# 51. *Thermodynamics of Ion Association. Part XI.*[1] *Some Transition-metal Glycine Salts.*

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Thermodynamic equilibrium constants for the association in aqueous solution of nickel, cobalt, and manganese cations with the glycine anion have been determined at temperatures from 0° to 45°, from the e.m.f.s of cells $H_2$,Pt/HA,NaOH,$MCl_2$/AgCl/Ag. $\Delta G$, $\Delta H$, $\Delta S$, and $\Delta C_p$ have been evaluated for the reactions $M^{2+} + A^- \rightleftharpoons MA^+$ and $MA^+ + A^- \rightleftharpoons MA_2$, and these are discussed.

Previous Parts of this series have been concerned with the study of complexes in which nickel, cobalt, and manganese ions associated with oxygen-containing ligands, forming quite stable chelate rings.[1] The present work extends the available thermodynamic information to complexes involving co-ordination to both a nitrogen and an oxygen atom. With glycine, HA, as ligand, the concentrations in the cell

$$H_2,Pt/HA, NaOH, MCl_2/AgCl/Ag \qquad (1)$$

have been arranged so as to limit the number of complex species present, enabling activity corrections to be made.

*Experimental.*—" AnalaR " salts were used and solutions were made up by weight with conductivity water. The e.m.f. apparatus and experimental procedure have been described previously.[2]

*Results and Discussion.*—In measurements involving the cell $H_2$,Pt/HA($m_1$), NaOH($m_2$), $MCl_2(m_3)$/AgCl/Ag the molality of hydrogen ion is given by $-\log [H^+] = (E - E^\circ)/k + \log 2m_3 + 2 \log \gamma_1$, where $m$ represents molality, $\gamma_1$ activity coefficient, and $k = 2{\cdot}3026\ \boldsymbol{R}T/\boldsymbol{F}$. As was done by Monk[3] and with the assumption that two complexes $MA^+$ and $MA_2$ were present in solutions containing $Co^{2+}$ or $Ni^{2+}$ ions, the molalities of ionic species were obtained from equations:

for total glycine ion,

$$m_1 = [H_2A^+] + [HA] + [A^-] + [MA^+] + 2[MA_2];$$

for total metal ion,

$$m_3 = [M^{2+}] + [MA^+] + MA_2];$$

for electroneutrality,

$$[H^+] + 2[M^{2+}] + [MA^+] + m_2 + [H_2A^+] = [A^-] + 2m_3;$$

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[1] Part X, McAuley, and Nancollas, *J.*, 1963, 989.
[2] Nair and Nancollas, *J.*, **1958**, 4144.
[3] Monk, *Trans. Faraday Soc.*, 1951, **47**, 292, 297.

and for the dissociation constants of glycine,

$$k_1 = [H^+][HA]/[H_2A^+], \text{ and } k_2 = [H^+][A^-]\gamma_1^2/[HA].$$

Values of $k_1$ and $k_2$ at the required temperatures were those obtained by Datta and Grzybowski [4] for similar cells.

| Temp.: | 0° | 15° | 25° | 35° | 45° |
|---|---|---|---|---|---|
| $10^3k_1$ (D. and G.) | 3·67 | 4·17 | 4·46 | 4·66 | 4·77 |
| $10^{10}k_2$ (D. and G.) | 0·327 | 0·896 | 1·67 | 2·97 | 5·06 |
| $10^{10}k_2$ (King) | — | 0·893 | 1·66 | 2·95 | 5·02 |

TABLE 1.

E.m.f. measurements.

*$K_1$ for nickel glycine.*

| Expt.: | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $10^3m_1$ | 9·2378 | 6·2971 | 6·9927 | 5·8195 | 5·5262 | 6·3292 | 5·9371 |
| $10^4m_2$ | 2·7142 | 1·8722 | 2·2291 | 1·0678 | 0·9834 | 1·0590 | 3·8055 |
| $10^3m_3$ | 0·6549 | 6·1272 | 0·8316 | 0·9847 | 0·7859 | 0·6374 | 2·9797 |

| | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|
| $10^3m_1$ | 6·1349 | 5·5410 | 6·0667 | 5·1350 | 5·4071 | 5·6186 | 6·3358 |
| $10^4m_2$ | 3·9347 | 2·7295 | 4·9962 | 2·6031 | 3·0628 | 3·1015 | 3·4016 |
| $10^3m_3$ | 4·0651 | 3·1635 | 5·3758 | 6·7398 | 5·4922 | 5·7036 | 5·9861 |

Temp. 0°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^7$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^6$ $[MA_2]$ | $10^{-6}$ $K_1$ |
|---|---|---|---|---|---|---|
| 2 | 37,613 | 18·163 | 0·211 | 2·180 | 0·69 | 2·93 |
| 3 | 46,587 | 2·273 | 1·449 | 2·166 | 5·48 | 3·00 |
| 5 | 43,342 | 2·253 | 0·646 | 1·034 | 1·15 | 2·87 |
| 6 | 46,170 | 1·801 | 0·854 | 1·095 | 1·65 | 2·92 |
| 7 | 42,420 | 8·556 | 0·725 | 3·792 | 4·41 | 2·93 |
| 8 | 41,069 | 11·795 | 0·575 | 3·966 | 3·56 | 2·89 |
| 10 | 40,471 | 15·622 | 0·572 | 5·010 | 4·34 | 2·92 |
| 11 | 38,321 | 19·941 | 0·251 | 2·774 | 1·01 | 2·93 |
| 12 | 39,448 | 16·157 | 0·346 | 3·175 | 1·66 | 2·90 |
| 13 | 39,240 | 16·786 | 0·342 | 3·226 | 1·66 | 2·89 |
| 14 | 38,953 | 17·602 | 0·359 | 3·547 | 1·91 | 2·92 |

Mean $K_1$ = 2·92 ± 0·02.

