

- (10) Z. Libus and H. Tialowska, *J. Solution Chem.*, **4**, 1011 (1975).
 (11) R. H. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 740 (1940).
 (12) G. Schorsh, *Bull. Soc. Chim. Fr.*, 1449 (1964).
 (13) A. O. Gubeli and J. Ste. Marie, *Can. J. Chem.*, **45**, 827 (1967).
 (14) T. Sekine, *Acta Chem. Scand.*, **19**, 1526 (1965).
 (15) P. Schindler, H. Althaus, and W. Feitnecht, *Helv. Chim. Acta*, **47**, 982 (1964).
 (16) L. G. Sillen and A. E. Martel, *Chem. Soc., Spec. Publ.*, No. 17 (1964).
 (17) T. Taketatsu, *Bull. Chem. Soc. Jpn.*, **36**, 549 (1963).
 (18) W. J. Hamer, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 24 (1968).
 (19) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
 (20) A. F. Clifford, *J. Am. Chem. Soc.*, **79**, 5404 (1957); *J. Phys. Chem.*, **63**, 1227 (1959).
 (21) R. M. Garrels and C. L. Christ, "Solution Minerals and Equilibria", Harper and Row, New York, N.Y., 1965, pp 96-98.
 (22) I. M. Klotz and R. M. Rosenberg, "Chemical Thermodynamics", 3rd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 386.

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Thermodynamics of the Manganese(II) Bicarbonate System

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The formation constant for the MnHCO_3^+ ion pair was determined at the temperatures 5, 10, 15, 25, 40, and 55 °C. The experimental pH change resulting from alternating additions of aqueous MnCl_2 and KHCO_3 to MnCl_2 - KHCO_3 mixtures in equilibrium with CO_2 was used to calculate the formation constant of the MnHCO_3^+ ion pair by a floating point method which does not require absolute pH and $P(\text{CO}_2)$ values. The logarithm of the formation constant of the MnHCO_3^+ ion pair is 1.27 at 25 °C and rises with temperature. These data are similar to previously determined log formation constants for CaHCO_3^+ , MgHCO_3^+ , and ZnHCO_3^+ ion pairs. From the temperature dependence of the log of the formation constant, it was possible to derive values for ΔH° for the MnHCO_3^+ ion pair. The values of ΔG° , ΔH° , and ΔS° at 25 °C for the MnHCO_3^+ ion pair are $-1.73 \text{ kcal mol}^{-1}$, $0.98 \text{ kcal mol}^{-1}$, and 9.1 eu , respectively. Thus, the formation of the MnHCO_3^+ ion pair is an example of an endothermic reaction made possible by favorable entropy changes.

Introduction

Metal ligand ion pairs were shown to be geochemically significant in Garrels and Thompson's model of seawater.¹ Garrels and Thompson showed that the MgHCO_3^+ and CaHCO_3^+ ion pairs contributed significantly to the control and distribution of the carbonate species in seawater. However, when they checked the validity of their model with the experimental values given by Sverdrup² they concluded that more HCO_3^- is tied up than could be accounted for by simply Ca^{2+} and Mg^{2+} complexation. Reasons for this could be the difficulty in determining accurate formation constants for the species of interest and the failure to consider all interactions. Indeed, a literature search^{3,4} proved that existing thermodynamic data for the MgHCO_3^+ and CaHCO_3^+ ion pairs did not span a range of geochemically interesting temperatures in general.

Previous work in our laboratories has determined the ion pairing constants for Mg^{2+} , Ca^{2+} , and Zn^{2+} with HCO_3^- . It was possible to obtain convergent values of equilibrium constants for these systems at temperatures between 10 and 90 °C. Therefore, we considered it worthwhile to explore the interaction between Mn^{2+} and HCO_3^- using techniques similar to those of the other studies. Mn(II) having an unfilled d shell would offer a model system for the study of transition-metal ion interactions with HCO_3^- .

Previously published values for the formation constant for the MnHCO_3^+ ion pair at 25 °C are shown in Table I. Comparing these values shows that the agreement between recent researchers is good, but the internal deviations in the reported values are rather high. Each of these researchers used a different type of potentiometric method, each of which has its respective faults. The above studies suffer another common problem—viz., that the formation constant was only determined at one temperature (25 °C).

