to suppress hydrolysis.

$Cu(ClO_4)_2$, $Zn(ClO_4)_2$, and $Cd(ClO_4)_2$. Known amounts of CuO wire (Baker Analysed), 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 $Fe(ClO_4)_2$, were standardized for metal-ion concentration using EDTA (Baker Analysed) with either Erichrome Black T or Xylenol Orange as indicator. The $Fe(ClO_4)_2$ solution was standardized by a thermometric titration of the Fe^{II} solution with acidic dichromate.[6] The results of the Fe^{II} determinations gave reproducibility of $\pm 0{\cdot}1\%$ using Fe^{II} concentrations as low as 8×10^{-3}M.

Proton Ionization from HG *and* H_2G^+.—Values of ΔH° for the reaction $HG = H^+ + G^-$ were determined at 10, 25, and 40° in the following manner using a calorimetric titration procedure.[7] Five duplicate glycine solutions (100 ml, $1{\cdot}100 \times 10^{-2}$M-HG) were titrated with 0·2087M-NaOH solutions at each temperature and the resulting heat changes, Q, were corrected for heat losses from the calorimeter, heats of dilution, and heats of stirring. Corrections at 10, 25, and 40° for the formation of H_2G^+ were made using literature pK[8] and ΔH°[9] values for the reaction $H_2G^+ = HG + H^+$. The pK[8] values at 10, 25, and 40° for the reaction $HG = H^+ + G^-$ were used to evaluate the mmoles of HG reacted. From the corrected Q values and mmoles of HG reacted, ΔH values were calculated at each temperature, and combined with heat of ionization of water values, *i.e.* 14·22 (ref. 10), 13·34 (ref. 11), and 12·70 (ref. 10) kcal/mol 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 value to $\mu = 0$ was the same as that used to correct the heat of ionization of water to $\mu = 0$.[10,11]

The heats of dilution of the NaOH titrant were taken from the literature[12] at 25° and were measured[13] at 10 and 40°.

---

* The results of other thermodynamic studies for the interaction of G^- with H^+ and with the metal ions studied here, *but not under the same conditions*, are given in expanded versions of Tables 1 and 2 which are deposited with the N.L.L. as Supplementary Publication No. 20353, 21 pp., 1 microfiche (see note concerning Supplementary Publications in Notice to Authors No. 7, *J. Chem. Soc. (A)*, Issue No. 20, 1970).

[1] R. M. Izatt, H. D. Johnston, D. J. Eatough, J. W. Hansen, and J. J. Christensen, *Thermochim. Acta*, 1971, **2**, 77.

[2] J. J. Christensen, M. D. Slade, D. E. Smith, R. M. Izatt, and J. Tsang, *J. Amer. Chem. Soc.*, 1970, **92**, 4164.

[3] J. J. Christensen, J. H. Rytting, and R. M. Izatt, *J. Chem. Soc. (B)*, 1970, 1643.

[4] J. J. Christensen, J. H. Rytting, and R. M. Izatt, *Biochemistry*, 1970, **9**, 4907.

[5] J. J. Christensen, J. H. Rytting, and R. M. Izatt, *J. Chem. Soc. (B)*, 1970, 1646.

[6] L. D. Hansen, J. J. Christensen, and R. M. Izatt, 'Applications of Thermometric Titrimetry to Analytical Chemistry in New Developments in Titrimetry,' ed. J. Jordan, Marcel Dekker, in the press.

[7] J. J. Christensen, R. M. Izatt, and L. D. Hansen, *Rev. Sci. Instr.*, 1965, **36**, 779.

[8] E. J. King, *J. Amer. Chem. Soc.*, 1951, **73**, 155.

[9] J. J. Christensen, J. L. Oscarson, and R. M. Izatt, *J. Amer. Chem. Soc.*, 1968, **90**, 5949.

[10] J. J. Christensen, G. L. Kimball, H. D. Johnston, and R. M. Izatt, *Thermochim. Acta*, in the press.

[11] J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605.

[12] C. E. Vanderzee and J. A. Swanson, *J. Phys. Chem.*, 1963, **67**, 2608.