Temp. 25°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^7$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^6$ $[MA_2]$ | $10^{-6}$ $K_1$ |
|---|---|---|---|---|---|---|
| 2 | 38,978 | 18·131 | 0·477 | 2·502 | 0·816 | 1·53 |
| 3 | 48,555 | 2·268 | 3·023 | 2·222 | 5·416 | 1·50 |
| 5 | 47,259 | 2·245 | 1·375 | 1·118 | 1·240 | 1·49 |
| 6 | 48,155 | 1·793 | 1·820 | 1·172 | 1·738 | 1·50 |
| 7 | 43,920 | 8·546 | 1·460 | 3·892 | 4·192 | 1·52 |
| 8 | 42,451 | 11·782 | 1·160 | 4·100 | 3·406 | 1·51 |
| 10 | 41,807 | 15·609 | 1·157 | 5·142 | 4·140 | 1·52 |
| 11 | 39,588 | 19·919 | 0·532 | 2·996 | 1·079 | 1·53 |
| 12 | 40,757 | 16·140 | 0·718 | 3·352 | 1·668 | 1·51 |
| 13 | 40,540 | 16·768 | 0·713 | 3·415 | 1·680 | 1·51 |
| 14 | 40,251 | 17·580 | 0·744 | 3·761 | 1·948 | 1·51 |

Mean $K_1$ = 1·51 ± 0·01.

Temp. 45°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^7$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^6$ $[MA_2]$ | $10^{-6}$ $K_1$ |
|---|---|---|---|---|---|---|
| 1 | 51,587 | 1·691 | 8·812 | 2·631 | 11·83 | 0·95 |
| 2 | 40,168 | 18·091 | 0·852 | 2·900 | 1·05 | 1·02 |
| 3 | 50,078 | 2·260 | 4·865 | 2·300 | 5·63 | 0·99 |
| 4 | 47,750 | 2·815 | 2·070 | 1·379 | 1·42 | 1·00 |
| 5 | 48,831 | 2·234 | 2·331 | 1·230 | 1·44 | 0·99 |
| 6 | 49,798 | 1·783 | 3·089 | 1·272 | 2·00 | 0·99 |
| 7 | 45,108 | 8·532 | 2·325 | 4·033 | 4·30 | 1·01 |
| 8 | 43,571 | 11·763 | 1·866 | 4·287 | 3·56 | 1·01 |
| 9 | 44,150 | 9·179 | 1·645 | 3·094 | 2·32 | 1·00 |

Mean $K_1$ = 1·00 ± 0·02.

Temp. 15°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^7$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^6$ $[MA_2]$ | $10^{-6}$ $K_1$ |
|---|---|---|---|---|---|---|
| 2 | 38,435 | 18·146 | 0·349 | 2·350 | 0·75 | 1·94 |
| 5 | 46,454 | 2·249 | 1·016 | 1·080 | 1·18 | 1·93 |
| 6 | 47,368 | 1·797 | 1·366 | 1·135 | 1·69 | 1·92 |
| 7 | 43,338 | 8·551 | 1·125 | 3·843 | 4·26 | 1·93 |
| 8 | 41,914 | 11·789 | 0·892 | 4·034 | 3·45 | 1·92 |
| 10 | 41,285 | 15·615 | 0·888 | 5·078 | 4·20 | 1·93 |
| 11 | 39,089 | 19·930 | 0·401 | 2·889 | 1·50 | 1·94 |
| 12 | 40,247 | 16·148 | 0·546 | 3·266 | 1·66 | 1·92 |
| 13 | 40,033 | 16·777 | 0·541 | 3·323 | 1·66 | 1·91 |
| 14 | 39,710 | 17·591 | 0·570 | 3·657 | 1·92 | 1·93 |

Mean $K_1$ = 1·93 ± 0·01.

Temp. 35°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^7$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^6$ $[MA_2]$ | $10^{-6}$ $K_1$ |
|---|---|---|---|---|---|---|
| 1 | 50,666 | 1·693 | 6·727 | 2·615 | 10·94 | 1·23 |
| 2 | 39,559 | 18·113 | 0·641 | 2·684 | 0·90 | 1·24 |
| 3 | 49,317 | 2·264 | 3·878 | 2·259 | 5·37 | 1·20 |
| 4 | 46,977 | 2·823 | 1·599 | 1·304 | 1·26 | 1·21 |
| 5 | 48,035 | 2·240 | 1·808 | 1·168 | 1·30 | 1·20 |
| 6 | 48,964 | 1·789 | 2·388 | 1·218 | 1·80 | 1·20 |
| 7 | 44,509 | 8·540 | 1·859 | 3·956 | 4·12 | 1·22 |
| 8 | 43,005 | 11·774 | 1·484 | 4·183 | 3·38 | 1·22 |
| 9 | 43,549 | 9·190 | 1·300 | 2·995 | 2·17 | 1·21 |

Mean $K_1$ = 1·21 ± 0·01.

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[4] Datta and Grzybowski, *Trans. Faraday Soc.*, 1958, **54**, 1179.

