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THERMODYNAMIC PROPERTIES OF THE ION PAIRS $MgCO_3^\circ$ AND $CaCO_3^\circ$ FROM 10 TO 50°C

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ABSTRACT. Potentiometric measurements in $MgCl_2$–K_2CO_3 and $CaCl_2$–K_2CO_3 solutions near 10, 25, 40, and 50°C yield dissociation pK values for the ion pairs $MgCO_3^\circ$ and $CaCO_3^\circ$ of 2.88 ± 0.05 and 3.15 ± 0.08, respectively, at 25°C. Recomputation of $pK(MgCO_3^\circ)$, using data measured by Garrels, Thompson, and Siever (1961), gives values in essential agreement with this study at 25°C but 0.55 pK units less than reported previously. Equations that fit the experimental data as a function of temperature (°K) are $pK(MgCO_3^\circ) = -21.39 + 3265/T + 0.04467T$ and $pK(CaCO_3^\circ) = -27.393 + 4114/T + 0.05617T$. Derived enthalpies of dissociation are −3230 ± 600 cal/mol for $MgCO_3^\circ$ and −4025 ± 800 cal/mol for $CaCO_3^\circ$ at 25°C.

INTRODUCTION AND PREVIOUS WORK

Garrels, Thompson, and Siever (1961) determined the dissociation constant of $MgCO_3^\circ$ from addition of various quantities of $MgCl_2$ solution to dilute solutions of Na_2CO_3 previously titrated with HCl to adjust the pH. The pH change upon addition of the salt was taken to reflect ion pairing of Mg^{2+} with CO_3^{2-}, disrupting the carbonate equilibria and causing HCO_3^- dissociation to H^+ and CO_3^{2-}. In this study similar procedures were used, except that Na_2CO_3 solutions were replaced by K_2CO_3 solutions, since interference due to the KCO_3^- ion pair is less significant than that caused by the $NaCO_3^-$ ion pair.

Nakayama (1971) reviewed the pK's for carbonate ion pairs in the MgO–CO_2–H_2O system and reported $pK(MgCO_3^\circ)$ values from 2.97 to 3.40. In the same paper, he gave pK = 3.26, determined potentiometrically between pH 6.00 and 8.60. The error interval for two standard deviations, although not reported by the author, was ± 0.16 pK units. There is, however, a serious inconsistency between his computed ionic strength and the charge balance equation. Either mCl^- formed by the addition of $MgCl_2$ to the test solutions was not considered in the ionic strength computations, or there is an error in his charge balance calculations. This inconsistency which amounts to as much as 25 percent of the computed ionic strength casts doubt on his reported pK.

Jacobson and Langmuir (1974) extensively reviewed published values of $pK(CaCO_3^\circ)$. They felt that $pK(CaCO_3^\circ)$ was still uncertain despite Lafon's (1970) paper but showed that its value must equal or be less than 3.20 to be consistent with calcite solubility measurements.

EXPERIMENTAL PROCEDURE

Solutions were prepared using distilled, deionized water and reagent grade K_2CO_3 which had been oven-dried for four hours. Initial solutions were analyzed for total molal base ($mHCO_3^- + 2mCO_3^{2-} + mOH^-$) titrimetrically with a solution of primary standard $KH(IO_3)_2$ and for

Ca^{2+} and/or Mg^{2+} by titration with Na-EDTA to ensure stoichiometry of the salts. Thereafter, solutions were prepared with weighed portions of the dried salts. Distilled, deionized water with a specific conductance < 1.0 micromhos was used throughout the experiments. Initially, CO_2-free water was prepared by boiling this water and bubbling it with N_2 gas. Solutions were thermostated within $\pm$ 0.1°C at different temperatures. The pH measurements were made on a Corning Model 12 Research Meter with combination pH-reference electrodes. Their reproducibility was $\pm$ 0.01 units based on double buffer checks. Activity coefficients for Mg^{2+}, Ca^{2+}, and OH^- were determined from curves obtained by merging values calculated using the Debye-Hückel equation at ionic strengths (I's) < 0.05 and the mean salt method based on $\gamma K^+ = \gamma Cl^- = \gamma_{\pm} KCl$ at I's > 0.3 using mean activity coefficients of $MgCl_2$, $CaCl_2$, and KOH respectively. The γHCO_3^- and γCO_3^{2-} values were from Walker, Bray, and Johnston (1927). Activity coefficients for neutrally-charged species were assumed equal to $\gamma H_2CO_3°$ calculated from the Setchenow expression, $\gamma H_2CO_3 = 10^{0.06I}$, as modified by Harned and Owen (1958). The first (K_1) and second (K_2) dissociation constants for carbonic acid were from Harned and Davis (1943) and Harned and Scholes (1941), respectively.

The experimental procedure was identical to that outlined by Garrels, Thompson, and Siever (1961). An aliquot of concentrated HCl was added to a solution of K_2CO_3 to bring the pH to around 10.0, so that $mCO_3^{2-}/mHCO_3^-$ would be near unity. To this solution, various quantities of solid $MgCl_2 \cdot 6H_2O$ or $CaCl_2 \cdot 2H_2O$ were added, and the pH change recorded.

THEORY

Procedures used to determine the amounts of $MgCO_3°$ or $CaCO_3°$ were identical. Therefore only the arguments pertaining to $MgCO_3°$ are presented here. To establish the $MgCO_3°$ present after addition of $MgCl_2$ it is necessary to know:

pH_1—Solution pH before salt addition
pH_2—Solution pH after salt addition
Mg_T—Molality of total magnesium added
C_T—Total carbonate defined at these pH's as $mHCO_3^- + mCO_3^{2-} + MgCO_3° + MgHCO_3^+$, since the $mH_2CO_3°$ formed or lost during a run is negligible (less than 1 percent of C_T for all runs).

