THERMOCHEMISTRY AND OXIDATION POTENTIALS OF MANGANESE AND ITS COMPOUNDS

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CONTENTS

I. INTRODUCTION

In this review we are primarily concerned with the chemical thermodynamics of manganese, its compounds, and its aqueous ions. The resulting thermodynamic data are of a kind that has long been known to be useful in electrochemistry, analytical chemistry, and many applications of chemical principles to other disciplines.

We have been critical in the tabulation of data and have recalculated many of the published results cited. When data from different sources are not in good agreement, we have attempted to justify our choices. We have been explicit about the sources of data and also our treatment of data from the literature so that interested readers can check the steps leading to the tabulated values of thermodynamic properties and form their own opinions about reliability and accuracy. When we have not read the original papers cited, we have listed the *Chemical Abstracts* reference or the name of the journal in which the article has been translated.

For several compounds and aqueous ions we have combined experimental data from a cited source with our estimate of some thermodynamic property. *Numerical values of our estimates are given in parentheses.*

Whenever possible, we have used auxiliary thermodynamic data from the National Bureau of Standards Technical Note 270-3.[1] Other auxiliary data are taken from sources such as NBS Circular 500[2] or Latimer's "Oxidation Potentials"[3] that are explicitly cited at appropriate places in the discussion.

The matter of uncertainties in thermodynamic properties is difficult to handle. For example, the uncertainty in a heat of formation calculated from a particular heat of reaction depends on the cumulative uncertainties of all of the heats of formation used in the calculation. Many errors in thermochemical investigations are due to difficulties in the compounds or processes being studied (*i.e.*, unidentified hydrolysis phenomena, nonhomogeneous phases, impurities, etc.), which are more difficult to assess than are measurement uncertainties. Our treatment of uncertainties is simply to list results to a "reasonable" number of figures. In some cases we have indicated that an uncertainty is larger than usual by placing an approximate sign ($\sim$) in front of the cited quantity.

Although this review is not primarily concerned with high-temperature chemistry for its own sake, we have made considerable use of data obtained at high temperatures in calculating desired thermodynamic properties. Methods of making such calculations have been described.[4]

In spite of considerable discussion[5-8] in recent years, general agreement is still lacking on "sign conventions" for potentials. Much of the confusion arises because "sign" can be either electrical or algebraic. *All potentials tabulated in this review are oxidation half-reaction potentials with algebraic signs.* This choice, which has been discussed previously,[9] permits straightforward use of the familiar $\Delta G° = -RT \ln K = -nFE°$. The half-reaction potentials are based on the usual references

$$H_2(g) = 2H^+(aq) + 2e^- \qquad E° \equiv 0 \text{ V}$$

$$H_2(g) + 2OH^-(aq) = 2H_2O(liq) + 2e^- \qquad E° = 0.828 \text{ V}$$
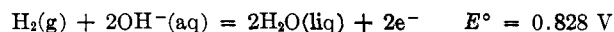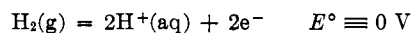
(1) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C. 1968.

(2) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(3) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

(4) G. N. Lewis and M. Randall (revised by K. S. Pitzer and L. Brewer), "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(5) F. C. Anson, *J. Chem. Educ.*, **36**, 394 (1959).

(6) A. J. deBethune, *J. Electrochem. Soc.*, **102**, 288c (1955).

(7) T. S. Licht and A. J. deBethune, *J. Chem. Educ.*, **34**, 433 (1957).

(8) J. B. Ramsay, *J. Electrochem. Soc.*, **104**, 255, 691 (1957); *J. Chem. Educ.*, **38**, 353 (1961).

(9) R. N. Goldberg and L. G. Hepler, *Chem. Rev.*, **68**, 229 (1968).

We have reserved the symbols $E°$ and K for potentials and equilibrium constants that have been determined in very dilute solutions or in such ways that activity coefficients could be considered in treating the experimental data. Similarly, we use $\Delta H°$ and $\Delta S°$ to indicate data that refer to the usual standard states[1,2,4] and use ΔH and ΔS to indicate data that refer to other states such as a solution maintained at constant ionic strength by means of some "inert" supporting electrolyte. The results of such investigations lead to equilibrium quotients represented by Q rather than equilibrium constants represented by K. We have used such symbols as $Q_{0.5}$ and $\Delta H_{0.5}$ to indicate that the equilibrium quotient or heat of reaction was determined in solutions having ionic strength 0.5.

II. DESCRIPTIVE CHEMISTRY

Species containing manganese in formal oxidation states ranging from -3 to $+7$ have been reported. We have no relevant data for the negative oxidation states and therefore limit our discussion to the zero and positive oxidation states.

For the zero oxidation state we have the well-characterized carbonyl compound of formula $Mn_2(CO)_{10}$. Related compounds such as $(CO)_5MnCo(CO)_4$ and $Mn(NO)_3CO$ are known, but we have no thermodynamic data for them. Reduction of $K_4Mn(CN)_6$ in liquid ammonia apparently yields $K_6Mn(CN)_6$, but we have no data for this substance.

Electrolytic or chemical reduction (with sodium amalgam) of $Mn(CN)_6{}^{4-}$ in aqueous solution yields $Mn(CN)_6{}^{-5}$ and thence such solids as $K_5Mn(CN)_6$ containing $Mn(I)$. Carbonyl halides of formula $Mn(CO)_5X$ are also represented as containing $Mn(I)$. We have no data for these compounds.

There is some evidence that the hydrocarbonyl $HMn(CO)_5$ is most realistically described as a hydrido complex containing $Mn(I)$. In this connection, it is interesting that $HMn(CO)_5$ ionizes to $H^+(aq)$ and $Mn(CO)_5{}^-(aq)$ with $pK \cong 7$.

Most of the compounds and ions for which we have data are those that contain manganese in the $+2$, $+4$, or $+7$ oxidation states. These compounds and ions account for most of the aqueous chemistry of manganese, and discussion of them is the principal subject of this review. We do, however, have some data for species in other less familiar positive oxidation states.

In most acidic solutions and under some other conditions $Mn(II)$ is the most stable oxidation state of manganese. Most salts of $Mn(II)$ are quite soluble in water, but a poorly defined sulfide and a well-defined hydroxide can be precipitated. Complexes of $Mn(II)$ are generally less stable than corresponding complexes of $Fe(II)$, $Co(II)$, etc.

Solids such as MnF_3 and various complexes of $Mn(III)$ are known. In general, the reasonably stable compounds of $Mn(III)$ are those that are only slightly soluble or slightly dissociated in solution.

Although several compounds of $Mn(IV)$ are known, MnO_2 is certainly the most important, both as a source of manganese in nature and as a useful oxidizing agent. Heating MnO_2 causes it to decompose to Mn_3O_2 or Mn_3O_4, depending upon conditions. The latter compound is apparently most realistically described as $Mn^{II}Mn^{III}_2O_4$ (a distorted spinel).

The dark green ion $MnO_4{}^{3-}$ contains $Mn(V)$. This ion, which is reasonably stable only in strongly alkaline solutions, has been postulated as an intermediate in various oxidation reactions.

For the $+6$ oxidation state, we have data for the dark green manganate ion, $MnO_4{}^{2-}$ which is stable only in alkaline solution.

The violet permanganate ion, $MnO_4{}^-$, and its salts contain $Mn(VII)$. Permanganate apparently gives $MnO_3{}^+$ in cold concentrated sulfuric acid, but it should be noted that solutions of permanganate in concentrated acids have exploded.

