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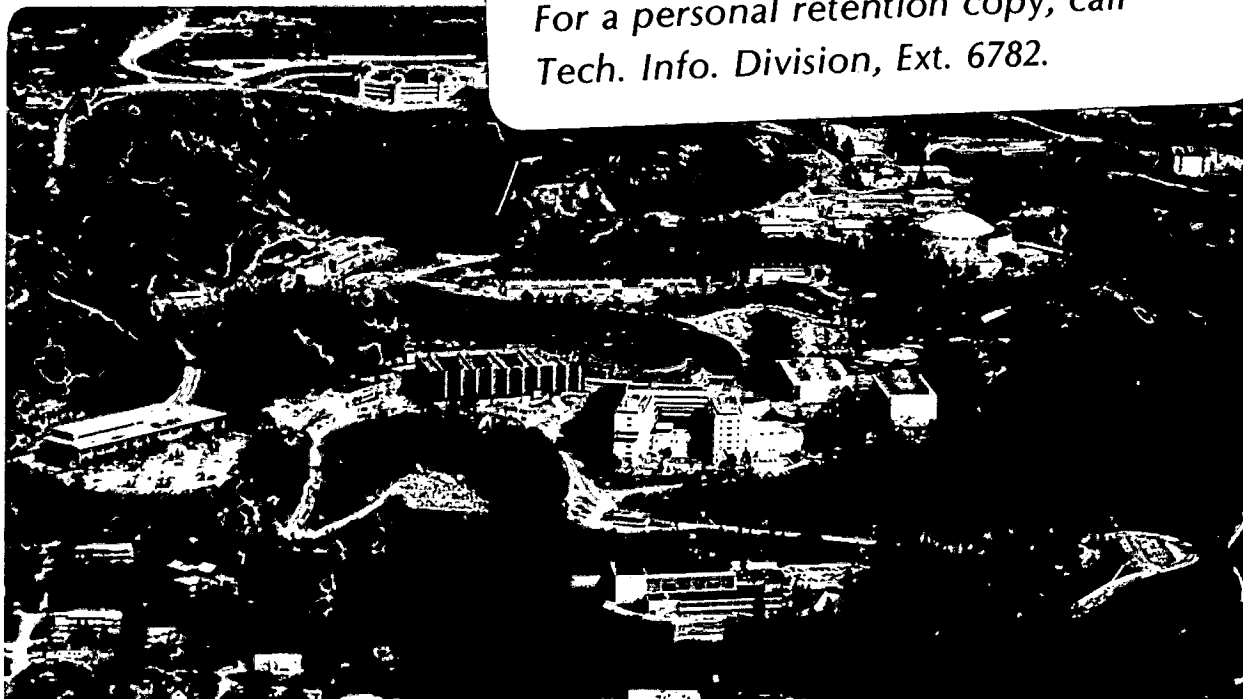
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USE OF BALANCED LIKE CHARGES APPROACH TO
METAL-BICARBONATE REACTIONS*

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February 1983

Formation reactions for several metal bicarbonate ion pairs were written as: $M^{2+} + H_2CO_3 = MHCO_3^+ + H^+$. Values of the equilibrium constants as a function of temperature could then be fit to a two-parameter equation of the form $\log K = A + B/T$. The resulting equations reproduce selected published experimental formation constants to an average of $\pm 0.5\%$ for the following ions: Mn, Mg, Ca, Zn and Cu.

Introduction

The temperature dependence of formation constants for metal-bicarbonate systems are important to sea water chemistry¹; geothermal energy studies² and nuclear waste disposal³. Usually the temperature dependence is described by fitting to nonlinear equations such as $\log K_f = A + B/T + C \ln T + DT^2$ in which either C or D may be zero^{1,2}. An example is that of Lesht and Bauman¹ who were unable to find a two-parameter equation consistent with their experimental $\log K_f$ values. We report here an approach whereby selected formation constants are fit to a two-term linear equation which permits estimating values at high temperatures by extrapolation. The approach is based on that recently used by Lindsay⁴, Cobble et al.⁵, Phillips and Silvester⁹ in which the charges on both sides of a chemical reaction are of like sign and are equal in number.