The amount of $MgCO_3°$ is then determined by solving the following 8 linearly independent equations by the Newton-Raphson method (Grove, 1966) and reiterating to a constant ionic strength. Brackets denote activities of the enclosed species, and K_w the ionization constant of H_2O.

$$mCO_3^{2-} = [HCO_3^-]K_2/(10^{-pH_2} \cdot \gamma CO_3^{2-}) \quad (1)$$

$$mMgOH^+ = [Mg^{2+}]mOH^-/K(MgOH^+) \quad (2)$$

$$mOH^- = [H_2O]K_w/(\gamma OH^- \cdot 10^{-pH_2}) \quad (3)$$

$$mHCO_3^- = C_T - (mCO_3^{2-} + mMgCO_3° + mMgHCO_3^+) \quad (4)$$

$$mMgCO_3° = Mg_T - (mMgOH^+ + mMg^{2+} + mMgHCO_3^+) \quad (5)$$

$$mMg^{2+} = 0.5(mOH^- + 2mCO_3^{2-} + mCl^- + mHCO_3^- - mK^+ - mMgOH^+ - mMgHCO_3^+) \quad (6)$$

$$mMgHCO_3^+ = [Mg^{2+}]mHCO_3^-/K(MgHCO_3^+) \quad (7)$$

$$K(MgCO_3°) = [Mg^{2+}][CO_3^{2-}]/[MgCO_3°] \quad (8)$$

To solve these relations, it was assumed that $\gamma MgOH^+ = \gamma OH^-$ and $\gamma MgHCO_3^+ = \gamma HCO_3^-$. Values for $K(MgOH^+)$ as a function of temperature were from McGee and Hostetler (1973); $K(CaOH^+)$ from Nancollas (1966), and $K(CaHCO_3^+)$ and $K(MgHCO_3^+)$ from Reardon, Jacobson, and Langmuir (1973). C_T in equation 4 can be determined from: (1) the total K_2CO_3 added, or (2) the pH of the solution before addition of the alkali earth salt (pH_1). Relevant equations for this second method are:

$$mCO_3^{2-} = [HCO_3^-]K_2/(10^{-pH_1} \cdot \gamma CO_3^{2-}) \quad (9)$$

$$mOH^- = [H_2O]K_w/(\gamma OH^- \cdot 10^{-pH_1}) \quad (10)$$

$$mHCO_3^- = mK^+ - (mCl^- + mOH^- + 2mCO_3^{2-}) \quad (11)$$

$$C_T = mHCO_3^- + mCO_3^{2-} \quad (12)$$

These equations are solved simultaneously and recycled to a constant ionic strength.

For this paper, C_T was obtained by the second method due to the possibility of CO_2 leakage from the atmosphere into the K_2CO_3 solution during its preparation, and because CO_2-free water was not always used in the experiments. C_T was initially calculated by both methods, however, to check experimental control. The percentage difference between the two methods is listed as %diff in table 1. C_T calculated by both methods should agree, if leakage of CO_2 into or out of the system is avoided. Precautions were taken in early runs to prevent such leakage, and agreement of the two methods was usually within ± 2 percent of the total carbonate present. In later runs, once experimental control was demonstrated, CO_2-free water was not used, resulting in a higher percentage difference between C_T added and calculated.

The pH was monitored in blank K_2CO_3–HCl solutions to determine the extent of CO_2 leakage into the solutions during an experimental run. The rate of pH change of uncorked K_2CO_3 solutions was greater, the lower the concentration of K_2CO_3 and the higher the pH, but no significant change was recorded for up to 20 min. Since run times were less than 15 min, this effect was considered negligible.

RESULTS

A large number of experimental runs were made to determine $pK(MgCO_3^\circ)$ and $pK(CaCO_3^\circ)$ at different pH's and ionic strengths by varying molalities of the initial K_2CO_3 solution, amounts of HCl titrant, and alkali earth salt added. This gave the maximum statistical scatter of the measurements and assuming only random errors should represent the maximum uncertainty. The experimental data are recorded in table 1. Tabulated pK's and molalities of significant species have been corrected for the ion pairs $MgOH^+$ or $CaOH^+$, $MgHCO_3^+$ or $CaHCO_3^+$, and for water additions from the $MgCl_2 \cdot 6H_2O$ or $CaCl_2 \cdot 2H_2O$.

The recomputed results of Garrels, Thompson, and Siever (1961) for $pK(MgCO_3^\circ)$ differ significantly from their reported pK of 3.40. They made no corrections for $MgHCO_3^+$ or $MgOH^+$ ion pairs and did not iterate to a constant ionic strength, but the discrepancy chiefly results from their assumption that $mCO_3^{2-} = mHCO_3^-$ at pH = 9.8 before addition of $MgCl_2$ solution. In fact $mCO_3^{2-} = 0.53\ mHCO_3^-$ at this pH.

DISCUSSION OF RESULTS

The $MgCO_3^\circ$ ion pair—Figure 1 is a plot of the experimental results as a function of pH along with recomputed values from Garrels, Thompson, and Siever (1961). There is considerable scatter in the data and significant trends at lower pH's. These trends are lessened, if one ignores the presence of $MgHCO_3^+$ ion pairs, but their existence in $Mg(HCO_3)_2$ solutions is firmly established (Greenwald, 1941; Hostetler, 1963; Nakayama, 1971; Reardon, Jacobson, and Langmuir, 1973). The upward trend of the data would be further accentuated, if a correction could be made for loss of $CO_2(g)$ at the lower pH's.

A plot of $pK(MgCO_3^\circ)$ versus I is given in figure 2. Although the scatter between runs is significant, within each run the same upward trend is evident for $I > 0.05$.