[13] H. D. Johnston, Ph.D. Dissertation, Brigham Young University, Provo, Utah, 1968 (*Diss. Abs.*, 1969, **29**, 4128B).

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 Ionalyser (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 ±0·1°.

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 at 10, 25, and 40° by the titration in each case of a solution of appropriate HG and $M(ClO_4)_2$ concentrations with a 0·2087M-NaOH solution. Concentrations of HG and $M(ClO_4)_2$ ranged from $1·7 \times 10^{-2}$ to $2·6 \times 10^{-2}$M and $5·9 \times 10^{-3}$ to $4·2 \times 10^{-3}$M, respectively. Between 20 and 25 titration curves were obtained for each system at each of the three temperatures studied. 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 iron(III) hydroxide. Use of a pure nitrogen atmosphere made it possible to obtain $\bar{n}$ (average number of bound ligands per metal ion) values of *ca.* 1·2 before precipitation of iron(III) hydroxide occurred, but this was not considered a large enough $\bar{n}$ value to calculate accurate constants for the formation of FeG_2. The agreement of the calculated log K values and the observed stabilities of the systems in the regions where MnG^+ and FeG^+ were predominant was taken as evidence that oxidation had not occurred in these regions. Thus, K_i values for the formation of FeG^+ and MnG^+, but not FeG_2 and MnG_2 are reported for these systems.

The K_i values for the interaction of G^- with the metal ions of group (*b*) were determined from 20 to 25 sets of pH titration data obtained by titrating each $M(ClO_4)_2$ solution with a sodium glycinate solution. Typical ranges of concentrations of metal ion and glycinate ion in solution were $M^{2+} = 8·0 \times 10^{-3}$—$9·0 \times 10^{-4}$M, $G^- = 0·390$—$0·400$M. In each case, except Cu^{2+}, three complexes, *i.e.* MG^+, MG_2(aq), and MG_3^-, were observed. In the case of Cu^{2+}, only CuG^+ and CuG_2(aq) were found for $G^- : Cu^{2+}$ 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 stoicheiometry predicted, or that some experimental parameter was in error. When $Zn(ClO_4)_2$ solutions were titrated with G^- solutions beyond a ratio of 2 G^- per Zn^{2+}, an apparent poisoning 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 complex formation for metal ions in group (*a*) (Mn^{2+} and Fe^{2+}) were determined by calorimetric titrations of metal perchlorate solutions containing an excess of glycine with NaOH solutions. Typical concentrations used were: titrate = $7·840 \times 10^{-3}$M-$Mn[ClO_4]_2$ and $5·210 \times 10^{-3}$M-$HClO_4$; titrant = 0·2086M-HG and 0·0195M-NaOH. Five runs were made for each metal ion. The resulting heat changes were then corrected for heats of dilution and the heat effects resulting from the formation of water [10,11] and proton ionization from HG [8,13] and H_2G^+.[9] This procedure allowed the reaction in the calorimeter to proceed without the formation of precipitates.

The heats of complex formation for metal ions in group (*b*) (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) were obtained from data measured by titrating the metal perchlorate solutions with sodium glycinate solutions. Typical concentrations used were: titrate = $7·639 \times 10^{-3}$M-$Cu(ClO_4)_2$ and $6·583 \times 10^{-3}$M-$HClO_4$; titrant = 0·3986M-HG and 0·3909M-NaOH. Five runs were made for each metal ion.

Calculations.—The equilibrium constants were calculated by a procedure that has been previously described [14] and later improved.[15] Equation (3) was used to convert all

$$\log \gamma = \frac{-Az^2\mu^{0·5}}{1 + B^\circ a\mu^{0·5}} + Cz^2\mu \qquad (3)$$

concentrations to activities and pH values to concentrations. All activity coefficients were determined using values of 4·4 Å and 0·3 for a and C, respectively, because equilibrium constants independent of μ were calculated when these parameters were used. The ion product of water was taken from the literature.[16]