TABLE 1. (*Continued.*)

$K_1$ *for cobalt glycine.*

| Expt.: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $10^3 m_1$ ... | 7·4284 | 7·3796 | 8·2576 | 8·2049 | 7·5728 | 6·4364 | 7·0639 | 6·6283 | 7·1659 | 5·8391 |
| $10^4 m_2$ ... | 1·5516 | 1·8040 | 1·6441 | 1·7241 | 1·3634 | 1·1744 | 1·3466 | 2·2921 | 1·2526 | 1·1185 |
| $10^3 m_3$ ... | 1·9699 | 2·3304 | 2·1885 | 2·5581 | 0·7795 | 0·5796 | 0·6220 | 0·5767 | 2·1214 | 2·3652 |

Temp. 0°.

| Expt. | $10^5 (E-E^\circ)$ | $10^3 I$ | $10^6$ [A⁻] | $10^4$ [MA⁺] | $10^6$ [MA₂] | $10^{-5} K_1$ |
|---|---|---|---|---|---|---|
| 1 | 47,819 | 5·756 | 6·227 | 1·531 | 1·373 | 1·85 |
| 2 | 47,478 | 6·812 | 6·310 | 1·779 | 1·596 | 1·84 |
| 3 | 47,293 | 6·400 | 6·156 | 1·645 | 1·447 | 1·83 |
| 4 | 46,676 | 7·502 | 5·494 | 1·710 | 1·326 | 1·85 |
| 5 | 51,680 | 2·207 | 1·299 | 1·305 | 2·583 | 1·90 |
| 6 | 53,051 | 1·626 | 1·470 | 1·113 | 2·527 | 1·93 |
| 7 | 52,851 | 1·737 | 1·589 | 1·273 | 3·114 | 1·95 |
| 8 | 55,118 | 1·519 | 3·565 | 2·034 | 11·22 | 1·86 |
| 9 | 46,937 | 6·239 | 0·446 | 1·250 | 0·799 | 1·94 |
| 10 | 46,691 | 6·983 | 0·365 | 1·119 | 0·579 | 1·92 |

Mean $K_1 = 1·89 \pm 0·04$.

Temp. 15°.

| Expt. | $10^5 (E-E^\circ)$ | $10^3 I$ | $10^6$ [A⁻] | $10^4$ [MA⁺] | $10^6$ [MA₂] | $10^{-5} K_1$ |
|---|---|---|---|---|---|---|
| 1 | 48,695 | 5·755 | 8·440 | 1·542 | 1·315 | 1·39 |
| 2 | 48,325 | 6·812 | 8·517 | 1·790 | 1·521 | 1·38 |
| 3 | 48,149 | 6·399 | 8·373 | 1·658 | 1·392 | 1·37 |
| 4 | 47,515 | 7·501 | 7·526 | 1·724 | 1·285 | 1·38 |
| 5 | 52,772 | 2·207 | 1·765 | 1·308 | 2·475 | 1·40 |
| 6 | 54,230 | 1·627 | 2·006 | 1·114 | 2·427 | 1·42 |
| 7 | 54,037 | 1·738 | 2·184 | 1·273 | 3·012 | 1·42 |
| 8 | 56,383 | 1·521 | 4·810 | 2·034 | 14·03 | 1·38 |
| 9 | 47,942 | 6·238 | 0·650 | 1·260 | 0·823 | 1·35 |
| 10 | 47,611 | 6·982 | 0·516 | 1·130 | 0·580 | 1·38 |

Mean $K_1 = 1·39 \pm 0·02$.

Temp. 25°.

| Expt. | $10^5 (E-E^\circ)$ | $10^3 I$ | $10^6$ [A⁻] | $10^4$ [MA⁺] | $10^6$ [MA₂] | $10^{-5} K_1$ |
|---|---|---|---|---|---|---|
| 1 | 49,238 | 5·754 | 10·050 | 1·554 | 1·256 | 1·18 |
| 2 | 48,854 | 6·811 | 10·137 | 1·802 | 1·450 | 1·17 |
| 3 | 48,678 | 6·398 | 9·988 | 1·672 | 1·330 | 1·17 |
| 4 | 48,036 | 7·500 | 9·027 | 1·740 | 1·238 | 1·17 |
| 5 | 53,448 | 2·207 | 2·095 | 1·313 | 2·345 | 1·20 |
| 6 | 54,955 | 1·627 | 2·380 | 1·116 | 2·297 | 1·21 |
| 7 | 54,777 | 1·738 | 2·612 | 1·275 | 2·873 | 1·20 |
| 8 | 57,173 | 1·522 | 5·685 | 2·039 | 10·05 | 1·18 |
| 9 | 48,489 | 6·237 | 0·783 | 1·275 | 0·798 | 1·14 |
| 10 | 48,156 | 6·981 | 0·623 | 1·143 | 0·565 | 1·16 |

Mean $K_1 = 1·18 \pm 0·02$.

Temp. 35°.

| Expt. | $10^5 (E-E^\circ)$ | $10^3 I$ | $10^6$ [A⁻] | $10^4$ [MA⁺] | $10^6$ [MA₂] | $10^{-5} K_1$ |
|---|---|---|---|---|---|---|
| 1 | 49,787 | 5·753 | 1·180 | 1·570 | 1·239 | 1·02 |
| 2 | 49,391 | 6·809 | 1·191 | 1·818 | 1·428 | 1·02 |
| 3 | 49,226 | 6·396 | 1·181 | 1·692 | 1·325 | 1·00 |
| 4 | 48,564 | 7·498 | 1·068 | 1·762 | 1·231 | 1·01 |
| 5 | 54,119 | 2·207 | 2·443 | 1·319 | 2·286 | 1·03 |
| 6 | 55,676 | 1·627 | 2·774 | 1·119 | 2·235 | 1·04 |
| 7 | 55,500 | 1·738 | 3·055 | 1·278 | 2·802 | 1·03 |
| 8 | 57,952 | 1·523 | 6·589 | 2·040 | 9·699 | 1·02 |
| 9 | 49,029 | 6·235 | 0·925 | 1·295 | 0·795 | 0·99 |
| 10 | 48,687 | 6·980 | 0·737 | 1·161 | 0·563 | 1·01 |

Mean $K_1 = 1·02 \pm 0·01$.