All data points derived from solutions in which $I < 0.05$ are shown in figure 3. There is little or no trend in the pK values with pH suggesting that the trend in figure 2 is related to ionic strength. The rising $pK(MgCO_3^\circ)$ trend at higher ionic strengths is too great to reflect liquid junction effects on the pH measurement which we have found less than 0.04 pH units. The trend may, however, result from erroneous values of $\gamma MgCO_3^\circ$ computed using the salting-out coefficient expression for neutral molecules, $\gamma MgCO_3^\circ = 10^{0.06I}$. A coefficient of 0.06 was obtained from Harned and Owen (1958) for $H_2CO_3^\circ$ in solutions of 1:1 salts. There is real basis for questioning the assumption that $\gamma MgCO_3^\circ = \gamma H_2CO_3^\circ$. $\gamma H_2CO_3^\circ$ as determined by the Setchenow expression is actually the net activity coefficient effect for $\gamma H_2CO_3^\circ$ and $\gamma CO_2(aq)$ arising from the fact that ΔG_r° for the reaction $CO_2(aq) + H_2O = H_2CO_3^\circ$ is taken by convention to be zero. It is entirely possible, considering the nature of the $MgCO_3^\circ$ ion pair (presumably Mg^{2+} and CO_3^{2-} ions separated by a sheath of water molecules), that its chemical potential in solution is reduced due to ionic interactions. The centers of charge

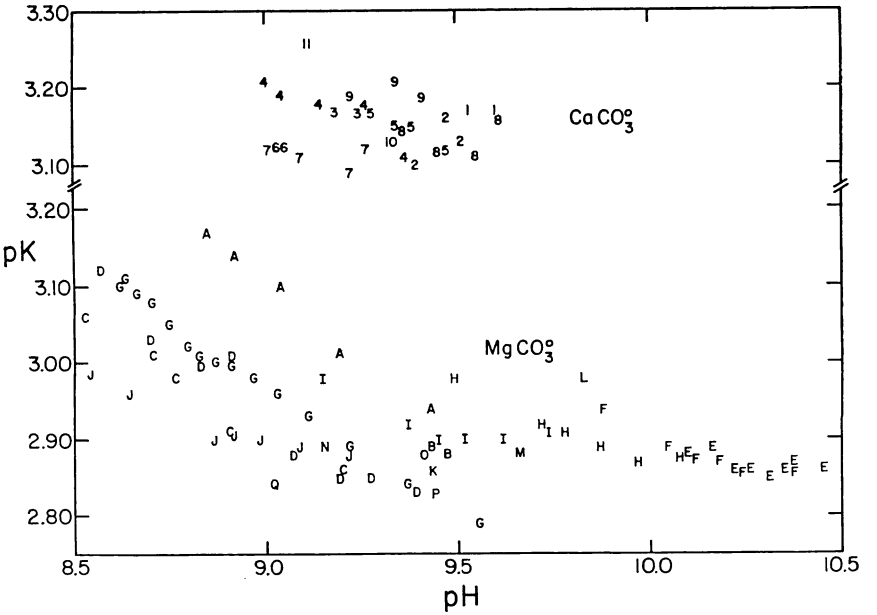

Fig. 1. Variation of $pK(MgCO_3^\circ)$ and $pK(CaCO_3^\circ)$ with solution pH after salt addition. Letters denote $pK(MgCO_3^\circ)$ values, and numbers $pK(CaCO_3^\circ)$ values in table 1.

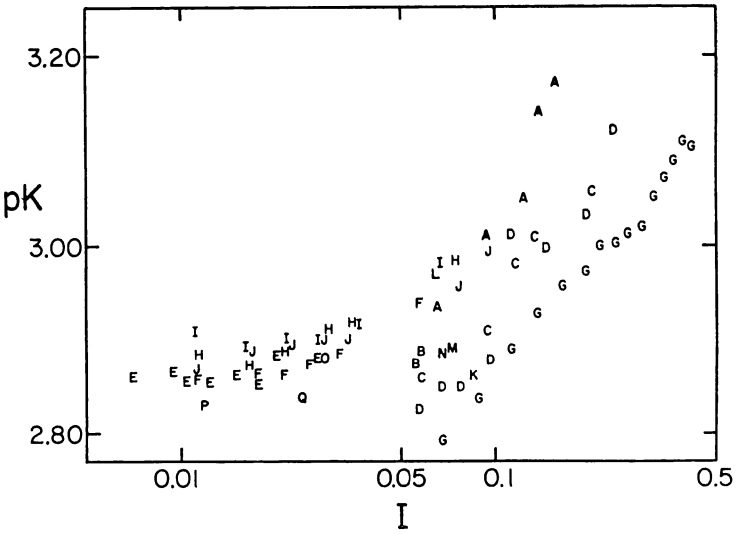

Fig. 2. Variation of $pK(MgCO_3^\circ)$ with I. Letters refer to values in table 1.

TABLE 1

A. Results of experimental runs for the determination of pK($MgCO_3°$). Columns headed –log mHCl and –log mK_2CO_3 give the moles of HCl and mK_2CO_3 added per liter of final solution. % diff = $[(C_T–K_2CO_3)/C_T] \times 100$, pH_1 is the pH before addition of $MgCl_2$ to the solution, pH_2 and molal values in succeeding columns are the solution composition after addition of $MgCl_2$ to initial K_2CO_3–HCl solutions.