III. "SIMPLE" COMPOUNDS AND AQUEOUS IONS

For the heat of sublimation of metallic manganese we follow Mah[10] and adopt $\Delta H°_{298} = 67.2$ kcal/mole from the work of McCabe and Hudson,[11] whose results are in substantial agreement with those of a more recent investigation.[12] This value is open to some question because higher values have been reported on the basis of other vapor pressure data and we can also calculate a higher (but less certain) value from the $\Delta H_f°$, heat of sublimation, and heat of dissociation of MnO. The $S°_{298}$ values for Mn(c) and Mn(g) are taken from Kelley and King,[13] and the $\Delta G_f°$ for Mn(g) is calculated by combination of its $\Delta H_f°$ with the entropies.

The $\Delta H_f°$ values for the gaseous ions of manganese are taken from NBS Circular 500[2] after adjustment for the new $\Delta H_f°$ for Mn(g) we have adopted.

We now consider the oxides MnO, Mn_2O_3, Mn_3O_4, and MnO_2. On the basis of earlier calorimetric investigations, Mah[10] has adopted $\Delta H_f°$ values for MnO(c), $Mn_3O_4(c)$, and $MnO_2(c)$, which we also adopt. We choose $\Delta H_f°$ of $Mn_2O_3(c)$ from the high-temperature equilibrium measurements of Otto.[14] Entropies of MnO(c), $Mn_2O_3(c)$, and $MnO_2(c)$ are taken from Kelley and King[13] while that for $Mn_3O_4(c)$ is taken from Otto.[14] Free energies are calculated by combination of heats

(10) A. D. Mah, U. S. Bureau of Mines Report of Investigations No. 5600, U. S. Government Printing Office, Washington, D. C., 1960.

(11) C. L. McCabe and R. G. Hudson, J. Metals (Japan), 9, 17 (1957).

(12) P. L. Woolf, G. R. Zellars, E. Foerster, and J. P. Morris, U. S. Bureau of Mines Report of Investigations No. 5634, U. S. Government Printing Office, Washington, D. C., 1960.

(13) K. K. Kelley and E. G. King, U. S. Bureau of Mines Bulletin No. 592, U. S. Government Printing Office, Washington, D. C., 1961.

(14) E. M. Otto, J. Electrochem. Soc., 111, 88 (1964).

and entropies. High-temperature emf data[15] lead to values for MnO in agreement with those adopted here.

Several high-temperature investigations of the manganese oxides have led to other thermodynamic data that we do not accept. For example, Matsushima and Thoburn[16] have employed DTA to obtain O_2 pressures at various high temperatures and have calculated $\Delta H°$ values by means of the van't Hoff equation. We have combined their reported $\Delta H°$ values (at 835 and 1200°K) with $H_T - H_{298}$ data from Kelley[17] to obtain $\Delta H°_{298}$ values which differ by about 15 kcal/mole from those we calculate from the adopted $\Delta H_f°$ values for the oxides.

On the basis of a review of earlier investigations and the excellent experimental work of Covington, Cressey, Lever, and Thirsk,[18] we adopt the following potential for the Mn^{2+}–MnO_2 half-reaction.

$$Mn^{2+}(aq) + 2H_2O(liq) = MnO_2(c) + 4H^+(aq) + 2e^-$$
$$E° = -1.239 \text{ V}$$
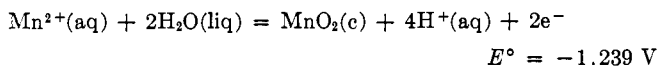
Combination of this potential with the $\Delta G_f°$ for $MnO_2(c)$ leads to $\Delta G_f° = -55.1$ kcal/mole for $Mn^{2+}(aq)$, and thence to the following calculated potential

$$Mn(c) = Mn^{2+}(aq) + 2e^- \qquad E° = 1.20 \text{ V}$$
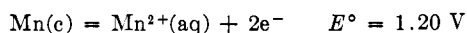
Cell measurements by Andrews and Brown[19] lead to the following potential for the MnO_2–MnO_4^- half-reaction in alkaline solution.

$$MnO_2(c) + 4OH^-(aq) = MnO_4^-(aq) + 2H_2O(liq) + 3e^-$$
$$E° = -0.588 \text{ V}$$
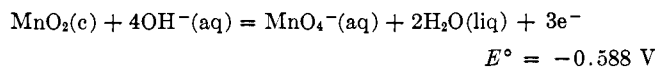
From this potential and the $\Delta G_f°$ of $MnO_2(c)$ cited above, we calculate $\Delta G_f° = -107.6$ kcal/mole for $MnO_4^-(aq)$.

Measurements by Carrington and Symons[20] on alkaline solutions lead to the following standard potential for the MnO_4^{2-}–MnO_4^- half-reaction.

$$MnO_4^{2-}(aq) = MnO_4^-(aq) + e^- \qquad E° = -0.558 \text{ V}$$
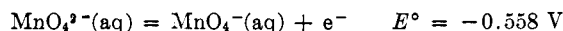
From this potential and the $\Delta G_f°$ above for $MnO_4^-(aq)$, we calculate $\Delta G_f° = -120.5$ kcal/mole for $MnO_4^{2-}(aq)$. Other measurements[20,21] with concentrated hydroxide solutions lead to an approximate standard potential for the MnO_4^{3-}–MnO_4^{2-} half-reaction and to $\Delta G_f° \leqq -127$ kcal/mole for $MnO_4^{3-}(aq)$.

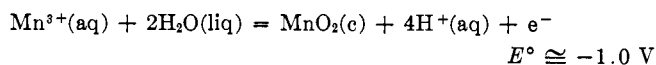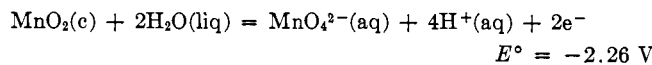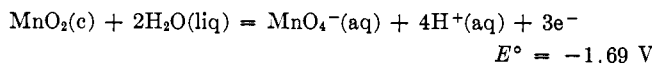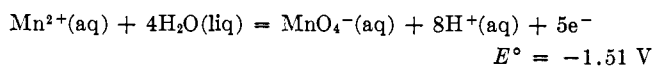$$MnO_4^{-3}(aq) = MnO_4^{2-}(aq) + e^- \qquad E° \cong -0.3 \text{ V}$$
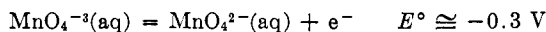
We follow Latimer[3] and write the following approximate potential for the Mn^{2+}/Mn^{3+} half-reaction in acidic solution.

$$Mn^{2+}(aq) = Mn^{3+}(aq) + e^- \qquad E° \cong -1.5 \text{ V}$$
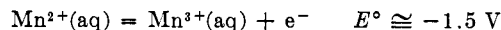
Combination of this potential with the $\Delta G_f°$ for $Mn^{2+}(aq)$ gives $\Delta G_f° \cong -21$ kcal/mole for $Mn^{3+}(aq)$.