Temp. 45°.

| Expt. | $10^5 (E-E^\circ)$ | $10^3 I$ | $10^6$ [A⁻] | $10^4$ [MA⁺] | $10^6$ [MA₂] | $10^{-5} K_1$ |
|---|---|---|---|---|---|---|
| 1 | 50,341 | 5·751 | 1·366 | 1·594 | 1·220 | 0·903 |
| 2 | 49,926 | 6·807 | 1·375 | 1·842 | 1·401 | 0·898 |
| 3 | 49,764 | 6·394 | 1·368 | 1·720 | 1·308 | 0·888 |
| 4 | 49,098 | 7·495 | 1·245 | 1·793 | 1·224 | 0·885 |
| 5 | 54,789 | 2·206 | 2·803 | 1·329 | 2·218 | 0·913 |
| 6 | 56,387 | 1·627 | 3·173 | 1·125 | 2·157 | 0·919 |
| 7 | 56,221 | 1·738 | 3·514 | 1·284 | 2·718 | 0·902 |
| 8 | 58,718 | 1·524 | 7·483 | 2·043 | 9·263 | 0·901 |
| 9 | 49,575 | 6·232 | 1·077 | 1·323 | 0·794 | 0·876 |
| 10 | 49,220 | 6·977 | 0·858 | 1·188 | 0·562 | 0·890 |

Mean $K_1 = 0·898 \pm 0·01$.

$K_1$ *for manganese glycine.*

| Expt.: | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $10^2 m_1$ .................. | 9·7058 | 8·6262 | 7·9700 | 7·3594 | 7·9639 | 7·1301 | 4·0712 |
| $10^4 m_2$ .................. | 5·8184 | 5·7306 | 4·6713 | 2·9607 | 3·6167 | 4·3108 | 4·0549 |
| $10^2 m_3$ .................. | 3·7319 | 3·3796 | 2·7622 | 1·8025 | 2·2210 | 2·9134 | 3·4246 |

Temp. 0°.

| Expt. | $10^5 (E-E^\circ)$ | $10^2 I$ | $10^5$ [A⁻] | $10^4$ [MA⁺] | $10^{-3} K_1$ |
|---|---|---|---|---|---|
| 1 | 43,695 | 11·142 | 2·715 | 5·600 | 1·56 |
| 2 | 44,316 | 10·087 | 2·843 | 5·486 | 1·57 |
| 3 | 44,799 | 8·245 | 2·637 | 4·443 | 1·57 |
| 4 | 45,492 | 5·382 | 2·137 | 2·782 | 1·63 |
| 5 | 45,101 | 6·631 | 2·412 | 3·413 | 1·54 |
| 6 | 44,670 | 8·701 | 2·356 | 4·107 | 1·56 |
| 7 | 45,122 | 10·237 | 1·908 | 3·878 | 1·63 |

Mean $K_1 = 1·58 \pm 0·03$.

Temp. 15°.

| Expt. | $10^5 (E-E^\circ)$ | $10^2 I$ | $10^5$ [A⁻] | $10^4$ [MA⁺] | $10^3 K_1$ |
|---|---|---|---|---|---|
| 1 | 43,794 | 11·142 | 2·947 | 5·643 | 1·49 |
| 2 | 44,435 | 10·087 | 3·069 | 5·513 | 1·49 |
| 3 | 44,942 | 8·245 | 2·845 | 4·467 | 1·50 |
| 4 | 45,630 | 5·382 | 2·265 | 2·815 | 1·59 |
| 5 | 45,263 | 6·631 | 2·604 | 3·441 | 1·46 |
| 6 | 44,807 | 8·701 | 2·542 | 4·129 | 1·49 |
| 7 | 45,281 | 10·237 | 2·057 | 3·880 | 1·55 |

Mean $K_1 = 1·51 \pm 0·03$.

TABLE 1. (*Continued.*)

Temp. 25°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^2 I$ | $10^5$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^{-3}$ $K_1$ |
|---|---|---|---|---|---|
| 1 | 43,852 | 11·142 | 3·105 | 5·708 | 1·45 |
| 2 | 44,500 | 10·086 | 3·215 | 5·560 | 1·46 |
| 3 | 45,020 | 8·245 | 2·974 | 4·509 | 1·47 |
| 5 | 45,367 | 6·631 | 2·739 | 3·485 | 1·43 |
| 6 | 44,888 | 8·701 | 2·665 | 4·167 | 1·46 |
| 7 | 45,360 | 10·237 | 2·142 | 3·894 | 1·52 |

Mean $K_1 = 1·47 \pm 0·02$.

Temp. 35°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^2 I$ | $10^5$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^{-3}$ $K_1$ |
|---|---|---|---|---|---|
| 1 | 43,916 | 11·141 | 3·253 | 5·822 | 1·44 |
| 2 | 44,573 | 10·086 | 3·351 | 5·644 | 1·45 |
| 3 | 45,120 | 8·244 | 3·112 | 4·582 | 1·45 |
| 5 | 45,475 | 6·630 | 2·861 | 3·564 | 1·42 |
| 6 | 44,971 | 8·701 | 2·775 | 4·236 | 1·45 |
| 7 | 45,449 | 10·237 | 2·222 | 3·921 | 1·50 |

Mean $K_1 = 1·45 \pm 0·02$.