TABLE 1

Thermodynamic quantities for the ionization of glycine in aqueous solution,[a] $HG = H^+ + G^-$

t (°C)	pK	ΔH° (kcal/mol)	ΔS° (cal/deg/mol)	ΔC°_p (cal/deg/mol)
10	(10·193) [b]	10·85 ± 0·03	−8·32	
		(10·73) [b]		
		(11·57) [c]		
		(10·73) [d]		
25	(9·780) [b]	10·55 ± 0·03	−9·36	
		(10·55) [b]		(−12) [b]
		(10·76) [c]		
		(10·57) [d–f]		(−11) [d]
40	(9·412) [b]	10·38 ± 0·03	−9·91	
		(10·37) [b]		
		(10·22) [c]		
		(10·40) [d]		
10—40				−16 ± 4

[a] The ΔH° values reported are the averages of several runs in each case with the uncertainties expressed as standard deviations among runs, $\mu = 0$. The uncertainty of the ΔC_p° value is estimated to be twice that which results when ΔC_p° values are calculated from ΔH° values at the extremes of their uncertainties. For a complete literature survey of earlier pK values see R. M. Izatt and J. J. Christensen in 'Handbook of Biochemistry and Selected Data for Molecular Biology,' Chem. Rubber Pub. Co., Cleveland, 2nd edn., 1970, pp. J-58—173. All data are valid at $\mu = 0$ except those from *c* ($\mu = 0·01$). The ΔH° values in *c*, *e*, and *f* were determined calorimetrically; those in *b* and *d* were calculated from the variation of pK with temperature. [b] Ref. 8. [c] Ref. 20. [d] S. P. Datta and A. K. Grzybowski, *Trans. Faraday Soc.*, 1958, **54**, 1188, values at 10 and 40° are interpolated from reported values at 5 and 15°, and 35 and 45°, respectively. [e] J. A. Partridge, J. J. Christensen, and R. M. Izatt, *J. Amer. Chem. Soc.*, 1966, **88**, 1649. [f] J. Sturtevant, *J. Amer. Chem. Soc.*, 1941, **63**, 88.

---

[14] F. J. C. Rossotti and H. Rossotti, 'The Determination of Stability Constants,' McGraw-Hill Book Co., New York, 1961, ch. 5.

[15] L. D. Hansen, J. A. Partridge, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, 1966, **5**, 569.

[16] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' 3rd edn., Reinhold Publishing Corp., New York, 1958, p. 754.

TABLE 2

Thermodynamic quantities [a] for the reaction of glycinate ion with selected metal ions in aqueous solution ($\mu = 0$)