Experimental Section

Solutions were prepared from Baker analyzed reagent KHCO_3 and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in deionized water distilled once from acidified di-

Table I. Literature Values for the Formation Constant of MnHCO_3^+ at 25 °C

ref	method	K_f	std dev
Nasanen, 1942 ⁵	potentiometry	3×10^3	
Hem, 1963 ⁶	potentiometry	63	21
Morgan, 1965 ⁷	potentiometry	86	26

Table II. Typical Reaction Conditions for a Determination of log K_f for the MnHCO_3^+ Ion Pair^a

addition	amt of KHCO_3 , g	amt of MnCl_2 , g	pH
1	13.80		5.022
2		24.69	4.978
3	12.66		5.141
4		23.95	5.107
5	13.24		5.228
6		24.45	5.199
7	13.43		5.294
8		24.66	5.267
9	13.19		5.343

^a Initial conditions: KHCO_3 , 13.70 g, 0.1009 m; MnCl_2 , 24.44 g, 0.5274 m; H_2O , 1609.5 g; gas phase pure CO_2 ; pH 4.730.

chromate. Solid KHCO_3 was dried over Drierite at room temperature. Solutions of MnCl_2 were adjusted to pH 5-6 by the addition of KOH, filtered, and analyzed to Cl^- with standardized $\text{Hg}(\text{NO}_3)_2$ with diphenylcarbazone as an indicator. The Mn^{2+} analysis was a standard EDTA procedure involving back-titration with Zn^{2+} and Eriochrome Black-T as an indicator.

The pH of the solution during Mn^{2+} and HCO_3^- additions was monitored with an Orion 801 pH meter using an Orion 90-02-00 double junction reference electrode (10% KNO_3 as the outer chamber solution) vs. a Beckman 39301 glass electrode. The electrodes were calibrated at 25 °C with commercial pH 4.008 and 6.865 buffers. Temperature corrections were supplied by NBS tables. Titrations were made after the pH was constant (± 0.001) for at least 0.5 h. A typical titration is shown in Table II. Approximately 5 min was allowed between each addition for mixing and thermal equilibrium. A buffer check was made at the end of each titration and a maximum difference of 1% change in slope was tolerated.

Table III. Experimental and Calculated Results for MnHCO_3^+ Determinations

$T, ^\circ\text{C}$	found		calcd		
	av log K_f	no. of runs	eq 1	eq 2	eq 3
5	1.261 ± 0.019^a	4	1.247	1.248	1.248
10	1.242 ± 0.010	4	1.248	1.248	1.248
15	1.235 ± 0.003	4	1.253	1.252	1.252
25	1.275 ± 0.004	13	1.271	1.270	1.270
40	1.330 ± 0.009	6	1.318	1.319	1.319
55	1.385 ± 0.015	10	1.390	1.391	1.391

^a Standard error of the mean at each temperature.

Reactions at 5, 10, and 15 $^\circ\text{C}$ were performed in a jacketed glass vessel of approximately 200-mL capacity linked in series to an auxiliary jacketed vessel and to a Forma Model 2095 constant-temperature circulating bath. A No. 11 rubber stopper in the top of the vessel was fitted with pH electrodes, gas delivery tube, gas outlet, and a septum for addition of reagents. A magnetic stirrer in conjunction with a Teflon-coated stir bar was used to mix the contents of the vessel. The auxiliary jacketed vessel contained two inner chambers which held buffers thermostated at the temperature of the run within ± 0.2 $^\circ\text{C}$. For reactions performed at 10 and 15 $^\circ\text{C}$, a gas washing bottle filled with deionized distilled water was inserted between the CO_2 gas storage tank and the gas delivery tube.

Reactions at 25, 40, and 55 $^\circ\text{C}$ were performed in a 2-L polypropylene reaction vessel, which was sealed gastight and thermostated to ± 0.1 $^\circ\text{C}$ in a 40-gallon constant-temperature water bath. The vessel's lid was fitted with a 250-W heater enclosed in a Vycor brand sheath, a gas dispersion tube, a gas outlet connected to a condensate catch tube and bubbler, a stainless steel thermistor probe, a septum for addition of reagents, pH electrodes, and another gas outlet tube connected to a bellows pump. The main temperature bath also held receptacles for buffers and a gas presaturator vessel. The gas circulation system consisted of pure CO_2 gas flowing at a rate of 100 mL/min through the gas presaturator and into the reaction vessel via the gas dispersion tube. The gas outlet tube was connected to a polyethylene bellows pump which withdrew the gas phase from the top of the reaction solution and pumped it at a rate of 2 L/min through 50 ft of heat exchange coil to the conically shaped bottom of the reaction vessel. The circulation of gas in this manner produced rapid equilibrium and excellent stirring of the reaction solution. The thermostated circulation system has been described by Siebert.^{4,8}