Temp. 45°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^2 I$ | $10^5$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^{-3}$ $K_1$ |
|---|---|---|---|---|---|
| 1 | 44,020 | 11·139 | 3·426 | 6·001 | 1·44 |
| 2 | 44,686 | 10·085 | 3·513 | 5·779 | 1·45 |
| 3 | 45,254 | 8·243 | 3·266 | 4·701 | 1·44 |
| 5 | 45,627 | 6·629 | 3·011 | 3·689 | 1·42 |
| 6 | 45,093 | 8·700 | 2·906 | 4·346 | 1·45 |
| 7 | 45,553 | 10·236 | 2·298 | 3·969 | 1·50 |

Mean $K_1 = 1·45 \pm 0·02$.

TABLE 2.

E.m.f. measurements.

*$K_2$ for nickel glycine.*

| Expt.: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $10^2 m_1$ | 3·7992 | 3·2694 | 3·6302 | 3·8354 | 4·5382 | 6·2537 | 5·4038 | 4·4874 |
| $10^3 m_2$ | 0·9139 | 1·0490 | 1·0942 | 0·8727 | 1·1191 | 1·2847 | 1·3672 | 1·1028 |
| $10^3 m_3$ | 0·7927 | 0·9694 | 1·0637 | 0·8726 | 1·0845 | 1·1448 | 1·4018 | 1·0580 |

Temp. 0°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3 I$ | $10^6$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-5}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 49,267 | 1·673 | 2·363 | 4·962 | 2·108 | 1·96 |
| 2 | 48,782 | 2·071 | 2·007 | 6·267 | 2·129 | 1·87 |
| 3 | 46,943 | 2·298 | 1·716 | 6·896 | 2·054 | 1·92 |
| 4 | 48,047 | 1·896 | 1·566 | 5·662 | 1·573 | 1·95 |
| 5 | 47,343 | 2·343 | 1·704 | 6·959 | 2·169 | 2·03 |
| 6 | 47,172 | 2·424 | 2·315 | 7·256 | 2·869 | 1·90 |
| 7 | 46,117 | 3·059 | 1·556 | 9·122 | 2·362 | 1·87 |
| 8 | 47,532 | 2·278 | 1·782 | 6·823 | 2·151 | 1·96 |

Mean $K_2 = 1·93 \pm 0·04$.

Temp. 15°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3 I$ | $10^6$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-5}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 50,671 | 1·671 | 3·838 | 5·031 | 2·081 | 1·18 |
| 2 | 50,075 | 2·069 | 3·150 | 6·309 | 2·117 | 1·18 |
| 3 | 49,252 | 2·292 | 2·761 | 7·000 | 2·017 | 1·16 |
| 4 | 49,361 | 1·891 | 2·519 | 5·743 | 1·552 | 1·18 |
| 5 | 48,640 | 2·336 | 2·765 | 7·069 | 2·139 | 1·22 |
| 6 | 48,426 | 2·420 | 3·705 | 7·297 | 2·886 | 1·19 |
| 7 | 47,301 | 3·051 | 2·480 | 9·208 | 2·365 | 1·17 |
| 8 | 48,809 | 2·273 | 2·855 | 6·900 | 2·137 | 1·20 |

Mean $K_2 = 1·19 \pm 0·02$.

Temp. 25°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3 I$ | $10^6$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-5}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 51,547 | 1·670 | 5·067 | 5·057 | 2·078 | 8·89 |
| 2 | 50,905 | 2·067 | 4·119 | 6·335 | 2·115 | 8·97 |
| 3 | 50,065 | 2·290 | 3·625 | 7·036 | 2·015 | 8·78 |
| 4 | 50,172 | 1·889 | 3·300 | 5·760 | 1·565 | 9·07 |
| 5 | 49,476 | 2·331 | 3·694 | 7·132 | 2·132 | 9·01 |
| 6 | 49,248 | 2·416 | 4·938 | 7·322 | 2·908 | 8·96 |
| 7 | 48,081 | 3·044 | 3·300 | 9·277 | 2·373 | 8·75 |
| 8 | 49,628 | 2·270 | 3·781 | 6·941 | 2·140 | 9·06 |

Mean $K_2 = 8·94 \pm 0·10$.

Temp. 35°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3 I$ | $10^6$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-5}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 52,437 | 1·669 | 6·571 | 5·082 | 2·078 | 6·83 |
| 2 | 51,770 | 2·065 | 5·335 | 6·380 | 2·104 | 6·85 |
| 3 | 50,910 | 2·286 | 4·711 | 7·092 | 2·007 | 6·69 |
| 4 | 51,078 | 1·883 | 4·382 | 5·843 | 1·546 | 6·66 |
| 5 | 50,290 | 2·327 | 4·780 | 7·160 | 2·152 | 7·01 |
| 6 | 50,082 | 2·413 | 6·456 | 9·335 | 2·946 | 6·95 |
| 7 | 48,864 | 3·037 | 4·295 | 9·327 | 2·403 | 6·78 |
| 8 | 50,446 | 2·266 | 4·891 | 6·967 | 2·159 | 7·06 |

Mean $K_2 = 6·85 \pm 0·11$.

Temp. 45°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3 I$ | $10^6$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-5}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 53,323 | 1·668 | 8·324 | 5·094 | 2·090 | 5·42 |
| 2 | 52,619 | 2·064 | 6·719 | 6·401 | 2·112 | 5·45 |
| 3 | 51,742 | 2·283 | 5·956 | 7·119 | 2·021 | 5·32 |
| 5 | 51,063 | 2·325 | 5·958 | 7·127 | 2·217 | 5·83 |
| 6 | 50,872 | 2·441 | 8·117 | 7·281 | 3·037 | 5·75 |
| 7 | 49,601 | 3·032 | 5·373 | 9·281 | 2·505 | 5·69 |
| 8 | 51,216 | 2·265 | 6·078 | 6·928 | 2·226 | 5·89 |

Mean $K_2 = 5·62 \pm 0·20$.