Run	T°C	–log mHCl	–log mK_2CO_3	–log Mg_T	% diff	pH_1	pH_2	I	–log mMg^{2+}	–log $mMgCO_3°$	–log mCO_3^{2-}	–log $mHCO_3^-$	pK
A	25.0	1.86	1.69	1.95	1.47	9.80	9.44	0.065	2.15	2.42	2.51	1.89	2.94
A	25.0	1.86	1.69	1.66	1.47	9.80	9.19	0.093	1.79	2.30	2.74	1.90	3.01
A	25.0	1.86	1.69	1.48	1.47	9.80	9.04	0.123	1.58	2.26	2.88	1.91	3.05
A	25.0	1.86	1.69	1.41	1.47	9.80	8.92	0.137	1.50	2.24	2.99	1.92	3.14
A	25.0	1.86	1.69	1.36	1.47	9.80	8.85	0.153	1.43	2.23	3.05	1.92	3.17
B	25.0	1.83	1.69	2.23	0.17	9.68	9.47	0.056	2.45	2.67	2.44	1.84	2.88
B	25.0	1.83	1.69	2.15	0.17	9.68	9.43	0.058	2.35	2.61	2.48	1.84	2.89
C	25.0	1.82	1.70	2.12	3.02	9.48	9.20	0.059	2.26	2.74	2.67	1.79	2.86
C	25.0	1.82	1.70	1.66	3.02	9.48	8.91	0.096	1.74	2.55	2.93	1.81	2.91
C	25.0	1.82	1.70	1.53	3.02	9.48	8.77	0.117	1.60	2.51	3.05	1.82	2.98
C	25.0	1.82	1.70	1.46	3.02	9.48	8.71	0.133	1.52	2.50	3.11	1.82	3.01
C	25.0	1.82	1.71	1.23	3.02	9.48	8.53	0.201	1.28	2.47	3.26	1.84	3.06
D	25.0	1.88	1.70	2.18	7.27	9.62	9.39	0.056	2.36	2.69	2.49	1.80	2.83
D	25.0	1.88	1.70	1.81	7.27	9.62	9.19	0.077	1.94	2.50	2.67	1.81	2.85
D	25.0	1.88	1.70	1.55	7.27	9.62	8.91	0.110	1.64	2.38	2.93	1.83	3.01
D	25.0	1.89	1.71	1.15	7.27	9.62	8.57	0.235	1.19	2.33	3.22	1.86	3.12
D	25.0	1.88	1.70	1.95	7.27	9.62	9.27	0.066	2.10	2.55	2.60	1.81	2.85
D	25.0	1.88	1.70	1.65	7.27	9.62	9.07	0.096	1.75	2.44	2.78	1.82	2.88
D	25.0	1.89	1.70	1.40	7.27	9.62	8.83	0.143	1.47	2.37	3.00	1.84	3.00
D	25.0	1.89	1.70	1.24	7.27	9.62	8.70	0.194	1.30	2.35	3.10	1.85	3.03
E	25.0	3.56	2.69	3.09	1.96	10.52	10.45	0.007	3.26	3.63	2.94	3.17	2.86
E	25.0	3.56	2.69	2.71	1.96	10.52	10.37	0.009	2.84	3.33	3.02	3.19	2.87
E	25.0	3.56	2.69	2.63	1.96	10.52	10.35	0.010	2.75	3.29	3.04	3.19	2.86
E	25.0	3.56	2.69	2.51	1.96	10.52	10.31	0.012	2.62	3.22	3.08	3.20	2.85
E	25.0	3.56	2.69	2.38	1.96	10.52	10.25	0.015	2.48	3.15	3.13	3.21	2.86
E	25.0	3.56	2.69	2.31	1.96	10.52	10.22	0.017	2.39	3.12	3.16	3.21	2.86
E	25.0	3.56	2.69	2.20	1.96	10.52	10.16	0.021	2.28	3.07	3.22	3.23	2.89
E	25.0	3.56	2.69	2.08	1.96	10.52	10.10	0.027	2.14	3.03	3.27	3.24	2.88