The floating point method, a potentiometric experimental technique which either eliminates or greatly reduces the sources of error of the previous potentiometric studies, was utilized in this investigation. Treatment of the floating point method has been discussed in detail by Siebert and Hostetler.⁸ This method allows the determination of the formation constant by the relative change in pH during a potentiometric titration of a millimolar KHCO_3 solution, in equilibrium with pure CO_2 gas, with alternating additions of 0.5 m MnCl_2 and 0.1 m KHCO_3 solutions without requiring absolute values for pH, $P(\text{CO}_2)$, or the acid dissociation constants for carbonic acid. This is accomplished by realizing that under isothermal and constant $P(\text{CO}_2)$ reaction conditions, the product of the bicarbonate ion activity and the hydrogen ion activity is a constant equal to the product $P(\text{CO}_2)K_0K_{a1}$. The constants K_0 and K_{a1} describe the solubility of CO_2 gas and the first dissociation of carbonic acid, respectively. Under isothermal and isobaric conditions, the formation constant for any species is constant throughout the titration sequence. Thus the MnHCO_3^+ formation constant, $K_{\text{MnHCO}_3^+}$, can be calculated by utilizing the electroneutrality equation, mass balance equations, and appropriate activity coefficients in conjunction with accurately measured relative pH changes between titration points and by varying (floating) the product $P(\text{CO}_2)K_0K_{a1}$ until convergent $K_{\text{MnHCO}_3^+}$ values are obtained for each addition in the titration sequence.

Results

The thermodynamic association constants calculated from experimental data covering a temperature range from 5 to 55 $^\circ\text{C}$ are summarized in Table III. An extensive error analysis considered errors due to the assumption that during a titration sequence the system could adequately be described by the aqueous species Mn^{2+} , Cl^- , HCO_3^- , MnHCO_3^+ , H^+ , K^+ , and

Table IV. Calculated ΔH° Values

$T, ^\circ\text{C}$	$\Delta H^\circ, \text{kcal mol}^{-1}$		
	eq 1	eq 2	eq 3
5	0.036	-0.093	-0.146
10	0.241	0.167	0.136
15	0.461	0.431	0.419
25	0.945	0.974	0.983
40	1.792	1.822	1.830
55	2.789	2.713	2.676

Table V. ΔS° Values Calculated from Values Listed in Tables III and IV

$T, ^\circ\text{C}$	$\Delta S^\circ, \text{cal}/(\text{deg mol})$		
	eq 1	eq 2	eq 3
5	5.83	5.38	5.19
10	6.56	6.30	6.19
15	7.33	7.23	7.18
25	8.99	9.08	9.11
40	11.75	11.85	11.88
55	14.86	14.63	14.55

OH^- and that other possible aqueous species such as MnCO_3^0 , $\text{MnCO}_3(\text{c})$, MnCl^+ , MnCl_2^0 , MnCl_3^- , MnOH^+ , or $\text{Mn}(\text{OH})_2(\text{c})$ need not be considered. Other assumptions were that the $P(\text{CO}_2)$ remained constant throughout the titration sequence, that pH change between titration points could be accurately measured, and that the single ion activity coefficients could be adequately defined. The resulting overall experimental uncertainty believed to encompass reasonable errors at all temperatures for $\log K_{\text{MnHCO}_3^+}$ was ± 0.05 log unit.

Discussion

While we have been unable to find a two-parameter equation that is consistent with our experimental $\log K_f$ values, we have found several three-parameter equations which satisfactorily describe our experimental $\log K_f$ values over a wide range of temperatures. Three equations of this type are described below.

The first equation considered represents the $\log K_f$ as the power series

$$\log K_f = A + BT + CT^2 \quad (1)$$

where $A = 5.5205$, $B = 3.0831 \times 10^{-2}$, and $C = 5.5601 \times 10^{-5}$. This equation leads to $\Delta H^\circ = 2.303R(2CT^3 + BT^2)$.