TABLE 2. (*Continued.*)

*$K_2$ for cobalt glycine.*

| Expt.: | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $10^2m_1$ .................. | 8·4170 | 6·4753 | 9·2361 | 6·5973 | 12·1177 | 12·6328 | 14·1085 |
| $10^3m_2$ .................. | 1·3904 | 1·1048 | 1·3370 | 1·1019 | 1·4619 | 1·5389 | 1·3279 |
| $10^3m_3$ .................. | 1·3658 | 0·9961 | 1·1797 | 0·9872 | 1·2936 | 1·3856 | 1·1513 |

Temp. 0°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^5$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-4}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 51,238 | 3·017 | 2·101 | 8·295 | 2·716 | 1·75 |
| 2 | 53,026 | 2·172 | 2·518 | 6·013 | 2·400 | 1·75 |
| 3 | 52,006 | 2·556 | 2·765 | 7·091 | 3·016 | 1·71 |
| 4 | 53,005 | 2·152 | 2·521 | 5·919 | 2·433 | 1·80 |
| 5 | 51,185 | 2·800 | 2·814 | 7·797 | 3·296 | 1·68 |
| 6 | 50,915 | 3·002 | 2·801 | 8·487 | 3·339 | 1·58 |
| 7 | 51,279 | 2·484 | 3·043 | 6·975 | 3·032 | 1·59 |

Mean $K_2 = 1·69 \pm 0·07$.

Temp. 15°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^4$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-4}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 52,369 | 3·022 | 2·926 | 8·420 | 2·625 | 1·20 |
| 2 | 54,201 | 2·182 | 3·432 | 6·078 | 2·329 | 1·24 |
| 3 | 53,141 | 2·566 | 3·792 | 7·173 | 2·936 | 1·20 |
| 4 | 54,196 | 2·161 | 3·460 | 5·999 | 2·352 | 1·25 |
| 5 | 52,321 | 2·808 | 3·931 | 7·924 | 3·197 | 1·15 |
| 6 | 52,001 | 3·011 | 3·858 | 8·574 | 3·265 | 1·11 |
| 7 | 52,409 | 2·494 | 4·232 | 7·080 | 2·945 | 1·10 |

Mean $K_2 = 1·18 \pm 0·05$.

Temp. 25°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^5$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-4}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 53,113 | 3·024 | 3·587 | 8·551 | 2·539 | 9·34 |
| 2 | 54,951 | 2·189 | 4·114 | 6·136 | 2·272 | 9·98 |
| 3 | 53,882 | 2·573 | 4·596 | 7·261 | 2·864 | 9·60 |
| 4 | 54,960 | 2·168 | 4·170 | 6·071 | 2·288 | 10·02 |
| 5 | 53,055 | 2·814 | 4·802 | 8·030 | 3·119 | 9·09 |
| 6 | 52,705 | 3·017 | 4·679 | 8·660 | 3·203 | 8·92 |
| 7 | 53,112 | 2·501 | 5·101 | 7·139 | 2·897 | 8·88 |

Mean $K_2 = 9·40 \pm 0·40$.

Temp. 35°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^4$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-4}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 53,789 | 3·030 | 4·209 | 8·592 | 2·507 | 7·84 |
| 2 | 55,666 | 2·196 | 4·786 | 6·167 | 2·233 | 8·41 |
| 3 | 54,581 | 2·580 | 5·387 | 7·307 | 2·820 | 8·03 |
| 4 | 55,684 | 2·175 | 4·867 | 6·109 | 2·244 | 8·39 |
| 5 | 53,737 | 2·821 | 5·654 | 8·077 | 3·083 | 7·60 |
| 6 | 53,373 | 3·024 | 5·504 | 8·700 | 3·175 | 7·50 |
| 7 | 53,808 | 2·509 | 6·032 | 7·187 | 2·864 | 7·39 |

Mean $K_2 = 7·88 \pm 0·34$.

Temp. 45°.

| Expt. | $10^5$ $(E-E^\circ)$ | $10^3I$ | $10^5$ $[A^-]$ | $10^4$ $[MA^+]$ | $10^4$ $[MA_2]$ | $10^{-4}$ $K_2$ |
|---|---|---|---|---|---|---|
| 1 | 54,485 | 3·033 | 4·815 | 8·673 | 2·460 | 6·57 |
| 2 | 56,392 | 2·203 | 5·505 | 6·221 | 2·185 | 7·11 |
| 3 | 55,285 | 2·587 | 6·226 | 7·367 | 2·773 | 6·79 |
| 4 | 56,429 | 2·182 | 5·636 | 6·179 | 2·185 | 6·99 |
| 5 | 54,438 | 2·828 | 6·591 | 8·146 | 3·042 | 6·40 |
| 6 | 54,055 | 3·030 | 6·398 | 8·757 | 3·148 | 6·37 |
| 7 | 54,530 | 2·516 | 7·081 | 7·256 | 2·827 | 6·17 |

Mean $K_2 = 6·63 \pm 0·29$.