F	25.0	3.26	2.56	2.69	0.63	10.51	10.37	0.011	2.85	3.23	2.88	3.05	2.86
F	25.0	3.26	2.56	2.34	0.63	10.51	10.24	0.017	2.46	3.02	3.00	3.07	2.86
F	25.0	3.26	2.56	2.22	0.63	10.51	10.18	0.021	2.32	2.97	3.06	3.08	2.87
F	25.0	3.26	2.56	2.10	0.63	10.51	10.11	0.026	2.18	2.92	3.12	3.09	2.88
F	25.0	3.26	2.56	2.00	0.63	10.51	10.05	0.032	2.07	2.88	3.17	3.10	2.89
F	25.0	3.26	2.56	1.74	0.63	10.51	9.88	0.056	1.78	2.82	3.32	3.12	2.94
H	25.0	3.02	2.56	2.68	3.91	10.26	10.08	0.011	2.82	3.28	2.99	2.88	2.88
H	25.0	3.02	2.56	2.40	3.91	10.26	9.97	0.016	2.49	3.12	3.09	2.89	2.87
H	25.0	3.02	2.56	2.21	3.91	10.26	9.87	0.022	2.29	3.04	3.18	2.90	2.89
H	25.0	3.02	2.56	2.06	3.91	10.26	9.78	0.029	2.12	2.98	3.26	2.90	2.91
H	25.0	3.02	2.56	1.96	3.91	10.26	9.72	0.035	2.01	2.96	3.31	2.91	2.92
H	25.0	3.02	2.56	1.63	3.91	10.26	9.49	0.072	1.66	2.89	3.50	2.93	2.98
I	25.0	2.83	2.56	2.70	5.66	9.95	9.74	0.011	2.80	3.43	3.18	2.73	2.91
I	25.0	2.83	2.56	2.41	5.66	9.95	9.62	0.016	2.47	3.28	3.29	2.74	2.90
I	25.0	2.83	2.56	2.23	5.66	9.95	9.52	0.022	2.28	3.21	3.37	2.74	2.90
I	25.0	2.83	2.56	2.09	5.66	9.95	9.45	0.028	2.13	3.17	3.43	2.75	2.90
I	25.0	2.83	2.56	1.97	5.66	9.95	9.37	0.036	2.00	3.14	3.50	2.75	2.92
I	25.0	2.83	2.56	1.66	5.66	9.95	9.15	0.069	1.68	3.08	3.67	2.77	2.98
J	25.0	2.71	2.57	2.70	11.05	9.44	9.22	0.011	2.74	3.80	3.57	2.59	2.87
J	25.0	2.71	2.57	2.41	11.05	9.44	9.09	0.016	2.44	3.65	3.67	2.59	2.89
J	25.0	2.71	2.57	2.23	11.05	9.44	8.99	0.022	2.26	3.59	3.75	2.60	2.90
J	25.0	2.71	2.57	2.10	11.05	9.44	8.92	0.028	2.12	3.55	3.82	2.60	2.91
J	25.0	2.71	2.57	2.01	11.05	9.44	8.87	0.034	2.02	3.53	3.86	2.60	2.90
J	25.0	2.71	2.57	1.67	11.05	9.44	8.65	0.068	1.69	3.46	4.03	2.62	2.96
J	25.0	2.71	2.57	1.52	11.05	9.44	8.54	0.095	1.52	3.44	4.12	2.63	2.99
K	9.9	2.06	1.80	1.66	1.73	9.96	9.67	0.087	1.76	2.39	2.58	2.05	2.72
K	25.3	2.06	1.80	1.66	1.73	9.96	9.43	0.085	1.77	2.34	2.66	2.05	2.86
K	41.2	2.06	1.80	1.66	1.73	9.96	9.22	0.083	1.79	2.31	2.77	2.06	3.01
K	51.3	2.06	1.80	1.66	1.73	9.96	9.09	0.081	1.80	2.29	2.85	2.06	3.12
L	9.7	2.06	1.70	1.91	0.54	10.17	10.02	0.065	2.20	2.23	2.27	2.05	2.93
L	25.0	2.06	1.70	1.91	0.54	10.17	9.83	0.064	2.21	2.22	2.29	2.05	2.97
L	42.0	2.06	1.70	1.91	0.54	10.17	9.65	0.062	2.26	2.19	2.35	2.05	3.11
L	52.0	2.06	1.70	1.91	0.54	10.17	9.54	0.059	2.31	2.15	2.41	2.04	3.24
M	10.3	1.96	1.68	1.87	1.47	10.01	9.85	0.072	2.08	2.31	2.31	1.95	2.81
M	25.3	1.96	1.68	1.87	1.47	10.01	9.66	0.071	2.10	2.28	2.35	1.95	2.88
M	41.2	1.96	1.68	1.87	1.47	10.01	9.47	0.068	2.15	2.23	2.42	1.95	3.04
M	51.3	1.96	1.68	1.87	1.47	10.01	9.35	0.065	2.19	2.20	2.49	1.95	3.18

TABLE 1A (continued)

Run	T°C	−log mHCl	−log mK_2CO_3	−log Mg_T	% diff	pH_1	pH_2	I	−log mMg^{2+}	−log $mMgCO_3^\circ$	−log mCO_3^{2-}	−log $mHCO_3^-$	pK
N	9.7	1.82	1.70	1.92	1.61	9.55	9.36	0.071	2.03	2.62	2.68	1.81	2.80
N	25.0	1.82	1.70	1.92	1.61	9.55	9.15	0.070	2.04	2.59	2.72	1.81	2.89
N	42.0	1.82	1.70	1.92	1.61	9.55	8.96	0.068	2.07	2.55	2.80	1.82	3.03
N	52.0	1.82	1.70	1.92	1.61	9.55	8.83	0.067	2.09	2.51	2.89	1.82	3.17
O	25.0	2.80	2.55	2.08	6.30	9.90	9.41	0.029	2.12	3.19	3.44	2.72	2.88
P	25.0	2.86	2.62	2.36	11.51	9.78	9.44	0.017	2.41	3.44	3.44	2.71	2.83
P	39.0	2.86	2.62	2.36	11.51	9.78	9.25	0.017	2.41	3.41	3.52	2.71	2.97
Q	9.5	2.82	2.66	2.17	12.90	9.67	9.27	0.024	2.18	3.69	3.74	2.69	2.72
Q	16.0	2.82	2.66	2.17	12.90	9.67	9.17	0.024	2.19	3.67	3.76	2.69	2.75
Q	25.0	2.82	2.66	2.17	12.90	9.67	9.02	0.024	2.19	3.65	3.81	2.69	2.84
Q	35.0	2.82	2.66	2.17	12.90	9.67	8.87	0.024	2.19	3.62	3.89	2.69	2.93
Q	40.0	2.82	2.66	2.17	12.90	9.67	8.79	0.024	2.19	3.61	3.94	2.69	3.00

B. Recomputation of $pK(MgCO_3^\circ)$ at 25°C from the experimental data of Garrels, Thompson, and Siever (1961). Columns headed −log mHCl and −log mNa_2CO_3 give the moles of HCl and Na_2CO_3 added per liter of final solution. For all runs labelled G in the figures, % diff = 11.35 and $pH_1 = 9.80$ before addition of $MgCl_2$ to the solution. pH_2 and molal values in succeeding columns are the solution composition after addition of $MgCl_2$ to initial Na_2CO_3–HCl solutions.

