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The solubility of $BaCO_3$(cr) (witherite) in CO_2-H_2O solutions between 0 and 90°C, evaluation of the association constants of $BaHCO_3^+$(aq) and $BaCO_3^0$(aq) between 5 and 80°C, and a preliminary evaluation of the thermodynamic properties of Ba^{2+}(aq)

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Abstract—One hundred and fifty new measurements of the solubility of witherite were used to evaluate the equilibrium constant of the reaction $BaCO_3(cr) = Ba^{2+}(aq) + CO_3^{2-}(aq)$ between 0 and 90°C and 1 atm total pressure. The temperature dependence of the equilibrium constant is given by

$$\log K = 607.642 + 0.121098T - 20011.25/T - 236.4948 \log T$$

where T is in degrees Kelvin. The log K of $BaCO_3$(cr), the Gibbs energy, the enthalpy and entropy of the reaction at 298.15 K are −8.562, 48.87 kJ · mol^{-1}, 2.94 kJ · mol^{-1} and −154.0 J · mol^{-1} · K^{-1}, respectively. The equilibrium constants are consistent with an aqueous model that includes the ion pairs $BaHCO_3^+$(aq) and $BaCO_3^0$(aq) Three different methods were used to evaluate the association constant of $BaHCO_3^+$(aq), and all yielded similar results. The temperature dependence of the association constant for the reaction $Ba^{2+}(aq) + HCO_3^-(aq) = BaHCO_3^+(aq)$ is given by

$$\log K_{BaHCO_3^+} = -3.0938 + 0.013669T.$$

The log of the association constant, the Gibbs energy, the enthalpy and entropy of the reaction at 298.15°K are 0.982, −5.606 kJ · mol^{-1}, 23.26 kJ · mol^{-1} and 96.8 J · mol^{-1} · K^{-1}, respectively. The temperature dependence of the equilibrium constant for the reaction $Ba^{2+}(aq) + CO_3^{2-}(aq) = BaCO_3^0(aq)$ is given by

$$\log K_{BaCO_3^0} = 0.113 + 0.008721T.$$

The log of the association constant, the Gibbs energy, the enthalpy and entropy of the reaction at 298.15°K are 2.71, −15.49 kJ · mol^{-1}, 14.84 kJ · mol^{-1} and 101.7 J · mol^{-1} · K^{-1}.

The above model leads to reliable calculations of the aqueous speciation and solubility of witherite in the system $BaCO_3$-CO_2-H_2O from 0 to more than 90°C. Literature data on witherite solubility were re-evaluated and compared with the results of this study.

Problems in the thermodynamic selections of Ba compounds are considered. Newer data require the revision of $\Delta_f H°$ and $\Delta_f G°$ of Ba^{2+}(aq) to −532.5 and −555.36 kJ · mol^{-1}, respectively, for agreement with solubility data.

INTRODUCTION

ALL NATURAL ALKALINE earth carbonate minerals demonstrate at least limited solid solution behavior. In order to begin to interpret the solubility and equilibrium controls on mineral-water reactions with these solid solutions, detailed knowledge of the end-member solubility products is required. We have already reported such data for calcite, aragonite, and strontianite (PLUMMER and BUSENBERG, 1982; BUSENBERG *et al.*, 1984). In preparing a thermodynamic study of the aragonite-witherite and witherite-strontianite solid solution series, we found that the witherite solubility product was not well known. Furthermore, there are contradictory data on the ion pair formation of Ba^{2+} with HCO_3^- and CO_3^{2-}, necessary to calculate the aqueous speciation of Ba in natural waters.

The solubility of witherite ($BaCO_3$) has been of interest to both geologists and chemists for the past one-hundred and thirty years. The solubility has been determined in pure water by BINEAU (1857), SCHLOESING (1872), HOLLMAN (1893), CANTONI and GOGUELIA (1905), KERNOT *et al.* (1908), WEISENBERGER (1914), HEYROVSKÝ and BEREZICKÝ (1929), and TOWNLEY *et al.* (1937). The solubility in pure water at various CO_2 partial pressures was determined by BINEAU (1857), SCHLOESING (1872), MCCOY and SMITH (1911), HAEHNEL (1924), GARRELS *et al.* (1960), and MALININ (1963). The solubility in various salt solutions was determined by CANTONI and GOGUELIA (1905), KERNOT *et al.* (1908), RAMANN and SALLINGER (1921), TOWNLEY *et al.* (1937), NÄSÄNEN (1946), BENĚS and SELECKÁ (1973), and MILLERO *et al.* (1984). Our recalculated values of the equilibrium constant from these literature data vary over three orders of magnitude, and the temperature dependence of the equilibrium constant is not known.