Some potentials for acidic solution calculated from $\Delta G_f°$ values already cited are the following.

$$Mn^{2+}(aq) + 4H_2O(liq) = MnO_4^-(aq) + 8H^+(aq) + 5e^-$$
$$E° = -1.51 \text{ V}$$

$$MnO_2(c) + 2H_2O(liq) = MnO_4^-(aq) + 4H^+(aq) + 3e^-$$
$$E° = -1.69 \text{ V}$$

$$MnO_2(c) + 2H_2O(liq) = MnO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$
$$E° = -2.26 \text{ V}$$

$$Mn^{3+}(aq) + 2H_2O(liq) = MnO_2(c) + 4H^+(aq) + e^-$$
$$E° \cong -1.0 \text{ V}$$

The $\Delta G_f°$ values already cited, along with $\Delta G_f° = -148$ kcal/mole for $Mn(OH)_2(c)$ and $\Delta G_f° \cong -190$ kcal/mole for $Mn(OH)_3(c)$ taken from later in this review, permit calculation of several potentials for alkaline solution.

$$Mn(c) + 2OH^-(aq) = Mn(OH)_2(c) + 2e^- \qquad E° = 1.58 \text{ V}$$

$$Mn(OH)_2(c) + OH^-(aq) = Mn(OH)_3(c) + e^- \qquad E° \cong 0.2 \text{ V}$$

$$Mn(OH)_3(c) + OH^-(aq) = MnO_2(c) + 2H_2O(liq) + e^-$$
$$E° \cong -0.1 \text{ V}$$

$$Mn(OH)_2(c) + 2OH^-(aq) = MnO_2(c) + 2H_2O(liq) + 2e^-$$
$$E° \cong 0.03 \text{ V}$$

$$Mn(OH)_2(c) + 6OH^-(aq) = MnO_4^-(aq) + 4H_2O(liq) + 5e^-$$
$$E° = -0.34 \text{ V}$$

$$MnO_2(c) + 4OH^-(aq) = MnO_4^{3-}(aq) + 2H_2O(liq) + e^-$$
$$E° \cong -0.9 \text{ V}$$

$$MnO_2(c) + 4OH^-(aq) = MnO_4^{2-}(aq) + 2H_2O(liq) + 2e^-$$
$$E° = -0.603 \text{ V}$$
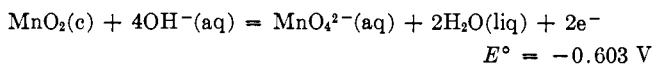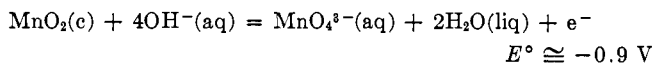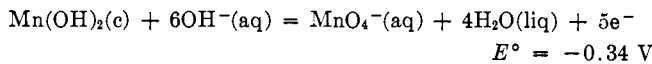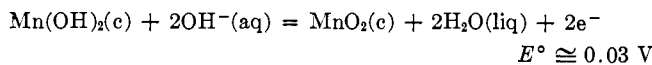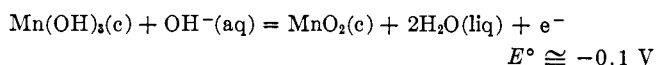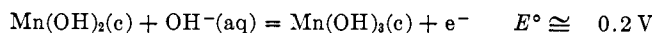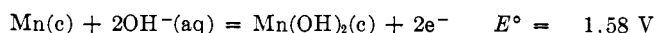
The potentials relating the various oxidation states of manganese in both acidic and basic solutions are summarized in the accompanying oxidation potential diagrams. As is now well known from the work of Latimer,[3] these diagrams present a considerable amount of chemical information in convenient form. Since the potential to the left of Mn^{3+} is more negative than that to the right, we know that Mn^{3+} is unstable with respect to disproportionation to Mn^{2+} and MnO_2. On the other hand, the potential to the left of $Mn(OH)_3$ is larger than that to the right, which indicates that $Mn(OH)_3$ is stable with respect to disproportionation. Similarly, the potential diagrams (Scheme I) show that MnO_4^{2-} is unstable with respect to MnO_2 and MnO_4^- in acidic solution. In alkaline solution MnO_4^{2-} is stable with respect to MnO_4^{3-} and MnO_4^-. The MnO_2–MnO_4^{2-} potential is slightly more negative than the MnO_4^{2-}–MnO_4^- potential, which indicates that the equilibrium constant for the disproportionation reaction

(15) C. B. Alcock and S. Zador, *Electrochim. Acta*, 12, 673 (1967).
(16) T. Matsushima and W. J. Thoburn, *Can. J. Chem.*, 43, 1723 (1965).
(17) K. K. Kelley, U. S. Bureau of Mines Bulletin No. 584, U. S. Government Printing Office, Washington, D. C., 1960.
(18) A. K. Covington, T. Cressey, B. G. Lever, and H. R. Thirsk, *Trans. Faraday Soc.*, 58, 1975 (1962).
(19) L. V. Andrews and D. J. Brown, *J. Am. Chem. Soc.*, 57, 254 (1935).
(20) A. Carrington and M. C. R. Symons. *J. Chem. Soc.*, 3373 (1956).
(21) R. Thiele and R. Landsberg, *Z. Physik. Chem.* (Leipzig), 236, 95 (1967); *Chem. Abstr.*, 68, 18081r (1968).

SCHEME I

Acidic Solution

Alkaline Solution
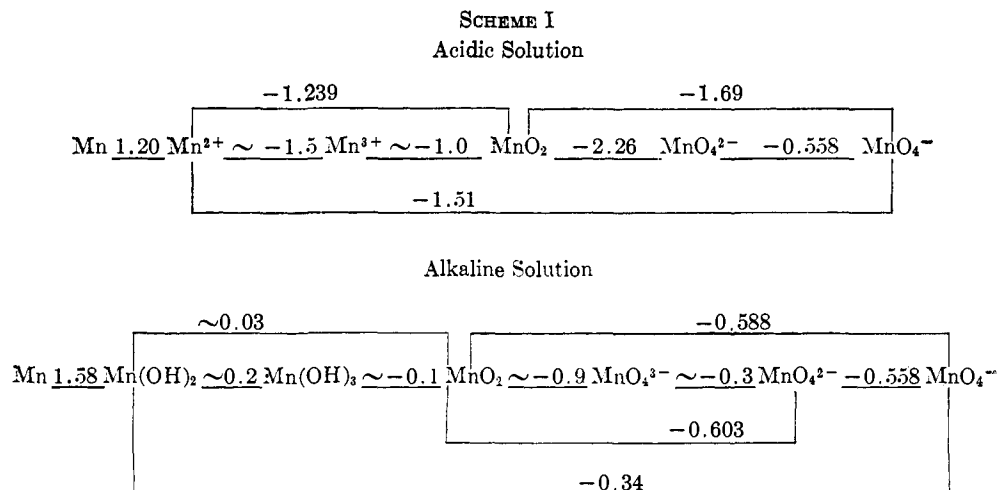
$3MnO_4^{2-}(aq) + 2H_2O = 2MnO_4^{-}(aq) + MnO_2(c) + 4OH^{-}(aq)$

is only slightly greater than unity. Thus MnO_4^{2-} is reasonably stable in solutions containing moderate concentrations of OH^- and becomes more stable as the pH increases. Although the equilibrium constant for disproportionation of MnO_4^{3-} is large, its instability is diminished by increasing concentration of OH^-.

Although there is no necessary simple relation between potentials and reaction mechanism, the potential diagram for acidic solution accounts for the ordinary reduction of MnO_4^- to Mn^{2+}, since every intermediate species that might be formed is also a strong oxidizing agent. On the other hand, reduction of MnO_4^- in alkaline solution commonly yields MnO_2, which is consistent with the observation that neither MnO_2 nor $Mn(OH)_3$ is a strong oxidizing agent in alkaline solution.