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Method of Calculation

The formation of a metal-bicarbonate ion pair for a divalent metal ion is written as



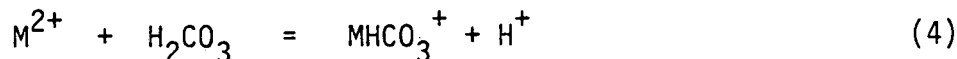
whence

$$K_f = \frac{[MHCO_3^+]}{[M^{2+}][HCO_3^-]} \quad (2)$$

Adding the dissociation reaction for H_2CO_3



to equation (1) gives equation (4)



It is seen that equation (4) has ions of identical sign on each side of the equation, and an equal number of charges. On the other hand, equation (1) has ions with unlike charges on the left hand side.

The heat capacity change may be small for reactions such as those in equation (4); so that a plot of $\log K$ versus $1/T$ closely approximates a straight line^{4,5,7,9}. Extrapolation to high temperatures is thereby much facilitated.

Data on formation constants for metal-bicarbonates from Lesht and Bauman¹ and Bauman⁶, (Fig. 1) and data on H_2CO_3 dissociation from Patterson, et al.⁷ (Fig. 2) were used to construct the following table according to equation (4):

TABLE I. Equilibrium Constants for Equation (4) Calculated From Data in References 1,6 and 7.

Species	Log K at Indicated Temperature, °C							
	5	10	15	25	40	55	70	90
MnHCO ₃ ⁺	-5.251	-5.215	-5.179	-5.073	-4.963	-4.892	--	--
CaHCO ₃ ⁺	--	-5.23	--	-5.12	-5.03	-4.97	-4.91	-4.85
CuHCO ₃ ⁺	--	-4.55	--	-4.27	-3.97	-3.70	--	--
ZnHCO ₃ ⁺	--	-5.04	--	-4.95	-4.82	-4.71	-4.66	--
MgHCO ₃ ⁺	--	-5.406	--	-5.282	-5.185	-5.117	-5.063	-5.016

Figure 3 is a plot of log K values in Table I as a function of temperature. The equilibrium constants in this table were fit to the following equation^{9,10}.

$$R \ln K = A + \frac{B}{T} + C \ln T + D T + E T^2 + F T^3 \quad (5)$$

where

$$A = \Delta S^\circ_\theta - (C_0 - \frac{\theta^2}{4} C_2 + \frac{10\theta^3}{72} C_3) - \ln \theta \quad (6)$$

$$(C_0 - \theta C_1 + \frac{\theta^2}{2} C_2 - \frac{\theta^3}{6} C_3)$$

$$B = -\Delta H^\circ_\theta + \theta C_0 - \frac{\theta^2}{2} C_1 + \frac{\theta^3}{6} C_2 - \frac{\theta^4}{24} C_3 \quad (7)$$

$$C = C_0 - \theta C_1 + \frac{\theta^2}{2} C_2 - \frac{\theta^3}{6} C_3 \quad (8)$$

$$D = \frac{C_1}{2} - \frac{\theta}{2} C_2 + \frac{\theta^2}{4} C_3 \quad (9)$$

$$E = \frac{C_2}{12} - \frac{\theta}{12} C_3 \quad (10)$$

$$F = \frac{C_3}{72} \quad (11)$$

and $C_0 = \Delta C_{p\theta}$, $C_1 = (d\Delta C_p/dT)_\theta$, $C_2 = (d^2\Delta C_p/dT^2)_\theta$, $C_3 = (d^3\Delta C_p/dT^3)_\theta$.
 $\theta = 298.15$.

Enthalpy and entropy values at 25°C were obtained from the computer fit to equation (5); adding a heat capacity change term did not improve the fit, so that the C, D, E and F coefficients were negligible. Table II summarizes the results.

TABLE II. Enthalpy, Entropy and A,B, Coefficients for Reactions According to Equation 4 Based on the Fit to Equation (5).

Species	$\Delta H, 298.15$	$\Delta S, 298.15$	A	B	* σ
	cal/mole	cal/deg/mole			
MnHCO ₃ ⁺	3165	-12.7	-2.772	- 691.75	0.0141
CaHCO ₃ ⁺	2243	-15.9	-3.486	- 490.16	0.0160
CuHCO ₃ ⁺	8127	+ 7.8	1.702	-1775.99	0.0214
ZnHCO ₃ ⁺	3014	-12.5	-2.726	- 658.66	0.0219
MgHCO ₃ ⁺	2359	-16.3	-3.565	- 515.51	0.0262

*Standard deviation of fit.