Reaction	t (°C)	Method	Log K	$\Delta H°$ (kcal/mol)	$\Delta S°$ (cal/deg/mol)	$\Delta C°_p$ (cal/deg/mol)
$Mn^{2+} + G^- = MnG^+$	10	pot, C	3·23 ± 0·02	−0·4 ± 0·02	13	
		pot, T	(3·18) [b]	(−0·50) [b]		
	25	pot, C	3·21 ± 0·02	−0·3 ± 0·1	14	
		pot T	(3·17) [c]	(−0·29) [c]	(13·5) [c]	(16) [c]
		sol	(3·44) [d]			
	40	pot, C	3·15 ± 0·02	−0·04 ± 0·13	14	
		pot, T	(3·16) [b]	(−0·03) [b]		
	10—40	C				12 ± 10
$Fe^{2+} + G^- = FeG^+$	10	pot, C	4·36 ± 0·03	−3·7 ± 0·2	6·8	
	25	pot, C	4·31 ± 0·02	−3·64 ± 0·15	7·5	
	40	pot, C	4·28 ± 0·02	−3·55 ± 0·16	8·2	
	10—40	C				7 ± 10
$Co^{2+} + G^- = CoG^+$	10	pot, C	5·16 ± 0·01	−3·00 ± 0·05	13·0	
		pot, T	(5·18) [b]	(−3·09) [b]		
	25	pot, C	5·07 ± 0·01	−2·86 ± 0·06	13·6	
		pot, T	(5·07) [c]	(−2·82) [c]	(13·7) [c]	(22) [c]
		sol	(5·23) [d]			
		pot	(5·016) [e]			
		C		(−2·48) [f]		
	40	pot, C	4·98 ± 0·01	−2·15 ± 0·03	15·9	
		pot, T	(4·98) [b]	(−2·44) [b]		
	10—40	C				28 ± 3
$CoG^+ + G^- = CoG_2(aq)$	10	pot, C	4·07 ± 0·01	−4·00 ± 0·02	4·5	
		pot, T	(4·12) [b]	(−3·85) [b]		
	25	pot, C	4·02 ± 0·01	−3·54 ± 0·03	6·5	
			(3·97) [c]	(−3·55) [c]	(6·3) [c]	(24) [c]
		sol	(4·02) [d]			
		pot	(3·971) [e]			
		C		(−2·55) [f]		
	40	pot, C	3·91 ± 0·01	−3·41 ± 0·02	7·0	
		pot, T	(3·86) [b]	(−3·13) [b]		
	10—40	C				20 ± 2
$CoG_2(aq) + G^- = CoG_3^-$	10	pot, C	2·67 ± 0·06	−3·63 ± 0·02	−0·6	
	25	pot, C	2·54 ± 0·04	−3·41 ± 0·06	0·2	
	40	pot, C	2·45 ± 0·05	−3·01 ± 0·04	1·6	
	10—40	C				21 ± 3
$Ni^{2+} + G^- = NiG^+$	10	pot, C	6·28 ± 0·01	−4·63 ± 0·11	12·4	
		pot	(6·34) [b]	(−4·27) [b]		
		pot, C	(6·36) [g]	(−5·2) [g]	(10·7) [g]	
	25	pot, C	6·13 ± 0·01	−4·38 ± 0·05	(13·4)	
		pot	(6·18) [c]	(−4·09) [c]	(14·5) [c]	(18)'
		sol	(6·18) [d]			
		C		(−4·14) [f]		
		pot, C	(6·18) [g]	(−4·9) [g]	(11·9) [g]	
	40	pot, C	6·00 ± 0·01	−3·77 ± 0·12	15·4	
		pot	(6·04) [b]	(−3·73) [b]		
		pot, C	(6·09) [g]	(−4·3) [g]	(14·2) [g]	
	10—40	C				28 ± 6
$NiG^+ + G^- = NiG_2(aq)$	10	pot, C	5·14 ± 0·01	−5·30 ± 0·04	4·8	
		pot	(5·14) [b]	(−5·03) [b]		
		pot, C	(5·29) [g]	(−5·8) [g]	(3·7) [g]	
	25	pot, C	4·92 ± 0·01	−4·97 ± 0·05	5·8	
		pot	(4·95) [c]	(−4·69) [c]	(6·9) [c]	(28) [c]
		sol	(4·96) [d]			
		pot, C	(5·07) [g]	(−4·7) [g]	(7·6) [g]	
	40	pot, C	4·76 ± 0·01	−4·60 ± 0·06	7·1	
		pot	(4·79) [b]	(−4·19) [b]		
		pot, C	(4·92) [g]	(−4·7) [g]	(7·4) [g]	
	10—40	C				23 ± 3
$NiG_2(aq) + G^- = NiG_3^-$	10	pot, C	3·51 ± 0·03	−5·64 ± 0·05	−3·9	
	25	pot, C	3·18 ± 0·03	−5·55 ± 0·03	−4·1	
	40	pot, C	3·00 ± 0·03	−5·50 ± 0·07	−3·8	
	10—40	C				5 ± 5
$Cu^{2+} + G^- = CuG^+$	10	pot, C	8·85 ± 0·02	−6·23 ± 0·06	16·9	
		pot, C	(8·85) [h]	(−7·28) [h]	(14·8) [h]	
	25	pot, C	8·57 ± 0·02	−5·82 ± 0·09	19·7	
		pot, C	(8·58) [h]	(−6·22) [h]	(18·4) [h]	
		sol	(8·62) [d]			
		C		(−6·0) [i]	(19) [i]	
		C		(−6·76) [f]		
		pot	(8·29) [j]			
	40	pot, C	8·33 ± 0·02	−5·47 ± 0·08	20·6	
		pot, C	(8·42) [h]	(−5·75) [h]	(20·2) [h]	
	10—40	C				25 ± 4