Mechanisms of oxidations by permanganate (and other high oxidation-state species of manganese) have been reviewed by Ladbury and Cullis.[22]

We now turn to consideration of ΔH_f° and S_2° values for the aqueous ions of manganese along with the related thermodynamic properties of compounds of manganese.

We combine the solubility[23] of $KMnO_4$ with $\gamma_\pm = (0.6)$ estimated by comparison with activity coefficients of other 1:1 electrolytes at the same concentration to obtain its K_{sp} and thence its ΔG° of solution. Then combination of this value with the ΔG_f° value for $MnO_4^-(aq)$ quoted earlier and ΔG_f° for $K^+(aq)$[1] gives $\Delta G_f^\circ = -176.8$ kcal/mole for $KMnO_4(c)$. We also calculate $S_2^\circ = 46.5$ gibbs/mole for $MnO_4^-(aq)$ by combining the ΔG° of solution with the heat of solution[24] and entropies of $K^+(aq)$[1] and $KMnO_4(c)$.[13]

The ΔG_f° and S_2° for $MnO_4^-(aq)$ lead to $\Delta H_f^\circ = -129.9$ kcal/mole for this ion.

We have several paths to the ΔH_f° of $Mn^{2+}(aq)$. From the calorimetric determination of the heat of reduction of MnO_4^- reported by Hugus and Latimer[25] and the ΔH_f° for $MnO_4^-(aq)$, we calculate $\Delta H_f^\circ = -53.4$ kcal/mole for $Mn^{2+}(aq)$. Another approach to this quantity is by way of ΔH_f° and ΔH° of solution of $MnCl_2(c)$. Two investigations[26,27] are in good agreement for the heat of solution, which we combine with a small estimated heat of dilution to obtain the desired $\Delta H^\circ = -17.5$ kcal/mole for solution of $MnCl_2(c)$. Koehler and Coughlin[28] have reported $\Delta H_f^\circ = -115.2$ kcal/mole for $MnCl_2(c)$, while high-temperature data[29,30] lead to $\Delta H_f^\circ = -116.9$ kcal/mole. Combination of these latter values with the heat of solution leads to $\Delta H_f^\circ = -52.8$ and -54.5 kcal/mole for $Mn^{2+}(aq)$. Walkley[31] has reported $\Delta H_f^\circ = -53.2$ (his best) and -52.8 (his second best, our recalculation) kcal/mole for $Mn^{2+}(aq)$. We also use the data of Southard and Shomate[32] for $MnSO_4(c)$ with the most recent auxiliary data[1] to calculate $\Delta H_f^\circ = -254.9$ kcal/mole for $MnSO_4(c)$. Next we combine the heat of solution reported by Thomsen[33] with corrections to 25° and infinite dilution estimated by comparison with

(22) J. W. Ladbury and C. F. Cullis, *Chem. Rev.*, **58**, 403 (1958).

(23) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1940.

(24) T. Nelson, C. Moss, and L. G. Hepler, *J. Phys. Chem.*, **64**, 376 (1960).

(25) G. Z. Hugus and W. M. Latimer, *J. Electrochem. Soc.*, **98**, 296 (1951).

(26) P. Ehrlich, F. W. Koknat, and H. J. Seifert, *Z. Anorg. Allgem. Chem.*, **341**, 281 (1965).

(27) P. Paoletti and A. Vacca, *Trans. Faraday Soc.*, **60**, 50 (1964).

(28) M. F. Koehler and J. P. Coughlin, *J. Phys. Chem.*, **63**, 605 (1959).

(29) L. Rossemyr and T. Rosenqvist, *Trans. AIME*, **224**, 140 (1962).

(30) H. Schafer, *Z. Anorg. Allgem. Chem.*, **278**, 300 (1955).

(31) A. Walkley, *J. Electrochem. Soc.*, **93**, 316 (1948); **94**, 41 (1948).

(32) J. C. Southard and C. H. Shomate, *J. Am. Chem. Soc.*, **64**, 1770 (1942).

(33) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

data[34] for $ZnSO_4$, $CdSO_4$, and $CuSO_4$ to obtain the standard heat of solution and thence $\Delta H_f° = -53.0$ kcal/mole for Mn^{2+}(aq). We adopt $\Delta H_f° = -53.2$ kcal/mole for Mn^{2+}(aq) and use this value in subsequent calculations.

We combine the $\Delta G_f°$ and $\Delta H_f°$ for Mn^{2+}(aq) to obtain its $\bar{S}_2° = -17$ gibbs/mole. All other paths to this entropy involve uncertain estimates of entropies of solid compounds.

Calorimetric data (± 1.5 kcal) from Hill and Williamson[35] lead to $\Delta H_f° = -157$ kcal/mole for MnO_4^{2-}(aq). By combination of the $\Delta G_f°$ and $\Delta H_f°$ values, we obtain $\bar{S}_2° = 14$ gibbs/mole for this ion, which is about the same as the more certain values for CrO_4^{2-}(aq) and MoO_4^{2-}(aq).

Using our values for the thermodynamic properties of the aqueous ions, we now turn to systematic discussion of compounds, beginning with the zero state and proceeding to the +7 state.

Although the solution chemistry of manganese carbonyl, $Mn_2(CO)_{10}$, has not been much investigated, its thermodynamic properties are of special interest because of the Mn–Mn bond. The heat of formation has been determined calorimetrically by Good, Fairbrother, and Waddington,[36] who report $\Delta H_f° = -400.9$ kcal/mole for $Mn_2(CO)_{10}$(c). Cotton and Monchamp[37] have made vapor pressure measurements and calculated $\Delta H° = 15.0$ kcal/mole for vaporization. We combine these data to obtain $\Delta H_f° = -385.9$ kcal/mole for $Mn_2(CO)_{10}$(g). Cotton and Monchamp[37] have used these data in calculating that the Mn–Mn bond energy is 34 ± 13 kcal/mole. A mass spectrometric investigation by Bidinosti and McIntyre[38] has led these workers to report 18.9 ± 1.4 kcal/mole for the Mn–Mn bond energy.

For manganous hydroxide we adopt $K_{sp} = 1.6 \times 10^{-13}$ from references cited by Sillen[39] and calculate the standard free energy of solution. Combination of this value with the free energies of the ions gives $\Delta G_f° = -148$ kcal/mole for solid manganous hydroxide represented by $Mn(OH)_2$(c). Two different calorimetric measurements by Thomsen give data[33] that we have combined with known and estimated heats of dilution in obtaining $\Delta H_f° = -167$ kcal/mole for $Mn(OH)_2$(c). These values lead to $S°_{298} = 23$ gibbs/mole for Mn-

$(OH)_2$(c). Berg and Kovyrzina[40] have investigated dissociation of solid $Mn(OH)_2$ into solid MnO and H_2O-(g). Their reported thermodynamic properties are not internally consistent, and their results are in poor agreement with the values already cited for thermodynamic properties of MnO(c) and $Mn(OH)_2$(c).

For MnF_2(c) we adopt the values cited by Mah[10] and Kelley and King.[18] Both the $\Delta G_f°$ and $\Delta H_f°$ values appear to be uncertain by several kilocalories/mole.