−log mHCl	−log mNa_2CO_3	−log Mg_T	pH_2	I	−log mMg^{2+}	−log $mMgCO_3^\circ$	−log mCO_3^{2-}	−log $mHCO_3^-$	pK
1.94	1.64	2.01	9.56	0.068	2.24	2.45	2.29	1.79	2.79
1.95	1.65	1.71	9.37	0.089	1.88	2.28	2.46	1.80	2.84
1.95	1.65	1.54	9.22	0.113	1.67	2.21	2.60	1.81	2.89
1.95	1.65	1.42	9.11	0.139	1.52	2.18	2.70	1.82	2.93
1.95	1.65	1.33	9.03	0.164	1.41	2.16	2.77	1.83	2.96
1.95	1.65	1.25	8.97	0.190	1.32	2.15	2.82	1.84	2.97
1.96	1.65	1.18	8.91	0.217	1.25	2.14	2.88	1.85	3.00
1.96	1.66	1.13	8.87	0.243	1.19	2.14	2.91	1.86	3.00
1.96	1.66	1.08	8.83	0.269	1.13	2.14	2.95	1.87	3.01
1.96	1.66	1.04	8.80	0.294	1.09	2.13	2.98	1.88	3.02
1.96	1.66	1.00	8.75	0.319	1.04	2.13	3.03	1.88	3.05
1.97	1.66	0.96	8.71	0.345	1.00	2.13	3.06	1.89	3.07
1.97	1.67	0.93	8.67	0.370	0.97	2.12	3.12	1.90	3.09
1.97	1.67	0.90	8.64	0.396	0.93	2.12	3.14	1.91	3.11
1.97	1.67	0.87	8.63	0.420	0.91	2.12	3.15	1.91	3.10

C. Results of experimental runs for the determination of $pK(CaCO_3^\circ)$. Columns headed $-\log mHCl$ and $-\log mK_2CO_3$ give the moles of HCl and mK_2CO_3 added per liter of final solution. % diff $= [(C_T - mK_2CO_3)/C_T] \times 100$, pH_1 is the solution pH before addition of $MgCl_2$, pH_2 and molal values in succeeding columns are the solution composition after addition of $MgCl_2$ to initial K_2CO_3–HCl solutions.

Run	T°C	$-\log mHCl$	$-\log mK_2CO_3$	$-\log Mg_T$	% diff	pH_1	pH_2	I	$-\log mMg^{2+}$	$-\log mMgCO_3^\circ$	$-\log mCO_3^{2-}$	$-\log mHCO_3^-$	pK
1	25.0	2.83	2.62	3.52	12.25	9.67	9.60	0.006	3.67	4.07	3.30	2.67	3.17
1	25.0	2.83	2.62	3.18	12.25	9.67	9.53	0.007	3.31	3.79	3.36	2.68	3.17
2	25.0	2.81	2.62	3.59	13.29	9.57	9.51	0.006	3.71	4.21	3.36	2.65	3.13
2	25.0	2.81	2.62	3.35	13.29	9.57	9.47	0.006	3.46	3.99	3.40	2.65	3.16
2	25.0	2.81	2.62	2.99	13.29	9.57	9.39	0.008	3.07	3.76	3.48	2.65	3.10
2	39.0	2.81	2.62	2.99	13.29	9.57	9.18	0.007	3.10	3.66	3.58	2.65	3.33
3	25.0	2.54	2.40	3.26	13.50	9.34	9.24	0.010	3.38	3.92	3.36	2.40	3.17
3	25.0	2.54	2.40	3.04	13.50	9.34	9.18	0.011	3.15	3.75	3.42	2.40	3.17
4	25.0	2.69	2.55	3.67	11.56	9.40	9.36	0.006	3.77	4.38	3.43	2.57	3.11
4	25.0	2.69	2.55	3.19	11.56	9.40	9.26	0.007	3.29	3.94	3.52	2.57	3.18
4	25.0	2.69	2.55	2.86	11.56	9.40	9.14	0.009	2.93	3.72	3.64	2.57	3.18
4	25.0	2.69	2.55	2.67	11.56	9.40	9.04	0.011	2.73	3.63	3.73	2.57	3.19
4	25.0	2.69	2.55	2.61	11.56	9.40	9.00	0.012	2.66	3.60	3.77	2.58	3.21
4	4.2	2.69	2.55	2.61	11.56	9.40	9.36	0.013	2.65	3.69	3.64	2.57	2.97
5	25.0	2.71	2.55	3.69	10.47	9.51	9.47	0.007	3.81	4.31	3.34	2.59	3.12
5	25.0	2.71	2.55	3.16	10.47	9.51	9.38	0.008	3.27	3.86	3.43	2.59	3.15
5	25.0	2.71	2.55	3.05	10.47	9.51	9.34	0.008	3.15	3.77	3.46	2.59	3.15
5	25.0	2.71	2.55	2.89	10.47	9.51	9.27	0.009	2.97	3.66	3.52	2.59	3.17
6	25.0	2.74	2.62	3.18	15.11	9.18	9.04	0.007	3.24	4.19	3.78	2.60	3.12
6	25.0	2.74	2.62	3.15	15.11	9.18	9.03	0.007	3.20	4.16	3.79	2.60	3.12
6	39.0	2.74	2.62	3.18	15.11	9.18	8.87	0.007	3.25	4.12	3.84	2.60	3.27
6	53.0	2.74	2.62	3.15	15.11	9.18	8.73	0.007	3.21	4.12	3.90	2.59	3.30

TABLE 1C (continued)