There has been only one determination at 25°C of the association constant of $BaHCO_3^+$(aq) (NAKAYAMA and RASNICK, 1969) and this value is significantly different from the values of all the other association constants of the alkaline-earth metals. Two determinations of the $BaCO_3^0$(aq) association constant are available at 25°C (BENĚS and SELECKÁ, 1973; PALMER and VAN ELDIK, 1983), but the two values differ by more than one order of magnitude.

The present study attempted to resolve all major problems in the aqueous model for the system $BaCO_3$(cr)-CO_2-H_2O between the temperatures of 0 and 90°C. In addition, a comparison was made of three different methods for the determination of the association constants of metal-bicarbonate complexes. The first method used potentiometric pH measurements, the second used specific conductance measurements, and the third used the determination of solubility as a function of CO_2 partial pressure (0.003 to 1 atm). In the solubility method, the association constant of the $BaHCO_3^+$(aq) was varied until all trends in the equilibrium constant of $BaCO_3$(cr) with P_{CO_2} were eliminated. The results of these calculations are given.

Finally, the thermodynamic properties of Ba^{2+}(aq) are re-examined for internal consistency with our observed witherite equilibrium constant.

EXPERIMENTAL

Analytical methods

Barium concentrations were determined using filtered barium bicarbonate solutions acidified with a few drops of HCl. The solutions were evaporated to dryness in Teflon[1] beakers at 110°C. The solid was redissolved in deionized water, was passed through a strong cation exchange column (Rexyn 101-H) and each Ba exchanged for two hydrogen ions. The released hydrogen ions were titrated with a standard base. This procedure was checked against standard Ca and Ba solutions that were acidified and evaporated to dryness by the above procedure. The standard solutions were prepared from J. T. Baker Chemical Co. 100.00 ± 0.01 percent Ultrex $CaCO_3$ and Aldrich Chemical Co., Inc. 99.999 percent $BaCO_3$. The accuracy of this procedure for the determination of Ba is about 0.2 percent.

The gas phase

Commercial liquified CO_2 and CO_2-N_2 mixtures were used. The CO_2 partial pressure was calculated from room barometric pressure using the equation

$$P_{CO_2} = \frac{(B - V + 0.4h/D)}{760} X_{CO_2} \qquad (1)$$

where B is the barometric pressure in mm Hg, V is the saturation water vapor pressure at the experimental temperature in mm Hg, and X_{CO_2} is the volume fraction of CO_2 in the gas. The term $0.4h/D$ represents the over-pressure of CO_2 and corrects for the depth of the bubbler in the solution (Hills and Ives, 1949). The depth of the bubbler (h) is in mm, and D is the specific gravity of Hg (13.6 $g \cdot cm^{-3}$). Equation 1 was found valid for CO_2 by Plummer and Busenberg (1982). Bubbling rates in all experiments were from about 100 to 200 ml per minute.

General procedures and apparatus

All experiments were performed in jacketed reaction vessels maintained to within 0.05°C of the desired temperature. The potentiometric instruments used in this study were previously described by Plummer and Busenberg (1982) and Busenberg *et al.* (1984). Potentials were measured to the nearest 0.01 mV simultaneously by up to four independently calibrated glass electrodes. The electrodes were calibrated with N.B.S. Standard Reference Material 185e (potassium hydrogen phthalate), 186c (potassium dihydrogen phosphate and disodium hydrogen phosphate) and 187b (Borax). The pH of the buffers at 25°C are 4.004, 6.863 and 9.183, respectively. The uncertainty in pH of these primary standards is estimated by N.B.S. not to exceed ±0.005 pH units below 50°C and ±0.010 pH units above 50°C.

Experimental procedures used to determine $BaHCO_3^+$(aq) and $BaCO_3^0$(aq)

The procedure used for the potentiometric determination of $BaHCO_3^+$(aq) has been previously used to determine the $SrHCO_3^+$(aq) and has been described in detail by Busenberg *et al.* (1984).