As can be seen, there is excellent agreement with King's data,[5] obtained by e.m.f. measurements. The association constants,

$$K_1 = [MA^+]/[M^{2+}][A^-]\gamma_2 \text{ and } K_2 = [MA_2]/[MA^+][A^-]\gamma_1^2,$$

were obtained by successive approximations for the ionic strength,

$$I = \tfrac{1}{2}\{[H^+] + [MA^+] + [H_2A^+] + [A^-] + m_2 + 2m_3 + 4[M^{2+}]\},$$

a DEUCE electronic computer being used. With the activity-coefficient expression,

$$-\log \gamma_z = Az^2\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - cI\}, \tag{2}$$

an approximate value of $K_2$ was used in the initial calculation of $K_1$ which in turn was used to obtain a more accurate $K_2$, and the process was repeated until both were constant. For the manganese glycine salt, it was necessary to take into account only one complex, $MnA^+$, as was found by Monk.[3] In order to determine the best value of $c$ in equation (2), calculations were made at each temperature with $c = 0·0$, 0·1, 0·2, 0·3, 0·4, 0·5, and 1·0. There was little to choose between values in the range 0·1—0·5 in the constancy of the $K$ values. The results given in Tables 1 and 2 were obtained with $c = 0·2$. In calculating the Debye–Hückel constant, $A$, consideration was given to the effect of the amino-acid in raising the dielectric constant, $\varepsilon$, of the water. The increase in $\varepsilon$, ~0·2 D,[6] had a negligible

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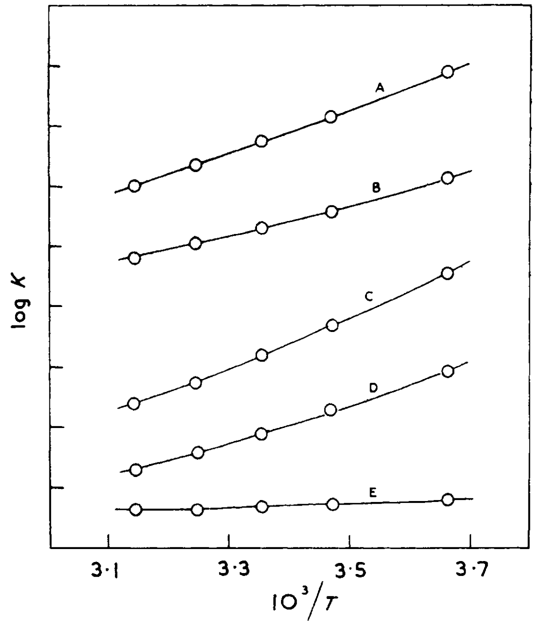
[5] King, *J. Amer. Chem. Soc.*, 1951, **73**, 155.

[6] Wyman and McMeekin, *J. Amer. Chem. Soc.*, 1933, **55**, 908.

effect on the calculated $\gamma_1$ and $\gamma_2$ values. $K_1$ and $K_2$ for nickel glycine salts are in very good agreement with $1{\cdot}51 \times 10^6$ and $9{\cdot}33 \times 10^4$, respectively, obtained by Monk[3] for potentiometric measurements at 25°. Albert,[7] at 20° and with $I = 0{\cdot}01$, obtained $K_1' = 1{\cdot}26 \times 10^6$. Introducing $\gamma$ values calculated from equation (2) gives thermodynamic $K_1 = 1{\cdot}9 \times 10^6$, in good agreement with $1{\cdot}93 \times 10^6$ obtained at 15° in the present work. For cobalt glycine salts at 25° Evans and Monk[8] obtained $K_1 = 1{\cdot}05 \times 10^5$ and $K_2 = 9{\cdot}33 \times 10^3$, which are very close to the values in Tables 1 and 2. For manganese glycine salt there is a much larger discrepancy between our value and Monk's[3] $K_1 = 2{\cdot}8 \times 10^3$.



Variation of log $K$ with $T^{-1}$ (each log $K$ division is 0·2 unit).

(A) $NiA^+$. (B) $CoA^+$. (C) $NiA_2$. (D) $CoA_2$. (E) $MnA^+$.

Plots of log $K$ against $T^{-1}$ (Figure) show marked curvature and may be expressed, with an accuracy of the order of 1% in $K_1$ and 2% in $K_2$, by the equation $\log K = a + bT + cT^2$. Values of the parameters, evaluated as described previously,[9] are given in Table 3.

TABLE 3.

Parameters for temperature-dependences of log $K_1$ and log $K_2$.

| | log $K_1$ | | | | log $K_2$ | | |
|---|---|---|---|---|---|---|---|
| | $a$ | $-10^2b$ | $10^5c$ | | $a$ | $-10^2b$ | $10^5c$ |
| $NiA^+$ ......... | 14·09 | 4·305 | 5·547 | $NiA_2$ ......... | 14·89 | 5·515 | 7·316 |
| $CoA^+$ ......... | 11·58 | 3·675 | 5·000 | $CoA_2$ ......... | 11·81 | 4·385 | 5·889 |
| $MnA^+$ ......... | 5·316 | 1·370 | 2·178 | | | | |

$\Delta G$, $\Delta H$, $\Delta C_p$, and $\Delta S$ calculated from the equations $\Delta G = -\boldsymbol{R}T \ln K$, $\Delta H = 2{\cdot}303\boldsymbol{R}T^2(b + 2cT)$, $\Delta C_p = 4{\cdot}606\boldsymbol{R}T(b + 3cT)$, and $\Delta S = (\Delta H - \Delta G)/T$ are given in Table 4.

It is not surprising that, as was found with the dicarboxylates,[9,10] precise measurements over a range of temperature indicate non-zero $\Delta C_p$ values. Pelletier,[11] in work with

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[7] Albert, *Biochem. J.*, 1950, **47**, 531; 1953, **54**, 646.

[8] Evans and Monk, *Trans. Faraday Soc.*, 1955, **51**, 1244.

[9] McAuley and Nancollas, *J.*, 1961, 2215.

[10] Nair and Nancollas, *J.*, 1961, 4367; McAuley and Nancollas, *J.*, 1961, 4458.