Run	T°C	−log mHCl	−log mK_2CO_3	−log Mg_T	% diff	pH_1	pH_2	I	−log mMg^{2+}	−log $mMgCO_3°$	−log mCO_3^{2-}	−log $mHCO_3^-$	pK
7	25.0	2.76	2.62	3.65	14.91	9.32	9.26	0.006	3.73	4.46	3.57	2.61	3.12
7	25.0	2.76	2.62	3.33	14.91	9.32	9.22	0.006	3.40	4.21	3.62	2.61	3.09
7	25.0	2.76	2.62	2.90	14.91	9.32	9.09	0.008	2.96	3.91	3.73	2.61	3.11
7	25.0	2.76	2.62	2.73	14.91	9.32	9.01	0.010	2.78	3.81	3.80	2.61	3.12
7	39.0	2.76	2.62	2.73	14.91	9.32	8.77	0.010	2.79	3.73	3.94	2.61	3.36
7	53.0	2.76	2.62	2.73	14.91	9.32	8.56	0.010	2.80	3.69	4.07	2.61	3.54
8	25.0	2.83	2.62	3.69	12.95	9.65	9.61	0.006	3.84	4.24	3.29	2.67	3.16
8	25.0	2.83	2.62	3.26	12.95	9.65	9.55	0.007	3.38	3.90	3.34	2.67	3.11
8	25.0	2.83	2.62	2.94	12.95	9.65	9.45	0.008	3.04	3.66	3.43	2.67	3.12
8	25.0	2.83	2.62	2.74	12.95	9.65	9.35	0.010	2.82	3.54	3.52	2.67	3.15
9	25.0	2.79	2.62	3.35	13.64	9.51	9.41	0.006	3.47	4.02	3.45	2.64	3.19
9	25.0	2.79	2.62	3.11	13.64	9.51	9.34	0.007	3.21	3.82	3.52	2.64	3.21
9	25.0	2.79	2.62	2.81	13.64	9.51	9.22	0.009	2.88	3.65	3.63	2.64	3.19
9	39.0	2.79	2.62	2.81	13.64	9.51	9.00	0.009	2.90	3.58	3.74	2.64	3.40
10	9.5	2.82	2.66	3.21	13.02	9.66	9.55	0.006	3.28	4.06	3.53	2.68	3.02
10	25.0	2.82	2.66	3.21	13.02	9.66	9.34	0.006	3.29	4.00	3.56	2.68	3.13
10	35.0	2.82	2.66	3.21	13.02	9.66	9.21	0.006	3.31	3.95	3.61	2.67	3.24
11	9.5	2.78	2.66	3.24	12.11	9.47	9.34	0.006	3.29	4.21	3.71	2.66	3.06
11	16.0	2.78	2.66	3.24	12.11	9.47	9.25	0.006	3.30	4.17	3.73	2.66	3.14
11	25.0	2.78	2.66	3.24	12.11	9.47	9.11	0.006	3.31	4.10	3.77	2.66	3.26
11	35.0	2.78	2.66	3.24	12.11	9.47	8.99	0.006	3.32	4.07	3.80	2.66	3.33
11	40.0	2.78	2.66	3.24	12.11	9.47	8.92	0.006	3.33	4.02	3.85	2.65	3.44

TABLE 2

Thermodynamic properties for the dissociation of $MgCO_3°$ and $CaCO_3°$ at 25°C.

Reaction	$\Delta G_r°$ (cal/mol)	$\Delta H_r°$ (cal/mol)	$\Delta S_r°$ (cal/mol deg)	S° ion pair
$MgCO_3° = Mg^{2+} + CO_3^{2-}$	3930 ± 70	−3230 ± 600	−24.0 ± 2.3	−21.8 ± 2.3
$CaCO_3° = Ca^{2+} + CO_3^{2-}$	4304 ± 110	−4025 ± 800	−27.9 ± 2.7	1.7 ± 2.9

of the two ions are far enough removed so that the ion pair does not behave as a "neutral" species. Component ions of the pair may strongly interact with H_2O molecules and other ions to reduce the activity coefficient of this species to about that of a monovalent ion. As shown by Reardon and Langmuir (1974) such a decreasing value for $\gamma MgCO_3°$ with I eliminates the $pK(MgCO_3°)$ trend. Possible errors in γMg^{2+} and γCO_3^{2-} are insufficient to level $pK(MgCO_3°)$ for $I > 0.05$.

Several determinations of $pK(MgCO_3°)$ were made at different temperatures with results tabulated in table 1. Although a plot of these pK data versus temperature shows scatter between the runs, slopes of the pK versus T curves for each run are quite similar. In order to obtain mean pK values at four temperatures (10, 25, 41, 51.5°C), the values for several runs near these temperatures were extrapolated, usually less than a degree. The resultant mean pK's are plotted in figure 4.

From figure 4, one can derive pertinent thermodynamic information for the reaction:

$$MgCO_3° = Mg^{2+} + CO_3^{2-}$$

Fitting the data to an equation of the general form $pK = a + b/T + cT$, where a, b, and c are constants, and T is in (°K), we obtain:

$$pK(MgCO_3°) = -21.39 + 3265/T + 0.04467T \qquad (13)$$

From the Van't Hoff equation, this leads to:

$$\Delta H_r° = 14{,}940 - 0.2044T^2 \qquad (14)$$

where $\Delta H_r°$ is the enthalpy of dissociation. Thus, at 25°C, $\Delta H_r° = -3230 \pm 600$ cal/mol. The free energy for the reaction given by the expression:

$$\Delta G_r° = -RT \ln K \qquad (15)$$

where R is the gas constant, yields $\Delta G_r° = 3930 \pm 70$ cal/mol at 25°C.

With thermochemical data for species in the MgO–CO_2–H_2O system from Langmuir (1965), we may compute the entropy of $MgCO_3°$ at 25°C using the relation:

$$\Delta G_r° = \Delta H_r° - T\Delta S_r° \qquad (16)$$

which gives $\Delta S_r° = -24.0 \pm 2.3$ cal/mol deg and since:

$$\Delta S_r° = (S°_{Mg^{2+}} + S°_{CO_3^{2-}}) - S°_{MgCO_3°} \qquad (17)$$

then $S°_{MgCO_3°} = -21.8 \pm 2.3$ cal/mol deg. This value is in fair agreement with -26.05 ± 8.0 cal/mol deg calculated by Lafon (ms) from:

$$S° \text{ neutral complex} = (-302/r - 116) - S°_{H_2O} \qquad (18)$$

This is an empirical equation that fits a plot of corrected entropies of neutral complexes versus the reciprocal of the interatomic distance (r) between the constituent ions of the complex.