In the solubility method, the solubility of $BaCO_3$(cr) was measured in 5 different CO_2-N_2 gas mixtures ranging from 317 ppm to 100 percent CO_2. Using an iterative computer program, the association constant of $BaHCO_3^+$(aq) was varied until all trends in the equilibrium constant of $BaCO_3$(cr) with P_{CO_2} were eliminated. This procedure is described in detail by Plummer and Busenberg (1982).

In the conductivity method, an Orion Research, Inc. (Model 101) conductivity meter was used. The output potential of this instrument was measured with a Fluke Manufacturing Co. model 8000A digital multimeter to the nearest 0.01 mV. The cell constant was determined with a 0.0100 M KCl standard solution. The linearity of the instrument's response was checked using a second standard 0.00500 M KCl solution. The calibration of the instrument was checked before and after all measurements. The temperature of the solutions was maintained at 25.00 ± 0.01°C. The conductivities were corrected to 25.00°C using the temperature coefficient of the solutions by the procedure described by Rand *et al.* (1976). The accuracy of the conductivity measurements is about 0.05 percent.

Procedures previously used to evaluate $CaCO_3^0$(aq) were also used in this study (Plummer and Busenberg, 1982) except that $BaCl_2$ was substituted for $CaCl_2$.

Preparation of $BaCO_3$(cr) and aging of the solid

The $BaCO_3$(cr) was prepared from a 0.1 M solution of $Ba(OH)_2$ and CO_2 gas at 78°C. The reagent grade $Ba(OH)_2$ was further purified by five successive recrystallizations. In this procedure, a saturated $Ba(OH)_2$ solution is prepared at 100°C, this solution is cooled to 2°C and the liquid is discarded. The procedure takes advantage of the 20-fold decrease in the solubility of $Ba(OH)_2$ between 100 and 2°C. The $BaCO_3$(cr) was prepared by gently bubbling 100 percent CO_2 for 24 hours into a 10 liter solution of 0.1 M $Ba(OH)_2$ at 78°C. The solid was aged in this solution at 78°C for thirty days, washed several times with deionized water, dried at 110°C for 48 hours and stored in a glass bottle. The solid consisted of highly uniform, elongated crystals of 3 × 24 μm size. This $BaCO_3$(cr) is significantly coarser than most commercial reagent grade material which consists of smaller crystals of less than about 1 × 1 μm size. Natural witherites often contain significant amounts of $MgCO_3$, $CaCO_3$ and $SrCO_3$ in solid solution. Reagent grade $BaCO_3$(cr) are solid solutions containing approximately 0.3 and 1.6 mole percent $CaCO_3$ and $SrCO_3$, respectively. The solid prepared in this study contains less than 0.05 and 0.1 mole percent $CaCO_3$ and $SrCO_3$, respectively.

Experimental procedures used to determine the solubility of $BaCO_3$(cr) are identical to those used for $SrCO_3$(cr) and $CaCO_3$(cr) and are described in detail by Plummer and Busenberg (1982) and Busenberg *et al.* (1984).

AQUEOUS MODEL

Individual ion activity coefficients were calculated by the modified Debye-Hückel equation of Truesdell and Jones (1974).

$$\text{Log}\,\gamma_i = (-Az_i^2\sqrt{I})/(1 + B\mathring{a}_i\sqrt{I}) + b_i I, \qquad (2)$$

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[1] The use of brand/firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

where A and B are temperature dependent constants (HAMMER, 1968), z_i is the charge of the ith ion, and I is the ionic strength ($I = 0.5 \sum m_i z_i^2$). The values of $\mathring{a}_i$ used for Ba^{2+}, $BaHCO_3^+$, HCO_3^-, CO_3^{2-}, H^+ and OH^- are 4.42, 5.4, 5.4, 5.4, 9.0, and 3.5, respectively. The values of the b term are 0.095 for Ba^{2+} and 0.0 for all the other ions. The values of $\mathring{a}_i$ and b_i for Ba^{2+} were calculated from the mean activity data of chloride salts by the mean salt method (MACINNES, 1919). The aqueous model is identical in all other details to that of PLUMMER and BUSENBERG (1982).