Results

Smoothed values were calculated at selected temperatures from equation (5) using the coefficients in Table II. These were converted to formation constants by subtracting values for the dissociation of H₂CO₃ at these temperatures, and compared with other values. Table III compares our results with those used to develop our correlation: Lesht and Bauman, Bauman, and Siebert and Hostetler; as well as earlier data published by Jacobson and Langmuir ¹².

TABLE III. Comparison of Formation Constants
Calculated from Eq (5) with Other Data.

* Species	Eq (5)	Bauman ⁶	Siebert and Hostetler ⁸	Lesht and Bauman ¹	Jacobson and Langmuir ¹²
CuHCO₃⁺					
10	1.89	^a 1.91			
25	2.09	2.08			
40	2.32	2.32			
55	2.57	2.58			
ZnHCO₃⁺					
10	1.41	^b 1.42			
25	1.42	1.40			
40	1.47	1.47			
55	1.55	1.57			
70	1.67	1.63			
MgHCO₃⁺					
10	1.076		1.051		
25	1.059		1.066		
40	1.085		1.108		
55	1.144		1.160		
70	1.228		1.230		
90	1.370		1.337		
MnHCO₃⁺					
5	1.258			1.261	
10	1.249			1.242	
15	1.248			1.235	
25	1.262			1.275	
40	1.315			1.330	
55	1.398			1.385	
CaHCO₃⁺					
10	1.25	^c 1.23			0.81
25	1.23	1.23			1.01
40	1.24	1.26			1.21
55	1.30	1.31			1.41
70	1.38	1.38			1.61
90	1.52	1.50			1.88

^aD. Rages, M.S. Thesis, University of Missouri-Columbia (1978).

^bFrom Reference 13.

^cW.R. Almon, M.S. Thesis, University of Missouri-Columbia (1973).

* At temperature, °C, indicated.

Values of $\log K_f$ calculated from equation (5) agree to an average of better than $\pm 1\%$ with those of Lesht and Bauman for MnHCO_3^+ ; and, the tabulation for Mg, Ca, Cu and Zn bicarbonate complexes given in Bauman⁶.

Formation constants according to equation (1) are recovered by subtracting equilibrium constants for the ionization of H_2CO_3 . In this way, we have fit $\log K_f$ values to equation (5) to obtain the thermodynamic data given in Table IV.

TABLE IV. Enthalpy, Entropy and Heat Capacity for Formation of Ion Pair Species Shown, and for Dissociation of H_2CO_3 , 298.15 K: $\text{M}^{2+} + \text{HCO}_3^- = \text{MHCO}_3^+$

Species	** ΔH 298.15	ΔS 298.15	C_p
MnHCO_3^+	985.4(983)	9.1	56.6
CaHCO_3^+	412.2(551)	7.0	53.9
MgHCO_3^+	785.8(779)	7.5	41.9
CuHCO_3^+	5550.0(5610)	28.1	127.9
ZnHCO_3^+	846.7	9.3	67.7
* H_2CO_3	2236.6	-21.6	-73.1

* Smith and Martell¹¹ select at 298.15, $\Delta H = 2000 \pm 100$, $\Delta S = -22$; Patterson et al.⁷ find $\Delta H = 2165.3$, $\Delta S = -21.8$, $\Delta C_p = -80.8$.

** Calculated values by Bauman⁶ given in parenthesis.

We then calculate A, B and C coefficients for a three-parameter equation in which now the heat capacity change for equation (1) is not negligible. Table V compares our results with those published by Bauman⁶.

TABLE V . Three-Parameter Fit to $\log K = A + B/T + C \log T$
Coefficients Calculated by Bauman are Shown
in Parenthesis.

<u>Species</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>*σ</u>
MnHCO ₃ ⁺	(-80.63) -80.87	(3462) 3473.16	(28.41) 28.49	0.015
CaHCO ₃ ⁺	(-79.08) -77.49	(3497) 3427.79	(27.71) 27.17	0.0011
CuHCO ₃ ⁺	(-168.7) -181.09	(6560) 7122.87	(60.13) 64.38	0.0089
ZnHCO ₃ ⁺	- 97.03	4225.52	34.06	0.027
MgHCO ₃ ⁺	(-59.85) -59.64	(2567) 2556.59	(21.14) 21.07	0.0023

* Standard deviation of fit.