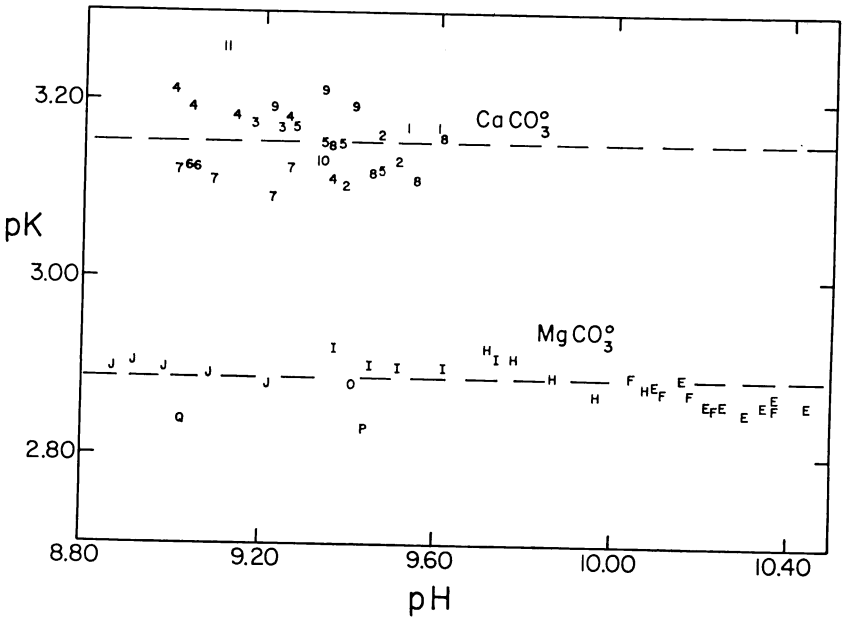

Fig. 3. Variation of pK($MgCO_3°$) (lettered) and pK($CaCO_3°$) (numbered) for runs with $I < 0.05$. Data from table 1. Broken lines represent mean pK values.

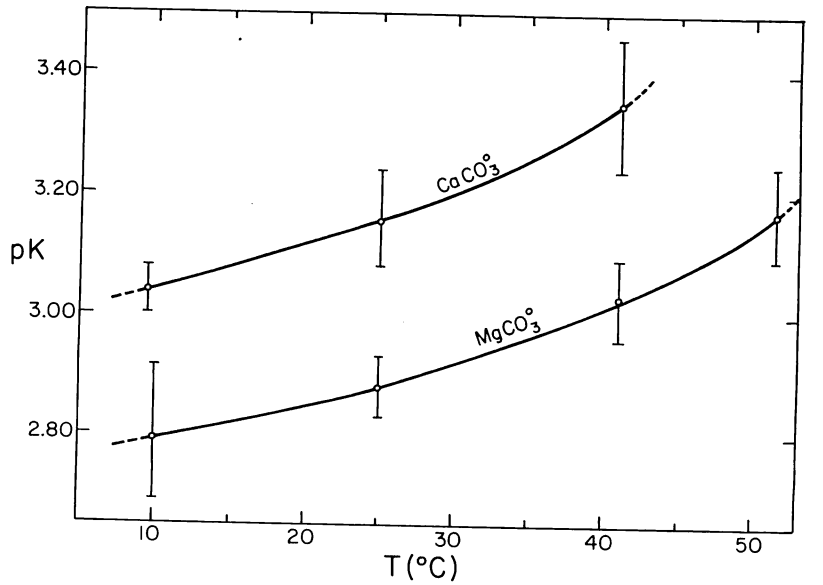

Fig. 4. Temperature variation of pK($MgCO_3°$) and pK($CaCO_3°$). Curves are plotted through mean pK values from table 1. Error bars show two standard deviations of the data.

The $CaCO_3°$ ion pair.—The $pK(CaCO_3°)$ data at 25°C are plotted in figure 3. The average of $pK(CaCO_3°) = 3.15 \pm 0.08$ is in essential agreement with 3.20 reported by Garrels and Thompson (1962). Recorded in table 1 are $pK(CaCO_3°)$ values as a function of temperature. The slopes of curves of pK versus T for individual runs exhibit more variation than those obtained for the $pK(MgCO_3°)$ runs. Many attempts to determine $pK(CaCO_3°)$ as a function of temperature were plagued by $CaCO_3$ precipitation, since it was necessary to work with solutions supersaturated with respect to calcite in order to produce significant $CaCO_3°$ ion pairing. $CaCO_3$ precipitation was evidenced by drift and large drops in the measured pH's and yielded a fine white-translucent material at the bottom of the flasks. Such runs were rejected. Because of $CaCO_3$ precipitation only two runs were completed at 51°C. These were in poor agreement, and so no attempt was made to compute a mean $pK(CaCO_3°)$ at this temperature.

The pK's determined at 9.5, 25, and 41°C were averaged in a manner similar to that described for $pK(MgCO_3°)$. The equation of the curve that fits these mean $pK(CaCO_3°)$ values (see fig. 4) is:

$$pK(CaCO_3°) = -27.393 + 4114/T + 0.05617T \qquad (19)$$

This leads to:

$$\Delta H_r°(\text{cal/mol}) = 18{,}828 - 0.2571T^2 \qquad (20)$$

and $\Delta H_r° = -4025 \pm 800$ cal/mol at 25°C. Based on expression (15), at 25°C, $\Delta G_r° = 4304 \pm 110$ cal/mol. With equation (16) we may compute at 25°C, $\Delta S_r° = -27.9 \pm 2.7$ cal/mol deg, and with the analogue of equation (17), $S° = 1.7 \pm 2.9$ cal/mol for $CaCO_3°$. Again, this value is in fair agreement with -1.78 ± 8.0 calculated by Lafon (ms).

Pertinent thermodynamic information for $MgCO_3°$ and $CaCO_3°$ at 25°C is summarized in table 2.

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