RESULTS

The association constant of $BaHCO_3^+(aq)$

The association constant of $BaHCO_3^+(aq)$ for the reaction

$$Ba^{2+}(aq) + HCO_3^-(aq) = BaHCO_3^+(aq), \qquad (3)$$

is defined by

$$K_{BaHCO_3^+} = \frac{a_{BaHCO_3^+}}{a_{Ba^{2+}} a_{HCO_3^-}}. \qquad (4)$$

The $BaHCO_3^+(aq)$ association constant determined by the potentiometric method was calculated from measurements of P_{CO_2}, total Ba and pH. The measured pH was corrected for liquid-junction potential using the Henderson equation (BATES, 1973; PLUMMER and BUSENBERG, 1982). The P_{CO_2}, total Ba, measured and corrected pH, and the association constants are given in supplementary material.[2] The results are summarized in Table 1. The iterative procedure used to calculate the association constant is described by BUSENBERG *et al.* (1984).

The conductivity method used to determine the $BaHCO_3^+(aq)$ association constant is similar to the method previously used by JACOBSON and LANGMUIR (1974) to determine log K of $CaHCO_3^+(aq)$. The theoretical conductivity of $Ba^{2+}(aq)$ plus two $HCO_3^-(aq)$, and $BaHCO_3^+(aq)$ plus one $HCO_3^-(aq)$ were calculated using the Onsager equation as modified by ROBINSON and STOKES (1954, 1970),

$$\Lambda_c = \Lambda^0 - \left[\frac{2.801 \times 10^6 |z_1 z_2| q \Lambda^0}{(\epsilon T)^{3/2}(1+\sqrt{q})} + \frac{41.25(|z_1|+|z_2|)}{\eta(\epsilon T)^{1/2}}\right] \times \frac{\sqrt{I}}{(1+\kappa a)} \qquad (5)$$

where $a = 4.75$ and is the mean near distance of closest approach of the hydrated cation and anion, I is the ionic strength, κ equals $50.29 \times 10^8 (\epsilon T)^{-1/2}\sqrt{I}$, $q = |z_1 z_2| / [(|z_1| + |z_2|)(|z_2| t_1^0 + |z_1| t_2^0)]$, t_1^0 is the cation transport number or $\lambda_1^0/(\lambda_1^0 + \lambda_2^0)$, the subscripts 1 and 2 represent cations and anions, respectively, T is in degrees Kelvin, z_1 is the charge of the cation, λ_1^0 is the limiting conductance of the cation, $\Lambda^0 = \lambda_1^0 + \lambda_2^0$, Λ^0 is the equivalent conductance, ϵ is the dielectric constant of water, and η is the viscosity of water. The λ^0 of $BaHCO_3^+$ is not known, but was assumed to be equal to the λ^0 of HCO_3^- based on the similarity of the two ions. All constants in Eqn. 5 needed for computation were obtained from ROBINSON and STOKES (1970).

Table 1. Summary of the average experimental and calculated values of log $K_{BaHCO_3^+}$.

t °C	Exp. log K $BaHCO_3^+$	Stand. Dev.	Calc.[1] log K $BaHCO_3^+$	No.[2]	Method[3] Used
5.0	0.764	0.074	0.708	10	P
25.0	0.935	0.063	0.982	51	P
25.0	1.049	0.022	0.982	18	C
25.0	0.95	0.05	0.982	5	S
25.0	0.978	0.062	0.982	3	A[4]
45.0	1.225	0.021	1.255	24	P
60.0	1.467	0.057	1.460	15	P
79.3	1.754	0.061	1.724	18	P
80.0	1.752	0.084	1.733	12	P

[1] Calculated using eqn. 7.
[2] Number of determinations.
[3] P = potentiometry, C = conductivity, S = variation of solubility as a function of P_{CO_2}, and A = average of 3 methods.
[4] This value was used at 25°C to calculate the least squares fit.

The calculated specific conductance (μ_c) was computed from the calculated equivalent conductance

$$\mu_c = \Lambda_c C \qquad (6)$$

where C is the concentration of the salt in equivalents per dm^3.