TABLE 2 (*Continued*)

Reaction	t (°C)	Method	Log K	$\Delta H°$ (kcal/mol)	$\Delta S°$ (cal/deg/mol)	$\Delta C_p°$ (cal/deg/mol)
$CuG^+ + G^- = CuG_2(aq)$	10	pot, C	7·52 ± 0·02	−7·20 ± 0·11	9·0	
		pot, C	(7·36) [h]	(−6·92) [h]	(9·2) [h]	
	25	pot, C	7·26 ± 0·02	−6·93 ± 0·07	10·0	
		pot, C	(7·09) [h]	(−6·96) [h]	(9·1) [h]	
		sol	(6·97) [d]			
		pot	(7·61) [j]			
		C		(−6·89) [f]		
		C		(−6·4) [i]	(11) [i]	
	40	pot, C	7·00 ± 0·02	−6·59 ± 0·05	11·0	
		pot, C	(6·85) [h]	(−7·33) [h]	(7·9) [h]	
		pot	(7·04) [i]			
	10—40	C				20 ± 5
$Zn^{2+} + G^- = ZnG^+$	10	pot, C	5·50 ± 0·02	−3·14 ± 0·07	14·2	
	25	pot, C	5·38 ± 0·02	−2·76 ± 0·05	15·4	
		sol	(5·52) [d]			
		C		(−3·39) [f]		
	40	pot, C	5·29 ± 0·02	−2·22 ± 0·07	17·1	
	10—40	C				31 ± 4
$ZnG^+ + G^- = ZnG_2(aq)$	10	pot, C	4·57 ± 0·02	−3·73 ± 0·03	7·7	
	25	pot, C	4·43 ± 0·02	−3·22 ± 0·04	9·5	
		sol	(4·44) [d]			
	40	pot, C	4·29 ± 0·01	−2·90 ± 0·03	10·4	
	10—40	C				28 ± 2
$ZnG_2(aq) + G^- = ZnG_3^-$	10	pot, C	2·63 ± 0·15	−3·53 ± 0·03	−0·4	
	25	pot, C	2·52 ± 0·15	−3·56 ± 0·03	−0·4	
	40	pot, C	2·40 ± 0·15	−3·64 ± 0·07	−0·6	
	10—40	C				−4 ± 3
$Cd^{2+} + G^- = CdG^+$	10	pot, C	4·73 ± 0·02	−2·26 ± 0·04	13·7	
	25	pot, C	4·69 ± 0·01	−2·12 ± 0·05	14·4	
		pot	(4·80) [e]			
	40	pot, C	4·60 ± 0·02	−1·95 ± 0·10	14·8	
	10—40	C				10 ± 4
$CdG^+ + G^- = CdG_2(aq)$	10	pot, C	3·76 ± 0·02	−3·74 ± 0·05	4·0	
	25	pot, C	3·71 ± 0·01	−3·24 ± 0·05	6·1	
		pot	(4·03) [e]			
	40	pot, C	3·60 ± 0·02	−2·95 ± 0·06	7·0	
	10—40	C				26 ± 3
$CdG_2(aq) + G^- = CdG_3^-$	10	pot, C	2·53 ± 0·05	−2·84 ± 0·11	1·5	
	25	pot, C	2·28 ± 0·05	−3·21 ± 0·06	−0·3	
	40	pot, C	2·00 ± 0·05	−3·39 ± 0·17	−1·7	
	10—40	C				−18 ± 7