[11] Pelletier, *Compt. rend.*, 1957, **244**, 894; 1959, **248**, 2567; *J. Chim. Phys.*, 1960, **57**, 295, 301, 310, 318.

methionine, arginine, serine, and valine, made no comment on the relation between log $K$ and temperature but apparently assumed a linear variation.

The relatively small $\Delta S$ values in Table 4 compared with those for the dicarboxylates [9,10] reflect the smaller charges of the associating ions. Writing

$$\Delta S_1 = \Delta S_g + \Delta S_{\text{hyd}}(\text{MA}^+) - \Delta S_{\text{hyd}}(\text{M}^{2+}) - \Delta S_{\text{hyd}}(\text{A}^-)$$

and

$$\Delta S_2 = \Delta S_g + \Delta S_{\text{hyd}}(\text{MA}_2) - \Delta S_{\text{hyd}}(\text{MA}^+) - \Delta S_{\text{hyd}}(\text{A}^-)$$

where $\Delta S_g$ and $\Delta S_{\text{hyd}}$ are, respectively, gaseous and hydration entropies, enables $\Delta S_{\text{hyd}}(\text{MA}^+)$ and $\Delta S_{\text{hyd}}(\text{MA}_2)$ to be derived as described previously,[12] with results given in Table 5. The aqueous entropy of the glycine anion ($S°_{\text{A}^-} = 31{\cdot}7$ cal. deg.$^{-1}$ mole$^{-1}$) was obtained from the crystal entropy of glycine [13] (26·1 cal. deg.$^{-1}$ mole$^{-1}$), the entropy of its dissociation (—8·8 cal. deg.$^{-1}$ mole$^{-1}$),[4] and its entropy of hydration computed from solubility measurements at a number of temperatures [14] [$\Delta S_{\text{hyd}}(\text{HA}) = 14{\cdot}4$ cal. deg.$^{-1}$ mole$^{-1}$]. $-\Delta S_{\text{hyd}}(\text{MA}^+)$ varies in the expected direction with the reciprocal of the cationic radii, $r_+^{-1}$, and the small positive values of $\Delta S_{\text{hyd}}(\text{MA}_2)$ reflect the solvent-structure-breaking influence of these relatively large uncharged complexes.

As has been found by other workers [15] from studies with ligands having nitrogen, sulphur, and oxygen as co-ordinating atoms, Table 4 indicates that the heat of reaction is more important than the entropy in determining the association constants. For the dicarboxylates, the endothermic heats of formation [9,10] oppose the reaction and this is not unusual with ionic ligands since the electrostatic forces will vary with temperature in the same way as does the macroscopic dielectric constant. The exothermic heat changes accompanying the formation of the glycine salts reflect the greater covalency resulting from the increased electron-donor properties of the co-ordinating nitrogen atom. The importance of $\Delta H$ in determining $\Delta G$ is even more marked in the further association reaction to form $\text{MA}_2$. Ligand-field stabilisation will increase in going from $\text{Mn}^{2+}$, for which the splitting factor $\Delta = 0$, to $\text{Ni}^{2+}$, and this is borne out by the increase in exothermicity shown in Table 4.

TABLE 4.

Thermodynamic properties.

| Reaction | $-\Delta G$ | $-\Delta H$ | $\Delta S$ | $\Delta C_p$ |
|---|---|---|---|---|
| $\text{Ni}^{2+} + \text{A}^-$ .................. | 8·43 ± 0·01 | 4·09 ± 0·03 | 14·5 ± 0·1 | 18 ± 2 |
| $\text{Co}^{2+} + \text{A}^-$ .................. | 6·29 ± 0·01 | 2·82 ± 0·12 | 13·7 ± 0·5 | 22 ± 14 |
| $\text{Mn}^{2+} + \text{A}^-$ .............. | 4·32 ± 0·01 | 0·29 ± 0·08 | 13·5 ± 0·3 | 16 ± 10 |
| $\text{NiA}^+ + \text{A}^-$ .............. | 6·75 ± 0·01 | 4·69 ± 0·30 | 6·9 ± 0·8 | 28 ± 25 |
| $\text{CoA}^+ + \text{A}^-$ .............. | 5·42 ± 0·02 | 3·55 ± 0·20 | 6·3 ± 0·6 | 24 ± 20 |

$-\Delta G$ and $-\Delta H$ in kcal. mole$^{-1}$. $\Delta S$ in cal. deg.$^{-1}$ mole$^{-1}$. $\Delta C_p$ in cal. deg.$^{-1}$.

TABLE 5.

Entropies (cal. deg.$^{-1}$ mole$^{-1}$).

| Complex | $S_g$ (complex) | $\Delta S$ | $S°$ (complex) | $-\Delta S_{\text{hyd}}$ (complex) | $r_+^{-1}$ (Å$^{-1}$) |
|---|---|---|---|---|---|
| $\text{NiA}^+$ .................. | 57·0 | 14·5 | 23·2 | 33·8 | 1·37 |
| $\text{CoA}^+$ .................. | 57·0 | 13·7 | 23·4 | 33·6 | 1·35 |
| $\text{MnA}^+$ .............. | 56·8 | 13·5 | 27·2 | 29·6 | 1·28 |
| $\text{NiA}_2$ .................. | 57·0 | 6·9 | 61·8 | −4·8 | 1·37 |
| $\text{CoA}_2$ .................. | 56·9 | 6·3 | 61·4 | −4·5 | 1·35 |

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[12] Nair and Nancollas, *J.*, 1958, 3706.

[13] Parks, Huffman, and Barmore, *J. Amer. Chem. Soc.*, 1933, **55**, 2736.

[14] Seidell, " Solubilities of Organic Compounds," Van Nostrand, New York, 1941.

[15] Ciampolini, Paoletti, and Sacconi, *J.*, 1960, 4553.