The concentrations of $Ba^{2+}(aq)$ and $BaHCO_3^+(aq)$ necessary to obtain the observed conductivities were calculated using an iterative computer program. Four measurements of conductivity were made at each of the 18 different solution concentrations of $Ba(HCO_3)_2$ and are shown in Fig. 1. Details of the conductivity measurements are given in the supplementary material.[2] The average value of log $K_{BaHCO_3^+}$ obtained from conductivity measurements is compared with the other values in Table 1.

In the third method used to determine $BaHCO_3^+(aq)$, the solubility of $BaCO_3(cr)$ was carefully measured at 5 different CO_2 partial pressures and 25°C. Figure 2 shows how the choice of log $K_{BaHCO_3^+}$ affects the calculated equilibrium product of $BaCO_3(cr)$ as a function of P_{CO_2}. Using the value of 1.52 for log $K_{BaHCO_3^+}$ obtained by NAKAYAMA and RASNICK (1969), the equilibrium constant of $BaCO_3(cr)$ varies with P_{CO_2}. All trends in log $K_{BaCO_3}(cr)$ with P_{CO_2} disappear if the value

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[2] See NAPS document no. 04424 for 8 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance in U.S. funds only $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each of 10 pages of material thereafter, $1.50 for microfiche postage.

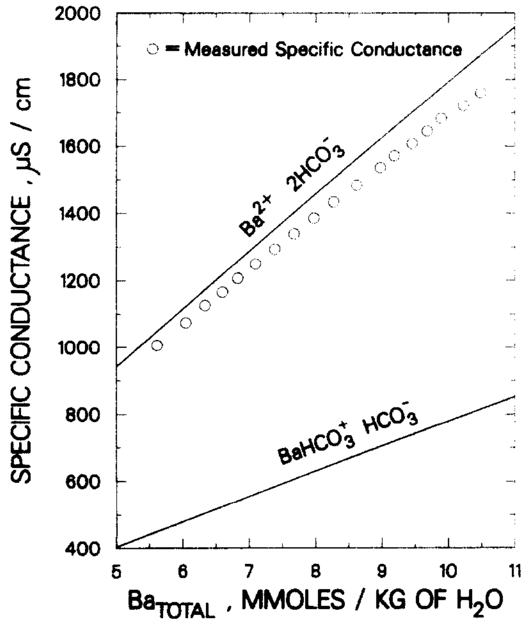

FIG. 1. Calculated specific conductances of $Ba(HCO_3)_2$ solutions assuming all Ba is present as $BaHCO_3^+(aq)$ or as $Ba^{2+}(aq)$. The observed results are shown.

of the association constant of $BaHCO_3^+(aq)$ is near 0.98 at 25°C. The results are compared in Table 1.

In summary, all three methods yield similar values for the log association constant of $BaHCO_3^+(aq)$ at 25°C, within the uncertainty of each method (Table 1 and Fig. 3).

The temperature dependence of the association constant is given by the equation

$$\log K_{BaHCO_3^+} = -3.0938 + 0.013669T, \qquad (7)$$

where T is in degrees Kelvin. The value of 0.982 for $\log K_{BaHCO_3^+}$ at 298.15°K obtained in this study is very similar to the values obtained for the bicarbonate association constants of the other alkaline-earth metals (BUSENBERG *et al.*, 1984) but significantly smaller than the 1.52 value obtained by NAKAYAMA and RASNICK (1969).

The association constant of $BaCO_3^0(aq)$

The association reaction is represented by the equation

$$Ba^{2+}(aq) + CO_3^{2-}(aq) = BaCO_3^0(aq). \qquad (8)$$

The equilibrium constant is defined by the equation

$$K_{BaCO_3^0} = \frac{a_{BaCO_3^0}}{a_{Ba^{2+}}a_{CO_3^{2-}}}. \qquad (9)$$

The procedures used to measure this association constant are identical to the procedures used to measure the association constants of $SrCO_3^0(aq)$ (BUSENBERG *et al.*, 1984) and $CaCO_3^0(aq)$ (PLUMMER and BUSENBERG, 1982). The association constants were determined from the change in pH of $KHCO_3$-K_2CO_3-KCl solutions when a small amount of $BaCl_2$ was added. The difference in pH resulting from the addition of $BaCl_2$ is believed to be more accurate than absolute pH values, because liquid-junction potentials are essentially unchanged between the initial and final solutions. The $\log K_{BaCO_3^0}$ was varied with the computer program PHREEQE (PARKHURST *et al.*, 1980) in order to reproduce the difference in pH between initial and final solutions. The difference between the observed and calculated pH of the initial solution was usually within 0.01 pH unit and rarely exceeded 0.02 pH units.