[a] Uncertainties of log K_i and $\Delta H°_i$ values are given as the standard deviation among runs. The uncertainties of the $\Delta S°_i$ values are estimated to be ±0·1 to ±0·4 $\Delta S°$ unit. The uncertainties of the $\Delta C°_{pi}$ values are estimated to be twice the uncertainty which results when ΔC_{pi} values are calculated from $\Delta H°_i$ values at the extremes of their stated uncertainties. The abbreviations and symbols used in the method column have the following meaning with respect to how log K and ΔH were measured: pot = potentiometry; C = calorimetry; T = temperature variations; and sol = solubility. [b] Data calculated from results in reference cited in footnote *c*. [c] J. R. Brannan, H. S. Dunsmore, and G. H. Nancollas, *J. Chem. Soc.*, 1964, **304**. [d] C. B. Monk, *Trans. Faraday Soc.*, 1951, **47**, 297. [e] W. P. Evans and C. B. Monk, *Trans. Faraday Soc.*, 1955, **51**, 1244. [f] S. Boyd, J. R. Brannan, H. S. Dunsmore, and G. H. Nancollas, *J. Chem. and Eng. Data*, 1967, **12**, 601. [g] K. P. Anderson, W. O. Greenhalgh, and E. A. Butler, *Inorg. Chem.*, 1967, **6**, 1056. [h] Ref. 20. [i] R. M. Izatt, J. J. Christensen, and V. Kothari, *Inorg. Chem.*, 1964, **3**, 1565. [j] R. M. Keefer, *J. Amer. Chem. Soc.*, 1948, **70**, 476.

The method used to calculate ΔH_i values from the calorimetric titration data has been described,[17,18] including modifications.[13] Since the μ values were low ($\mu < 0·03$) in all cases, the ΔH values were taken to be $\Delta H°$ values valid at $\mu = 0$.

The $\Delta C°_{pi}$ values were calculated by fitting the $\Delta H°_i$ values to a quadratic function of temperature and differentiating with respect to temperature. A non-linear function was chosen because from a similar calorimetric study as a function of temperature of the reaction $H^+ + OH^- = H_2O$, Ackermann[19] found ΔC_p to be a non-linear function (probably quadratic) of temperature and indicated that other reactions might be expected to behave in a similar fashion.

RESULTS

Values of log K_i (pK in the case of HG) $\Delta H°_i$, $\Delta S°_i$, and $\Delta C°_{pi}$ valid at $\mu = 0$ for reactions (1) and (2) are summarized in Tables 1 and 2 together with comparative literature values. The calorimetric titration and pH titration data from which the values in Tables 1 and 2 were calculated are available.[13]

DISCUSSION

The pK, log K_i, $\Delta H°_i$, and $\Delta C°_{pi}$ values determined in this study are generally in good agreement with those determined previously at or near $\mu = 0$.

---

[17] L. D. Hansen, Ph.D. Dissertation, Brigham Young University, Provo, Utah, 1965 (*Diss. Abs.*, 1966, **26**, 5000).

[18] J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, *J. Phys. Chem.*, 1966, **70**, 2003.

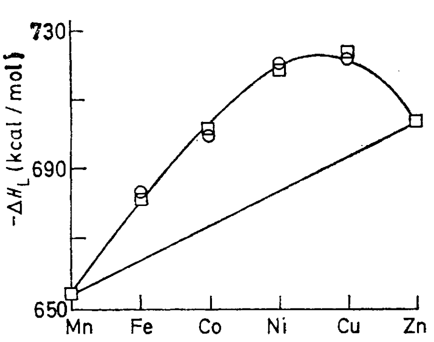
[19] T. Ackerman, *Z. Elektrochem.*, 1958, **62**, 411.

[20] K. P. Anderson, W. O. Greenhalgh, and R. M. Izatt, *Inorg. Chem.*, 1966, **5**, 2106.

The variations in log K_i, ΔH°_i, and ΔS°_i with atomic number for the M^{n+}–G^- complexes studied here have been discussed.[21] Lack of reliable ΔH data for metal complex formation reactions has caused others to assume that ΔG is proportional to ΔH when making comparisons of ligand-field effects on the various metal ions. Since this study contains a consistent set of reliable, measured ΔH values, a comparison was made between these values and the predicted stabilization energies calculated by George and McClure [22] using ΔG as a reference state. The ligand stabilization for glycine complexes is seen in the Figure where ΔH_L, calculated as shown in equation (4), is plotted *vs.* M^{2+} for the elements Mn through Zn.

$$M^{2+}\ (g) + G^-\ (aq) = MG^+\ (aq)\ \Delta H_L = \Delta H_{hydration} + \Delta H_{complex\ formation} \quad (4)$$

Values for $\Delta H_{hydration}$ are taken from NBS Circular 500 [23] and Brewer, *et al.*,[24] and those for $\Delta H_{complex\ formation}$ are taken from Table 2. The values reported by George and McClure 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 the Figure. The agreement of the two sets of values is excellent, being about ±1·5 kcal/mol in each case.