The second three-parameter equation considered is the Harned-Robinson equation⁹

$$\log K_f = A + BT + C/T \quad (2)$$

which leads to a fit similar to eq 1 where $A = -1.0078 \times 10^1$, $B = 2.0227 \times 10^{-2}$, and $C = 1.5852 \times 10^3$. This equation leads to $\Delta H^\circ = 2.303R(BT^2 - C)$.

The Everett and Wynne-Jones equation⁹

$$\log K = A + B \log T + C/T \quad (3)$$

where $A = -8.0629 \times 10^1$, $B = 2.8405 \times 10^1$, and $C = 3.4625 \times 10^3$ also leads to a fit similar to eq 1. This equation leads to $\Delta H^\circ = R(BT - 2.303C)$.

Values for $\log K_f$, ΔH° , and ΔS° calculated from eq 1-3 as a function of temperature are listed in Tables III-V, respectively. A comparison of the values listed for $\log K_f$, ΔH° , and ΔS° shows that values obtained by eq 1-3 are quite similar over the temperature range considered. Figure 1 shows a plot of $\log K_f$ vs. T fitted with the least-squares curve corresponding to eq 3. This equation has the advantage of yielding unbiased

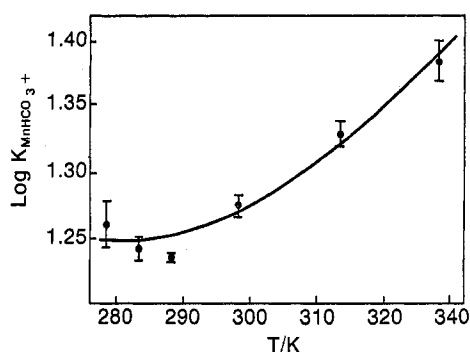
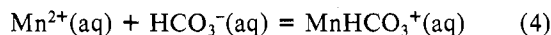


Figure 1. Log K formation of MnHCO_3^+ vs. temperature in Kelvin. Solid line represents the equation $\log K = -80.629 + 28.405 \log T + 3462.5/T$.

estimates of ΔG° , ΔH° , and ΔC_p° while requiring only three parameters.

The thermodynamic data listed in Tables III–V for the manganese bicarbonate species indicate that eq 4 is an en-



dothemic reaction made possible by favorable entropy changes. It should be pointed out that there is nothing in the thermodynamic data to indicate the type of ion pairing, inner or outer sphere, present in the manganese bicarbonate species.

Previous research^{3,4} indicated that purely electrostatic bonding predominated in the CaHCO_3^+ and MgHCO_3^+ ion pairs. Purely electrostatic bonding can be expected to predominate in ion pairs formed from cations with a noble gas configuration such as Ca^{2+} or Mg^{2+} . However, cations such as Mn^{2+} or Zn^{2+} which have a half-filled and filled d subshell, respectively, are more polarizable than Ca^{2+} or Mg^{2+} and are more apt to form ion pairs which have some covalent character.

The work of ion pair formation may be regarded as consisting of two parts: W_{env} representing long range electrostatic forces dependent upon environment and increasing with temperature, and W_{non} representing short-range or quantum mechanical forces, insensitive to environment and independent of temperature.¹⁰ The factors that determine the magnitudes

of W_{env} and W_{non} are quite separate and independent, and there is no reason why a small W_{non} should not be accompanied by a large W_{env} or a large W_{non} accompanied by a small W_{env} .¹¹

If W_{env} is zero or near zero, then the ion pair behavior should be described by W_{non} and thus be independent of temperature. This is clearly not the case in the present study. Gurney¹¹ has shown that the term W_{env} can be considered to be almost entirely electrostatic in nature and may be represented by W_{el} which is proportional to the dielectric constant, ϵ , of the solvent. If we now consider the case of pure electrostatic forces, that is $W_{\text{non}} = 0$, the values of $\log K$ would lie on a curve passing through a minimum at 219 K, the characteristic constant for water. Analysis of the experimental data via eq 1 indicates a minimum at 277 K.