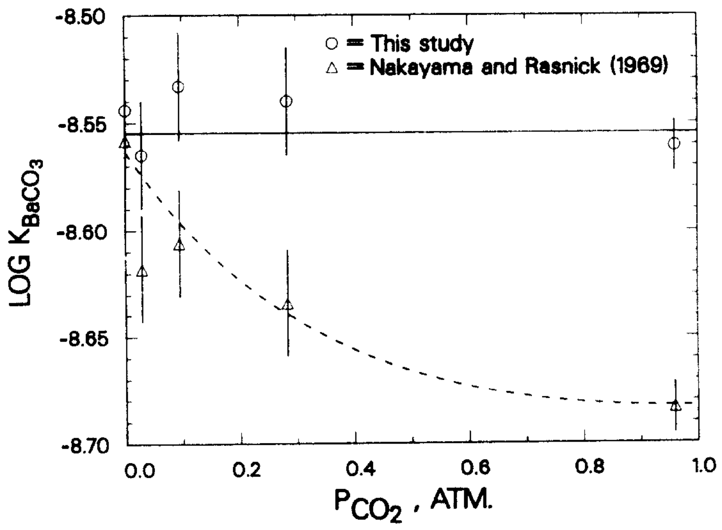

FIG. 2. The effect of the log association constant of $BaHCO_3^+(aq)$ used (0.98, this study; 1.52, NAKAYAMA and RASNICK, 1969) on the calculated equilibrium constant of witherite as a function of CO_2 partial pressure at 25°C. Error bars are ±2 standard deviations.

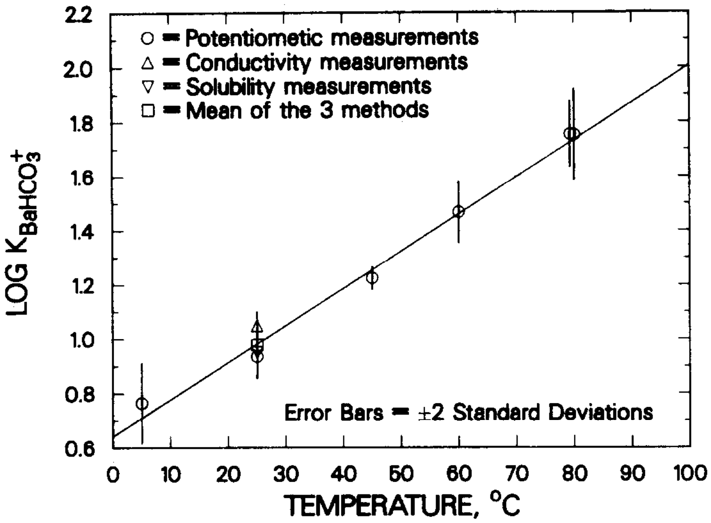

FIG. 3. The temperature dependence of the log association constant of $BaHCO_3^+(aq)$.

The initial and final compositions of the solutions, the difference in pH and the computed association constants for $BaCO_3^0(aq)$ are given in the supplementary material. The results are summarized in Table 2 and shown in Fig. 4.

The variation of log K of $BaCO_3^0(aq)$ with temperature is given by the equation

$$\log K_{BaCO_3^0} = -0.113 + 0.008721T. \qquad (10)$$

Equation (10) gives 2.71 for log $K_{BaCO_3^0}$ at 298.15°K, which is in good agreement with the value of 2.78 reported by PALMER and VAN ELDIK (1983), and significantly different from the value of 3.78 obtained by BENĚS and SELECKÁ (1973).

The equilibrium constant of witherite, $BaCO_3(cr)$

The solubility of $BaCO_3(cr)$ is given by the reaction

$$BaCO_3(cr) = Ba^{2+}(aq) + CO_3^{2-}(aq). \qquad (11)$$

The equilibrium constant is defined by the equation

$$K_{BaCO_3}(cr) = a_{Ba^{2+}} a_{CO_3^{2-}}. \qquad (12)$$

Table 2. Summary of the average experimental and calculated values of log $K_{BaCO_3^0}$.

t°C	Exp. log K $BaCO_3^0$	Stand. Dev.	Calc.[1] log K $BaCO_3^0$	No.[2]
5.0	2.556	0.021	2.536	28
25.0	2.697	0.048	2.710	36
40.0	2.786	0.041	2.841	40
60.0	3.012	0.042	3.016	16
80.0	3.227	0.044	3.190	20

[1] Calculated using Eqn. 10.
[2] Number of determinations.