It is concluded that use of the balanced like charges approach permits linearization of the temperature dependence of formation constants for selected metal-bicarbonate reactions. The resulting two-parameter equation facilitates extrapolation of log K values to high temperatures, and should simplify computer-assisted and other calculations for these reactions.

Acknowledgment

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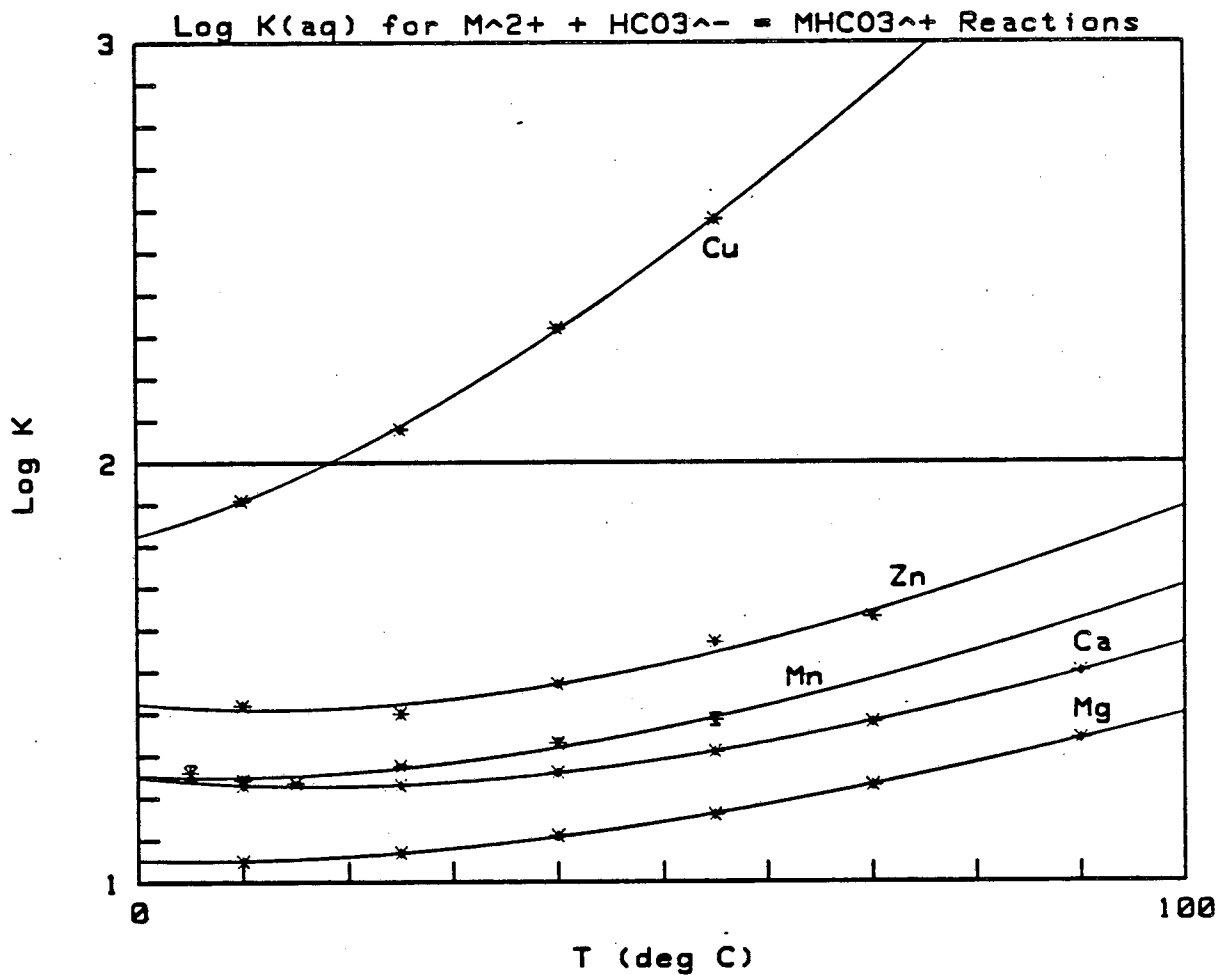


Figure 1. Effect of temperature on ion-pair formation constants for reaction: $M^{2+} + HCO_3^- = MHCO_3^+$. The lines are fits to experimental values (*).