Combination of the previously cited heat of solution[26,27] with the $\Delta H_f°$ of Mn^{2+}(aq) leads to $\Delta H_f° = -115.6$ kcal/mole for $MnCl_2$(c), which is the value we adopt. This value falls between the values cited earlier.[28–30] Combination of this $\Delta H_f°$ with $S°_{298}$ from Chisholm and Stout[41] gives $\Delta G_f° = -105.9$ kcal/mole for $MnCl_2$(c).

Mah[10] has cited earlier calculations of $\Delta H_f°$ of $MnBr_2$(c) from *gaseous* bromine. The more recently determined heat of solution[42] of this compound combined with an estimated heat of dilution and our $\Delta H_f°$ of Mn^{2+}(aq) permits us to calculate $\Delta H_f° = -92.6$ kcal/mole for formation of $MnBr_2$(c) from *liquid* bromine. We combine this $\Delta H_f°$ with our estimated $S°_{298}$ to obtain the tabulated $\Delta G_f°$.

For MnI_2(c) we adopt $\Delta H_f° = -64.2$ kcal/mole from the heat of solution[43] combined with our estimated heat of dilution and $\Delta H_f°$ values for Mn^{2+}(aq) and I^-(aq).[1] Our estimated $S°_{298}$ with $\Delta H_f°$ leads to the tabulated $\Delta G_f°$.

Results of several investigations[2,31,33] of hydrates of manganous halides are in poor agreement and we do not tabulate thermodynamic properties for these compounds.

Hayes and Martin[44] have determined the solubility of $Mn(IO_3)_2$(c) at several temperatures and report $K_{sp} = 4.79 \times 10^{-7}$, $\Delta G° = 8.61$ kcal/mole, $\Delta H° = 2.28$ kcal/mole, and $\Delta S° = -21.1$ gibbs/mole for the solution reaction at 298°K. We combine these values with data for IO_3^- (aq)[1] and Mn^{2+}(aq) to obtain $\Delta G_f° = -124.9$ kcal/mole, $\Delta H_f° = -161.3$ kcal/mole, and $S°_{298} = 61$ gibbs/mole for $Mn(IO_3)_2$(c). Heat capacity data leading to a third-law entropy are needed and would thence lead to a new $\bar{S}_2°$ for Mn^{2+}(aq).

Manganous sulfide, MnS, has been investigated by a number of workers. Kelley[45] has calculated $\Delta G°_{29} = 18.4$ kcal/mole, $\Delta H°_{298} = 28.9$ kcal/mole, and $\Delta S°_{298} = 35.3$ gibbs/mole for

(34) J. W. Larson, P. Cerutti, H. K. Garber, and L. G. Hepler, *J. Phys. Chem.*, 72, 2902 (1968).

(35) R. A. W. Hill and J. F. Williamson, *J. Chem. Soc.*, 2417 (1957).

(36) W. D. Good, D. M. Fairbrother, and G. Waddington, *J. Phys. Chem.*, 62, 853 (1958).

(37) F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 533 (1960).

(38) D. R. Bidinosti and N. S. McIntyre, *Chem. Commun.*, 555 (1966).

(39) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(40) L. G. Berg and V. P. Kovyrzina, *Zh. Neorg. Khim.*, 8, 2041 (1963); *Russ. J. Inorg. Chem.*, 8, 1065 (1963).

(41) R. C. Chisholm and J. W. Stout, *J. Chem. Phys.*, 36, 972 (1962).

(42) P. Paoletti, *Trans. Faraday Soc.*, 61, 219 (1965).

(43) P. Paoletti, A. Sabatini, and A. Vacca, *ibid.*, 61, 2417 (1965).

(44) A. M. Hayes and D. S. Martin, *J. Am. Chem. Soc.*, 73, 4853 (1951).

(45) K. K. Kelley, U. S. Bureau of Mines Bulletin No. 406, U. S. Government Printing Office, Washington, D. C., 1937; reprinted as Bureau of Mines Bulletin No. 601, 1962.

$$MnCl_2(c) + H_2S(g) = MnS(c) + 2HCl(g)$$
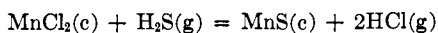
from the high-temperature data of Jellinek and Pod-jaski. We use our data for $MnCl_2$ with the above $\Delta G°$ and $\Delta H°$ values in calculating $\Delta G_f° = -50.0$ kcal/mole and $\Delta H_f° = -47.5$ kcal/mole for MnS. The third-law $\Delta S°_{298}$ for this reaction is 30.5 gibbs/mole, which differs significantly from that cited above. We have therefore combined this latter $\Delta S°_{298}$ with the $\Delta G°_{298}$ calculated by Kelley[45] to obtain $\Delta H°_{298} = 27.5$ kcal/mole for the reaction and thence $\Delta H_f° = -48.9$ kcal/mole for MnS(c). Since this last value depends on the free energy of reaction but not its temperature derivative, it may be more reliable than the first value given here.

We have recalculated the results of calorimetric measurements by Thomsen and Berthelot[33] to obtain $\Delta H_f° = -48$ and -49 kcal/mole for MnS. Combination of these values with the third-law $S°_{298} = 18.7$ gibbs/mole leads to $\Delta G_f° = -49$ and -50 kcal/mole for MnS. Mah[10] has adopted $\Delta H_f° = -49.5$ kcal/mole from the calorimetric work of Jeffes, Richardson, and Pearson. Combination of this value, which may be the most reliable of those we have cited, with the entropy leads to $\Delta G_f° = -50.5$ kcal/mole for MnS.

We adopt $\Delta G_f° = -50.5$ kcal/mole, $\Delta H_f° = -49.5$ kcal/mole, and $S°_{298} = 18.7$ gibbs/mole for MnS(c). Combination of this $\Delta G_f°$ with that for $S^{2-}(aq)^{1,46}$ leads to $K_{sp} = 2 \times 10^{-12}$ for MnS. Solubility measurements have led various investigators to report[39] "experimental" K_{sp} values covering a wide range, but it appears to us that the "best" values are in reasonable agreement with this calculated value.

A recent investigation of MnS is that of Adami and King[47] who have reported $\Delta H_f° = -51.0$ kcal/mole for MnS (alabandite). Taking $S_{298}° = 18.7$ gibbs/mole as before, we obtain $\Delta G_f° = -52.0$ kcal/mole and calculate $K_{sp} = 2 \times 10^{-13}$ for the alabandite modification of MnS. It might also be noted that Sato[48] has taken $\Delta G_f° = -50.0$ kcal/mole for alabandite from Robie. This $\Delta G_f°$ leads to $K_{sp} = 5 \times 10^{-12}$.

Although it is known that MnS can exist in several forms and solubilities have been reported for both pink and green forms, we have been unable to distinguish thermodynamically between these forms.

For $MnSO_4(c)$, we adopt $\Delta H_f° = -254.9$ kcal/mole^{1,32} as mentioned earlier. Combination of this $\Delta H_f°$ with the entropy[10,13] leads to $\Delta G_f°$.