Table 3 gives the experimental solubility of $BaCO_3(cr)$ as a function of temperature and CO_2 partial pressure. The calculated pH and log equilibrium constants are also given. A summary of the average log K values for each temperature is presented in Table 4 and these values were used to calculate the temperature dependence of the equilibrium constant, as given by the equation

$$\log K_{BaCO_3}(cr) = 607.642 + 0.121098T - 20011.25/T - 236.4948 \log T \qquad (13)$$

where T is in degrees Kelvin. Equation 13 is valid from 0 to 90°C.

There are approximately 20 reported studies of the solubility of $BaCO_3(cr)$ in various solutions and temperatures and most of these give sufficient data for the recalculation of the equilibrium constants. The recalculated log $K_{BaCO_3}(cr)$ values are given in the supplementary material and compared with our values in Fig. 5. Several points falling outside the boundaries of Figure 5 are not shown.

There is excellent agreement between the values for log $K_{BaCO_3}(cr)$ determined in this study and those of MILLERO *et al.* (1984) at 25°C (−8.56), MCCOY and SMITH (1911) at 25°C (−8.58), HOLLMAN (1893) at 24.2°C, 18°C and 8.8°C (−8.57, −8.56 and −8.68, respectively) and SCHLOESING (1872) at 16°C (−8.62). All other log $K_{BaCO_3}(cr)$ differ by more than 0.05 log units. Values as small as −8.8 (TOWNLEY *et al.*, 1937) and as large as −5.5 (BENĚS and SELECKÁ, 1973) have been reported for the equilibrium constant at 25°C. The only high temperature study is that of MALININ (1963). Malinin's data at 100°C and various CO_2 partial pressures are about 0.5 log units smaller than the value of the equilibrium constant calculated from the data of this study. The lower values are not surprising because other hydrothermal bomb studies for carbon-

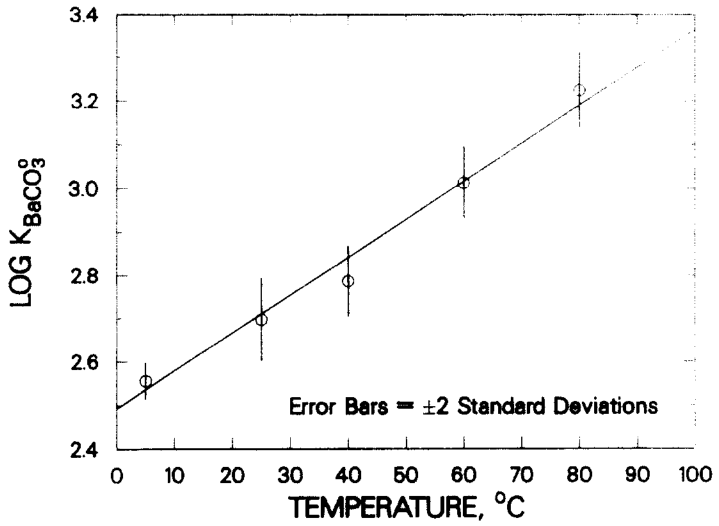

FIG. 4. The temperature dependence of the log association constant of $BaCO_3^0(aq)$.

ate minerals have yielded similar lower values (PLUMMER and BUSENBERG, 1982; BUSENBERG *et al.*, 1984).

The thermodynamic properties of the reactions (3), (8) and (11) at 298.15 K were evaluated from the temperature dependence of the equilibrium constants. The results are summarized in Table 5.

Table 3. Experimental solubility of $BaCO_3(cr)$ in CO_2-H_2O solutions as a function of temperature. Concentration of Ba is in mmoles.kg^{-1} of solution.