Plot of ΔH_L *vs.* M^{2+} (Mn–Zn) for the reaction M^{2+} (g) + G^- (aq) = MG^+ (aq). Data are taken from Table 2, ○, and George and McClure [22] □

A value for the ligand-field stabilization energy was computed for each metal ion studied by taking the difference between the ΔH_L value determined experimentally for each M^{n+} and that which it would have in the absence of any ligand-field stabilization. The latter quantity was estimated from the straight line in the Figure by assuming that the increase in ΔH_L with atomic number between Mn^{2+} and Zn^{2+} (which have no stabilization energies associated with their ground states) would be linear in the absence of ligand-field effects.[22] The calculated stabilization energies are 19·5, 25·7, 36·7, and 28·8 kcal/mol for the FeG^+, CoG^+, NiG^+, and CuG^+ systems, respectively. If all the ligand-field effects are considered to be directed in a symmetrical octahedral field, values for the splitting parameter, Δ, are calculated to be 58, 32, 30, and 48 kcal/mol for the FeG^+, CoG^+, NiG^+, and CuG^+ systems, respectively.

A simple electrostatic model [25] has been used to attempt to explain proton ionization in solution. The model predicts for ion–ion interaction that ΔG is proportional to ΔS for all reactions of similar charge types and that $\Delta C_p = 0$ for reaction (5). The proportionality

$$MG_2 + G^- = MG_3^- \quad (5)$$

for ΔG *vs.* ΔS is not observed for the metal glycinates nor was it observed for the metal cyanide complexes of Zn^{2+}, Ni^{2+}, Cd^{2+}, and Hg^{2+}.[1] Also, ΔC°_p values for reaction (5) are 20, 5, −4, and −18 in the cases of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}, respectively, which are the only cases where data for the MG_3^- species are available. The electrostatic model does not, therefore, predict metal glycinate behaviour.

Comparisons of ΔC_p values have the advantage over ΔS comparisons that there is no cratic or statistical term contributing to the magnitude of ΔC_p. This means that ΔC_p provides a more direct measure of the solute–solvent interaction. The M^{2+}–G^- systems studied have similar ΔC_p values which indicates that in these 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 corrected for ligand-field effects should correlate relative bond strengths of metal-ligand bonds.

Because ΔC_p values vary considerably for stepwise metal-ligand co-ordination (*e.g.* Ni^{2+}–G^-, $\Delta C^\circ_{p_1} = 28$, $\Delta C^\circ_{p_2} = 23$, $\Delta C^\circ_{p_3} = 5$), relative magnitudes of ΔG and ΔH values at temperatures far from 25° may be quite different than those reported here. It would then follow that many data correlations made at a single temperature, and interpretations based on such correlations, may not be valid in other temperature regions.

We thank the National Institutes of Health for financial support and for Public Health Service Research Career Development Awards (to R. M. I. and J. J. C.).

[1/2397 *Received*, 13*th December*, 1971]

---

[21] S. J. Ashcroft and C. T. Mortimer, ' Thermochemistry of Transition Metal Complexes,' Academic Press, New York, 1970, pp. 97—111.

[22] P. George and D. S. McClure in ' Progress in Inorganic Chemistry,' vol. 1 (ed. F. A. Cotton), Interscience, New York, 1959, p. 428.

[23] ' Selected Values of Chemical Thermodynamic Properties,' Nat. Bur. of Stand. (U.S.) Cir. 500, U.S. Government Printing Office, Washington, D.C., 1952.

[24] L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, in L. L. Quill, ed., ' Chemistry and Metallurgy of Miscellaneous Meterials: Thermodynamics,' McGraw-Hill, New York, 1950, p. 76.

[25] E. J. King, ' Acid Base Equilibria,' The Macmillan Co., New York, 1965.