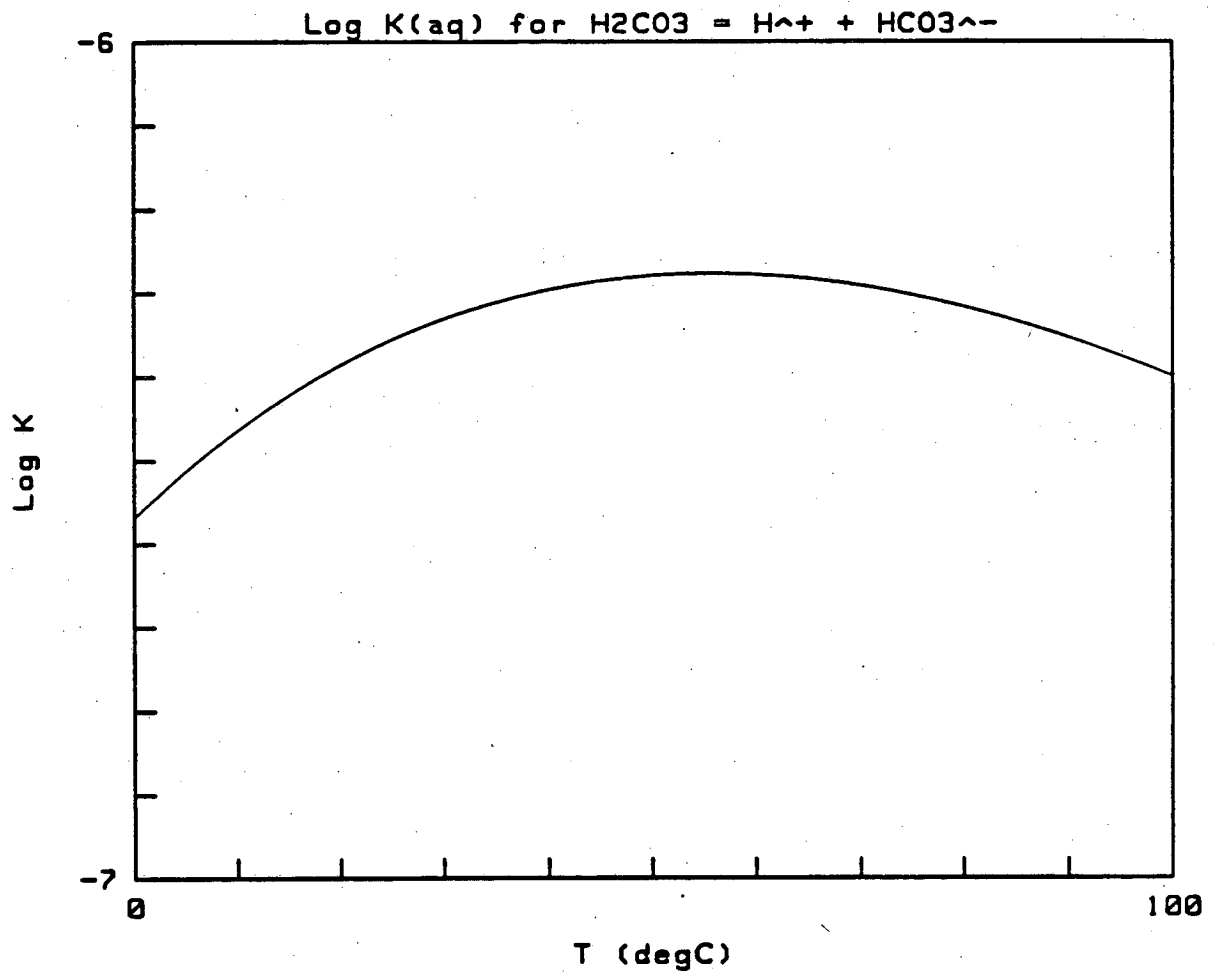


Figure 2. Dissociation constant for $\text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+$ over the range 0 - 100°C.