Heats of solution measured by Thomsen[33] lead to $\Delta H° = -6.0$ kcal/mole for

$$MnSO_4(c) + H_2O(liq) = MnSO_4 \cdot H_2O(c)$$
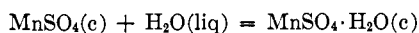
This value gives $\Delta H_f° = -329.2$ kcal/mole for $MnSO_4 \cdot H_2O(c)$. Kelley[45] quotes an equilibrium dissociation pressure of 2.64×10^{-2} atm at 25°. This pressure leads to $\Delta G° = 2.15$ kcal/mole for the dissociation reaction

$$MnSO_4 \cdot H_2O(c) = MnSO_4(c) + H_2O(g)$$
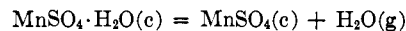
Combination of this $\Delta G°$ with $\Delta H°$ from $\Delta H_f°$ values leads to $\Delta S°_{298} = 48$ gibbs/mole for the dissociation. We have reliable $S°_{298}$ values for both $MnSO_4(c)$ and $H_2O(g)$ and are confident that an estimated $S°_{298} = (37)$ gibbs/mole is satisfactory for $MnSO_4 \cdot H_2O(c)$, leading to $\Delta S°_{298} = 35$ gibbs/mole for the dissociation. We combine this $\Delta S°$ with $\Delta H_f°$ values to obtain $\Delta G°_{298} = 6.1$ kcal/mole for the dissociation reaction and thence a dissociation pressure of 3×10^{-5} atm. This pressure seems more consistent with the stability of the hydrate than does the larger pressure cited above. Our own interpretation of the equilibrium data of Carpenter and Jette[49] cited by Kelley[45] suggests that the quoted dissociation pressure actually refers to a higher hydrate. We adopt a $\Delta G_f°$ for $MnSO_4 \cdot H_2O(c)$ based on the $\Delta H_f°$ and our estimated $S°$.

Although there are data for higher hydrates of $MnSO_4$, there are so many uncertainties that we are not listing thermodynamic properties for these compounds.

For $Mn(NO_3)_2 \cdot 6H_2O(c, liq)$, we combine the results of Shomate and Young[50] with the most recent auxiliary data[1] to obtain $\Delta H_f° = -566.9$ and -557.3 kcal/mole, respectively. Although there have been difficulties associated with determining the melting point of this compound, it is certainly close to the 25.8° cited in NBS Circular 500.[2] For $Mn(NO_3)_2(c)$ and $Mn(NO_3)_2 \cdot 3H_2O(c)$ we adopt $\Delta H_f° = -167$ and -355 kcal/mole, respectively, from data of uncertain accuracy cited in NBS Circular 500.[2]

For $MnCO_3(c)$ we adopt $\Delta H_f° = -214$ kcal/mole on the basis of investigations cited in NBS Circular 500.[2] Our recalculations with the data of Thomsen and Berthelot[33] lead to $\Delta H_f° = -211$ kcal/mole for $MnCO_3$-(ppt), in agreement with the value listed in NBS Circular 500.[2] Anderson's low-temperature data have led NBS Circular 500,[2] Kelley and King,[13] and Mah[10] to adopt $S°_{298} = 20.5$ gibbs/mole for $MnCO_3(c)$. Kostryukov and Kalinkina[51] have reported $S°_{298} = 27.0$ gibbs/mole for a "synthetic" sample (rather than the mineral used by Anderson) of $MnCO_3$. This entropy is larger than entropies of similar carbonates, but we know of no other reason to question it.

Although it is not entirely clear how the $\Delta H_f°$ and $S°_{298}$ values above should be combined, we have chosen to associate the lower entropy^{2,10,13} with $MnCO_3(c)$

(46) J. W. Kury, A. J. Zielen, and W. M. Latimer. *J. Electrochem. Soc.*, 100, 468 (1953).

(47) L. W. Adami and E. G. King, U. S. Bureau of Mines Report of Investigations No. 6495, U. S. Government Printing Office, Washington, D. C., 1964.

(48) M. Sato, *Electrochim. Acta*, 11, 361 (1966).

(49) C. D. Carpenter and E. R. Jette, *J. Am. Chem. Soc.*, 45, 578 (1923).

(50) C. H. Shomate and F. E. Young, *ibid.*, 66, 771 (1944).

(51) V. N. Kostryukov and I. N. Kalinkina, *Zh. Fiz. Khim.*, 38, 780 (1964).

and the larger entropy[51] with $MnCO_3$(ppt). Thus we obtain $\Delta G_f° = -196$ kcal/mole for $MnCO_3$(c) and $\Delta G_f° = -194$ kcal/mole for $MnCO_3$(ppt.) The corresponding solubility products are $K_{sp} = 10^{-11}$ for $MnCO_3$(c) and $K_{sp} = 10^{-10}$ for $MnCO_3$(ppt). Previously reported[39,45] solubility products fall between 3×10^{-10} and 2×10^{-11}. It should also be noted that Garrels and Christ[52] quote $\Delta G_f° = -195.7$ kcal/mole for natural rhodochrosite, which corresponds to $K_{sp} = 3 \times 10^{-11}$.

Calorimetric measurements by Barany[53] give $\Delta H_f° = -284.8$ kcal/mole for $MnMoO_4$(c). Combination of this value with our estimated entropy leads to the tabulated $\Delta G_f°$. We use this $\Delta G_f°$ with that for MoO_4^{2-}(aq)[54] to calculate $K_{sp} = 10^{-8}$ on the assumption that the solid phase in equilibrium with saturated solution is indeed $MnMoO_4$(c)

We have several highly uncertain paths to $\Delta G_f°$ for $Mn(OH)_3$. First, we may combine the $\Delta H_f° = -212$ kcal/mole for $Mn(OH)_3$ listed in NBS Circular 500[2] with our estimated $S°_{298} = (24)$ gibbs/mole to obtain $\Delta G_f° \cong -181$ kcal/mole. We may also adjust the heat of formation listed by Bichowsky and Rossini[33] for different $\Delta H_f°$ values for reference compounds to obtain $\Delta H_f° \cong -224$ kcal/mole and thence $\Delta G_f° \cong -193$ kcal/mole for $Mn(OH)_3$. All of these values are from the calorimetric data of Petersen, which are difficult to interpret. Our view inclines toward the more exothermic value. Still another approach is to take the $\Delta G°$ for hydration of Mn_2O_3 to $Mn(OH)_3$ by liquid water to be small, which leads to $\Delta G_f° \cong -190$ kcal/mole for $Mn(OH)_3$. Adopting an uncertainly weighted average $\Delta G_f° \cong -190$ kcal/mole, we obtain potentials cited earlier and also calculate $K_{sp} \cong 10^{-42}$ for $Mn(OH)_3$. Although this K_{sp} is smaller than several published estimates, it is not unreasonable, and we know of no experimental data that contradict (or confirm) this value.

For the solubility of barium manganate ($BaMnO_4$), Latimer[3] has given $K_{sp} = 1.5 \times 10^{-10}$. Combination of this K_{sp} with our $\Delta G_f°$ for MnO_4^{2-}(aq) and $\Delta G_f°$ for Ba^{2+}(aq)[2] gives $\Delta G_f° = -268$ kcal/mole for $BaMnO_4$(c). We estimate $S°_{298} = (37)$ gibbs/mole for this compound and combine with the $\Delta G_f°$ to obtain its $\Delta H_f° = -293$ kcal/mole. The $\Delta H_f° = -282$ kcal/mole listed in NBS Circular 500[2] appears to be in error.