Therefore, the behavior of the MnHCO_3^+ ion pair cannot be fully described by simple electrostatic interactions. Gurney¹¹ found that the addition of a nonelectrostatic contribution W_{non} to W_{el} will shift the position of the minimum to a higher temperature, that is to say, toward room temperature. With this as a criterion, it can be said that the bonding in the MnHCO_3^+ ion pair is a composite of both electrostatic and nonelectrostatic interactions.

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References and Notes

- (1) R. M. Garrels and M. E. Thompson, *Am. J. Sci.*, **260**, 57 (1962).
- (2) H. V. Sverdrup, M. W. Johnson, and R. H. Fleming, "The Oceans", Prentice-Hall, New York, N.Y., 1942.
- (3) W. R. Almon, M.A. Thesis, University of Missouri—Columbia, 1973.
- (4) R. M. Siebert, Ph.D. Thesis, University of Missouri—Columbia, 1974.
- (5) R. Nasanen, *Z. Phys. Chem., Abt. A*, **191**, 54 (1942).
- (6) J. D. Hem, USGS Water Supply Paper 1667-A (1963).
- (7) J. J. Morgan in "Principles and Applications of Water Chemistry", S. D. Faust and J. V. Hunter, Ed., Wiley, New York, N.Y., 1967, pp 561–624.
- (8) R. M. Siebert and P. B. Hostetler, *Am. J. Sci.*, **277**, 697 (1977).
- (9) P. D. Bolton, *J. Chem. Educ.*, **47**, 638 (1970).
- (10) G. H. Nancollas, "Interactions in Electrolyte Solutions", Elsevier, New York, N.Y., 1966.
- (11) R. W. Gurney, "Ionic Processes in Solution", Dover, New York, N.Y., 1962.

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Mixed Phosphine 2,2'-Bipyridine Complexes of Ruthenium

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Two types of mixed complex, e.g., $[(\text{bpy})_2\text{Ru}(\text{PPh}_3)\text{Cl}]^+$ and $[(\text{bpy})_2\text{Ru}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]^{2+}$, have been prepared from the appropriate group 5 ligand and $(\text{bpy})_2\text{RuCl}_2$ ($\text{bpy} = 2,2'$ -bipyridine). A complete study of the electronic spectral and redox properties indicates that phosphorus ligands stabilize the Ru(II) forms of these ions to a greater extent than pyridine-type ligands, which is consistent with the greater π -acid nature of the tertiary phosphine ligands. The impressive chemical stability and high reduction potentials for the Ru(III) form of these ions in acetonitrile solution make them ideal candidates as stoichiometric oxidants in inorganic or organic syntheses.

In the known mono- and diphosphine, -arsine, and -stibine complexes of ruthenium, the remaining ligands in the inner coordination sphere are usually the strong π -acid ligands of organometallic chemistry, i.e., CO, NO, phosphine, arsine, and unsaturated hydrocarbons,¹ or the hydride ligand.^{2,3} Considerably fewer complexes have been reported which contain both group 5 ligands and ligands like NH_3 , 2,2'-bpy or 1,10-phen which are more normally associated with classical coordination complexes. Complexes of the latter kind which have been reported, e.g., $[\text{Ru}_2\text{Cl}_2(\text{P}(\text{C}_6\text{H}_5)_3)_4(\text{bpy})_2]\text{Cl}_2$,⁴ *mer*-($\text{bpy})\text{Ru}(\text{P}(\text{C}_6\text{H}_5)_3)_3$,⁵ and $(\text{bpy})_2\text{Ru}(\text{P}(\text{C}_6\text{H}_5)_3)_3$

($\text{P} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$), have been prepared by the displacement of ligands from *trans*- P_3RuCl_2 or *trans*- P_4RuCl_2 .

We describe here the preparations of mono- and bis-substituted complexes of the types $(\text{bpy})_2\text{Ru}(\text{P})\text{Cl}^+$ and $(\text{bpy})_2\text{RuP}_2^{2+}$ (where P is tertiary phosphine, arsine or stibine) which are based on the known chemistry of *cis*-($\text{bpy})_2\text{RuCl}_2$ developed previously by ourselves^{6,7} and by Dwyer and his co-workers.^{8,9} There is by now a considerable synthetic chemistry of bis(bipyridyl)ruthenium(II) complexes, and electrochemical and spectral studies have given insight into the nature of the Ru(II)-ligand bond. One of the goals of this