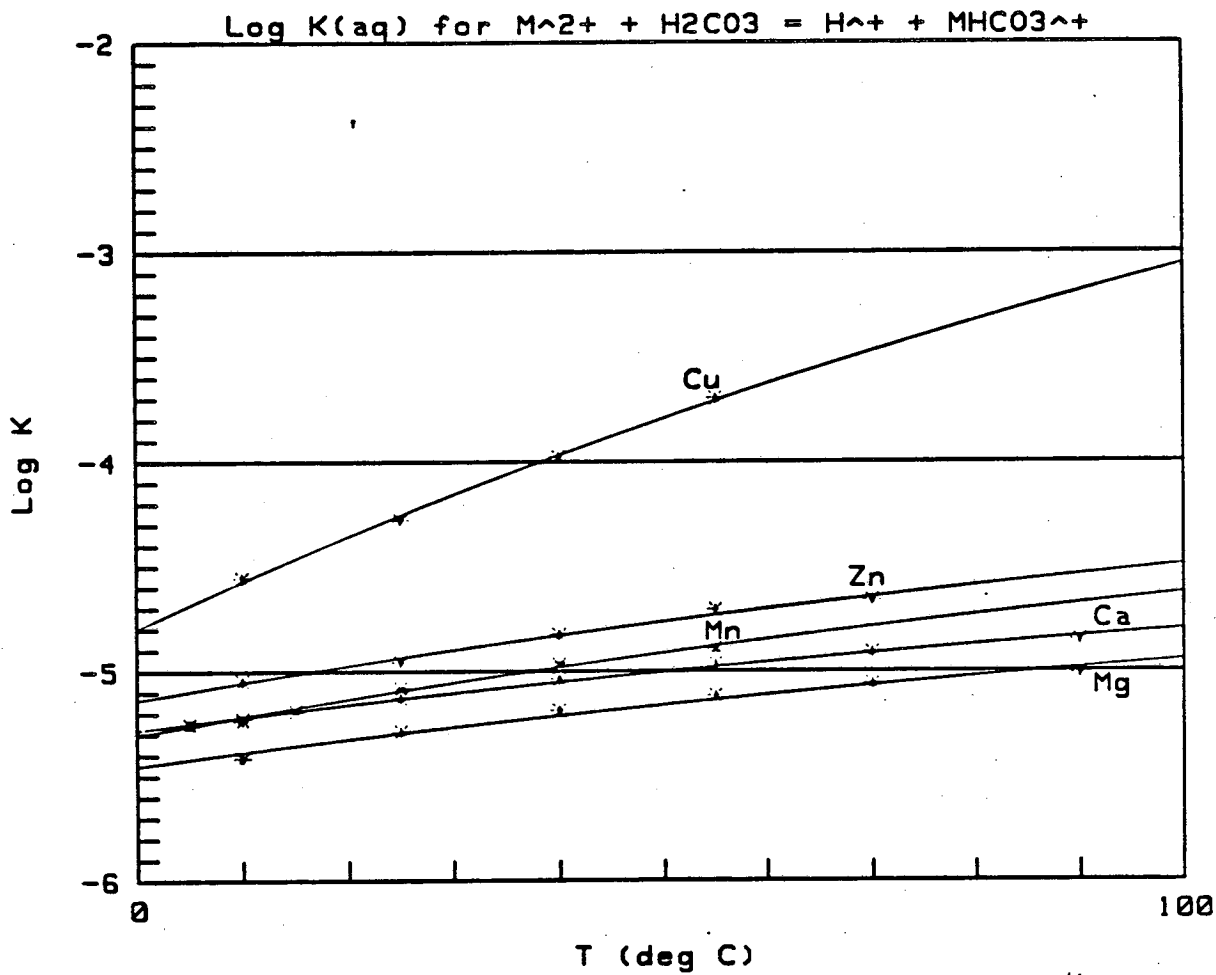


Figure 3. Variation in formation constants for "balanced charge" reactions: $M^{2+} + H_2CO_3 = MHCO_3^+ + H^+$ over temperature range 0 - 100°C.

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