We have no further data for solid manganates, but a comment on estimation of $\Delta H_f°$ of K_2MnO_4(c) may be worthwhile. Hill and Williamson[35] have combined

experimental data on MnO_4^{2-}(aq) with their estimate that the heat of solution of K_2MnO_4(c) is about 10 kcal/mole [as it is for $KMnO_4$(c)[24]] to calculate $\Delta H_f°$ of K_2MnO_4(c). It seems more reasonable to estimate $\Delta H° = (4)$ kcal/mole [by analogy to K_2CrO_4(c)[55,56]] for the heat solution of K_2MnO_4(c), which leads to its $\Delta H_f° = -282$ kcal/mole.

The heat of formation of $KMnO_4$(c) is calculated from its heat of solution[24] and combined with its entropy[10,13] to yield its $\Delta G_f°$.

IV. COMPLEX COMPOUNDS AND IONS

The best data on hydrolysis of Mn^{2+}(aq) appear to be those of Perrin,[57] who has reported the following.

Mn^{2+}(aq) + H_2O(liq) = $MnOH^+$(aq) + H^+(aq)

$$K = 2.6 \times 10^{-11}$$
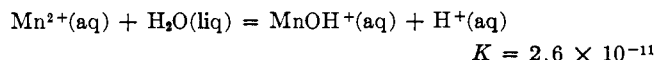
We use this equilibrium constant in calculating $\Delta G°_f = -97.3$ kcal/mole for $MnOH^+$(aq). Perrin[57] also reported K values at other temperatures, but we do not believe the accuracy justifies calculation of $\Delta H_f°$ or $\bar{S}_2°$ for $MnOH^+$(aq).

In addition to the stability data and references cited by Sillen and Martell,[39] we call attention to some other investigations of complex ions of Mn^{2+}. Cell measurements by Nair and Nancollas[58] have led to $\Delta G° = -3.07$, $\Delta H° = 3.37$ kcal/mole, and $\Delta S° = 21.6$ gibbs/mole for the association of Mn^{2+} with SO_4^{2-} as in

Mn^{2+}(aq) + SO_4^{2-}(aq) = $MnSO_4$(aq ion pair) $K = 181$
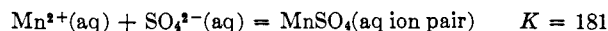
Combination of these data with our data for Mn^{2+}(aq) and those for SO_4^{2-}(aq)[1] lead to the tabulated values for $MnSO_4$(aq ion pair). Atkinson and Petrucci[59] have measured conductances of manganous sulfate and manganous m-benzenedisulfonate in water and mixed solvents. Their data indicate that the latter may be very close to a true strong electrolyte in dilute aqueous solution, while the former was found to be associated, in satisfactory agreement with the results cited above.[58] We also call attention to recent ultrasonic investigations[60,61] of solutions of these same salts. Although the experimental results and their interpretation are still controversial, the method is ultimately capable of providing detailed information about association of ions in solution.

Nair and Nancollas[62] have investigated association of Mn^{2+}(aq) with malonate at several temperatures and have calculated $\Delta H° = 3.53 \pm 0.2$ kcal/mole for the association reaction. Later, McAuley and Nancollas[63]

(52) R. M. Garrels and C. L. Christ, "Solutions, Minerals and Equilibria," Harper and Row, Publishers, New York, N. Y., 1965.

(53) R. Barany, U. S. Bureau of Mines Report of Investigations No .6618, U. S. Government Printing Office, Washington, D. C., 1965.

(54) R. L. Graham and L. G. Hepler, J. Am. Chem. Soc., 78, 4846 (1956).

(55) L. G. Hepler, ibid., 80, 6181 (1958).

(56) C. N. Muldrow and L. G. Hepler, ibid., 79, 4045 (1957).

(57) D. D. Perrin, J. Chem. Soc., 2197 (1962).

(58) V. S. K. Nair and G. H. Nancollas, ibid., 3934 (1959).

(59) G. Atkinson and S. Petrucci, J. Am. Chem. Soc., 86, 7 (1964).

(60) G. Atkinson and S. K. Kor, J. Phys. Chem., 70, 314 (1966).

(61) L. G. Jackopin and E. Yeager, ibid., 70, 313 (1966).

(62) V. S. K. Nair and G. H. Nancollas, J. Chem. Soc., 4367 (1961).

(63) A. McAuley and G. H. Nancollas, ibid., 989 (1963).

investigated the same system calorimetrically and reported $\Delta H° = 3.68 \pm 0.12$ kcal/mole for the same association reaction. McAuley and Nancollas[64,65] have also investigated association of Mn^{2+}(aq) with succinate in these same ways and reported $\Delta H° = 2.95 \pm 0.1$ kcal/mole and $\Delta H° = 3.02 \pm 0.15$ kcal/mole. This agreement of results obtained by different methods is characteristic of the best investigations, but is all too uncommon. Other data for association reactions are presented in a book by Nancollas.[66]
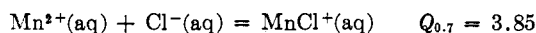
Brannan, Dunsmore, and Nancollas[67] have investigated association of Mn^{2+}(aq) with glycine, and Desai and Nair[68] have done an unusually thorough investigation of complexes with phthalate. Atkinson and Bauman[69] and Davies and Dunning[70] have employed emf and calorimetric measurements in investigating association of Mn^{2+} with 2,2'-bipyridine. Data for oxalate complexes have been reported.[71]

Ciampolini, Paoletti, and Sacconi[72,73] have carried out detailed calorimetric investigations of the association of Mn^{2+} (and ions of other transition elements) with ethylenediamine and various other amines. The association of manganous thiocyanate has been studied by Nancollas and Torrance.[74] Thermodynamic parameters for the association of Mn^{2+}(aq) with adenosine triphosphate[75] and histidine[76,77] have also been reported.

Various studies of the association of Mn^{2+}(aq) with aqueous halide ions have been made. Ciavatta and Grimaldi[78] have investigated the competition of Mn^{2+}-(aq) and H^+(aq) for F^-(aq). They report the following.

$$Mn^{2+}(aq) + F^-(aq) = MnF^+(aq) \qquad Q_2 = 6.2$$
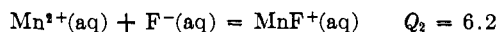
Morris and Short[79] have reported

$$Mn^{2+}(aq) + Cl^-(aq) = MnCl^+(aq) \qquad Q_{0.7} = 3.85$$

Approximate equilibrium quotients for complexes con-

(64) A. McAuley and G. H. Nancollas, *J. Chem. Soc.*, 4458 (1961).

(65) A. McAuley, G. H. Nancollas, and K. Torrance, *Inorg. Chem.*, 6, 136 (1967).

(66) G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier Publishing Co., Amsterdam, 1966.

(67) J. R. Brannan, H. S. Dunsmore, and G. H. Nancollas, *J. Chem. Soc.*, 304 (1964).

(68) I. R. Desai and V. S. K. Nair, *ibid.*, 2360 (1962).

(69) G. Atkinson and J. E. Bauman, *Inorg. Chem.*, 1, 900 (1962); 2, 64 (1963).

(70) R. L. Davies and D. W. Dunning, *J. Chem. Soc.*, 4168 (1965).

(71) A. McAuley and G. H. Nancollas, *ibid.*, 2215 (1961).

(72) M. Ciampolini, P. Paoletti, and L. Sacconi, *Nature*, 186, 880 (1960); *J. Chem. Soc.*, 4553 (1960); 2994, 5115 (1961); 3589 (1963).

(73) P. Paoletti and M. Ciampolini, *Inorg. Chem.*, 6, 64 (1967).

(74) G. H. Nancollas and K. Torrance, *ibid.*, 6, 1567 (1967).

(75) M. M. T. Kahn and A. E. Martell, *J. Am. Chem. Soc.*, 88, 668 (1966).

(76) H. Kroll, *ibid.*, 74, 2032 (1952).

(77) D. Perrin and V. S. Sharma, *J. Chem. Soc.*, A, 724 (1967).

(78) L. Ciavatta and M. Grimaldi, *J. Inorg. Nucl. Chem.*, 27, 2019 (1965).

(79) D. F. C. Morris and E. L. Short, *J. Chem. Soc.*, 5149 (1961).

TABLE I
THERMODYNAMIC DATA FOR MANGANESE AT 298°K[a]

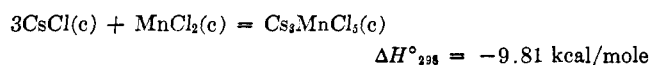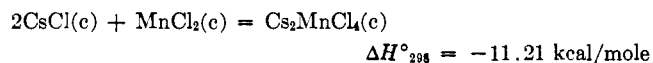| Substance	$\Delta H_f°$, kcal/mole	$\Delta G_f°$, kcal/mole	$S°$, gibbs/mole
Mn(c, α)	0	0	7.64[13]
Mn(c, γ)			7.72[13]
Mn(g)	67.2[10]	57.1	41.49[13]
Mn^+(g)	239.7[2]		
Mn^{2+}(g)	600.4[2]		
Mn^{2+}(aq)	−53.2[25,27−30]	−55.1[10,18]	−17
$MnOH^+$(aq)		−97.3[57]	
$MnSO_3$(aq ion pair)	−267.1[58]	−236.1[58]	9[58]
Mn^{3+}(aq)		∼−21[3]	
MnO_4^{3-}(aq)		∼−127[20]	
MnO_4^{2-}(aq)	−157[35]	−120.5[20]	∼14
MnO_4^-(aq)	−129.9[24]	−107.6[19]	46.5[13,24]
MnO(c)	−92.0[10]	−86.7	14.3[13]
Mn_2O_3(c)	−228.7[14]	−210.1	26.4[13]
Mn_3O_4(c)	−331.3[10]	−306.2	36.8[14]
MnO_2(c)	−124.4[10]	−111.3	12.68[13]
$Mn(OH)_2$(c)	−167[33]	−148[39]	∼23
$Mn(OH)_3$(c)	∼−221	∼−190	(24)
MnF_2(c)	∼−190[10]	∼−179[10]	22.25[10,13]
$MnCl_2$(c)	−115.6[26,27]	−105.9	28.26[41]
$CsMnCl_3$(c)	−228.8[26]		
Cs_2MnCl_4(c)	−333.8[26]		
Cs_3MnCl_5(c)	−435.9[26]		
$RbMnCl_3$(c)	−224.7[26]		
$KMnCl_3$(c)	−223.4[26]		
$NaMnCl_3$(c)	−214.5[26]		
$MnBr_2$(c)	−92.6[42]	−89	(33)
MnI_2(c)	−64.2[43]	−65	(37)
$Mn(IO_3)_2$(c)	−161.3[44]	−124.9[44]	61[44]
MnS(c)	−49.5[10]	−50.5[10]	18.7[10,13]
MnS(alabandite)	−51.0[47]		
$MnSO_4$(c)	−254.9[1,32]	−229.1	26.8[10,13]
$MnSO_4 \cdot H_2O$(c)	−329.2[33]	−289.9	(37)
$Mn(NO_3)_2$(c)	−167[2]		
$Mn(NO_3)_2 \cdot 3H_2O$(c)	−355[2]		
$Mn(NO_3)_2 \cdot 6H_2O$(c)	−566.9[50]		
$Mn(NO_3)_2 \cdot 6H_2O$(liq)	−557.3[50]		
$MnCO_3$(c)	−214[2]	−196[51]	20.5[2,10,13]
$MnCO_3$(ppt)	−211[33]	−194	27.0[51]
$MnMoO_4$(c)	−284.8[53]	−261	(32)
K_2MnO_4(c)	(−282)		
$KMnO_4$(c)	−200.6[24]	−176.8	41.0[13]
$BaMnO_4$(c)	−293	−268[3]	(37)
$Mn_2(CO)_{10}$(c)	−400.9[36]		
$Mn_2(CO)_{10}$(g)	−385.9[36,37]		

[a] Superscript numbers are references.

taining more Cl^- indicate that these species are significant only in concentrated solutions.

Heat of solution measurements by Ehrlich, Koknat, and Seifert[26] permit calculation of $\Delta H°_{298} = -9.73$, -6.21, -3.63, and -0.71 kcal/mole for reactions of type

$$MCl(c) + MnCl_2(c) = MMnCl_3(c)$$

in which M represents Cs, Rb, K, and Na. We use these results with our $\Delta H_f°$ for $MnCl_2$(c) and data for MCl(c) compounds from NBS Circular 500[2] to calculate our tabulated $\Delta H_f°$ values. Their heats of solution permit calculation of the following.

$$2CsCl(c) + MnCl_2(c) = Cs_2MnCl_4(c)$$

$$\Delta H°_{298} = -11.21 \text{ kcal/mole}$$

$$3CsCl(c) + MnCl_2(c) = Cs_3MnCl_5(c)$$

$$\Delta H°_{298} = -9.81 \text{ kcal/mole}$$

We also calculate $\Delta H_f°$ values for $Cs_2MnCl_4(c)$ and $Cs_3MnCl_5(c)$. The ΔH data are relevant to the interesting phase diagram[22] for the $CsCl-MnCl_2$ system.

Heats of solution of compounds of type $(NR_4)_2$-MnX_4 have been determined[27,42,43] and discussed, but auxiliary data required for calculation of heats of formation are not available.

Wells and Davies[80] have investigated the hydrolysis of $Mn^{3+}(aq)$ and report

$$Mn^{3+}(aq) + H_2O(aq) = MnOH^{2+}(aq) + H^+(aq)$$
$$Q_{4.0} = 0.88$$
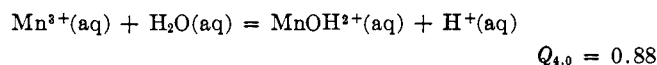
It thus appears than Mn^{3+} is more extensively hydrolyzed than any other $+3$ ion. Wells and Davies[80] also determined the equilibrium quotient $(Q_{4.0})$ at several other temperatures and calculated ΔH and ΔS values for the hydrolysis reaction in this solvent system. Data required to convert their values to our standard state are not available, so we tabulate no values for $MnOH_2^+(aq)$.

Suwyn and Hamm[81] report results of interesting kinetic and equilibrium investigations of the reaction

$$Mn^{III}EDTA(OH_2)^-(aq) + N_3^-(aq) = Mn^{III}EDTA(N_3)^{2-}(aq)$$
$$Q_{0.25} = 32.1$$
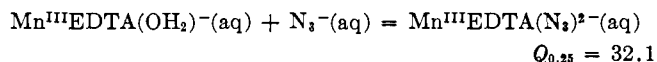
ΔH and ΔS values for this reaction are also given. They[81] also review and discuss evidence for seven-coordination of $Mn(III)$.

Table I presents a summary of thermodynamic data for manganese at $298°K$.

(80) C. F. Wells and G. Davies, *Nature*, **205**, 692 (1965).

(81) M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, **6**, 2150 (1967).