	PCO_2	Total	Calc.	log K		PCO_2	Total	Calc.	log K		PCO_2	Total	Calc.	log K
t °C	atm.	Ba	pH	$BaCO_3(cr)$	t°C	atm.	Ba	pH	$BaCO_3(cr)$	t °C	atm.	Ba	pH	$BaCO_3(cr)$
-0.2	0.9936	10.30	5.930	-8.735	27.2	0.9513	8.149	5.990	-8.565	54.9	0.8429	5.685	6.080	-8.639
-0.2	0.9913	10.24	5.929	-8.741	27.2	0.9428	8.157	5.994	-8.560	54.9	0.8445	5.678	6.079	-8.642
-0.2	0.9970	10.26	5.927	-8.741	27.6	0.9567	8.187	5.991	-8.558	54.9	0.8373	5.712	6.085	-8.631
-0.2	0.9825	10.26	5.933	-8.735	27.6	0.9604	8.149	5.988	-8.564	55.0	0.8313	5.614	6.082	-8.646
-0.2	0.9846	10.20	5.930	-8.742	27.6	0.9454	8.190	5.997	-8.552	55.0	0.8345	5.643	6.082	-8.642
5.0	0.9812	9.756	5.934	-8.701	27.6	0.9632	8.232	5.991	-8.554	60.1	0.7914	5.224	6.110	-8.669
5.0	0.9812	9.927	5.941	-8.681	27.6	0.9559	8.215	5.993	-8.553	60.1	0.7925	5.211	6.109	-8.672
5.0	0.9834	9.992	5.942	-8.675	27.6	0.9554	8.189	5.992	-8.557	60.1	0.8012	5.211	6.104	-8.677
5.0	0.9862	10.00	5.942	-8.675	29.8	0.9636	7.924	5.988	-8.570	60.1	0.7933	5.253	6.111	-8.664
5.0	0.9832	9.997	5.943	-8.674	29.8	0.9600	7.944	5.991	-8.566	60.1	0.7912	5.248	6.112	-8.664
5.0	0.9888	9.997	5.940	-8.676	29.8	0.9578	7.954	5.993	-8.564	64.8	0.7483	4.805	6.135	-8.707
5.0	0.9912	9.997	5.939	-8.678	29.8	0.9433	7.967	6.000	-8.555	64.8	0.7486	4.803	6.135	-8.708
10.0	0.9928	9.605	5.944	-8.642	29.8	0.9424	8.015	6.003	-8.548	64.8	0.7524	4.819	6.134	-8.706
10.0	0.9870	9.664	5.949	-8.632	29.8	0.9489	8.056	6.002	-8.545	64.8	0.7574	4.778	6.133	-8.713
10.0	0.9725	9.570	5.952	-8.637	29.8	0.9572	8.045	5.997	-8.551	64.8	0.7591	4.840	6.131	-8.705
10.0	0.9782	9.666	5.953	-8.628	35.0	0.9407	7.52	6.010	-8.559	64.8	0.7546	4.854	6.135	-8.700
10.0	0.9864	9.626	5.948	-8.636	35.0	0.9317	7.49	6.013	-8.559	64.8	0.7514	4.797	6.132	-8.711
15.0	0.9780	9.30	5.963	-8.595	35.0	0.9307	7.47	6.012	-8.562	64.8	0.7412	4.816	6.140	-8.700
15.0	0.9691	9.29	5.966	-8.592	35.0	0.9401	7.453	6.007	-8.569	64.8	0.7338	4.771	6.141	-8.706
15.0	0.9680	9.25	5.965	-8.596	35.0	0.9389	7.523	6.011	-8.558	65.0	0.7479	4.81	6.137	-8.137
15.0	0.9682	9.245	5.960	-8.602	35.0	0.9338	7.508	6.008	-8.572	69.8	0.6989	4.391	6.165	-8.749
15.0	0.9763	9.303	5.963	-8.594	35.0	0.9313	7.420	6.009	-8.570	69.9	0.6986	4.386	6.165	-8.749
15.0	0.9713	9.265	5.964	-8.596	35.0	0.9440	7.536	6.010	-8.558	69.9	0.6920	4.401	6.171	-8.742
15.0	0.9687	9.269	5.965	-8.594	40.3	0.9145	6.993	6.028	-8.572	70.0	0.6791	4.342	6.174	-8.748
15.0	0.9784	9.158	5.956	-8.612	40.3	0.9155	6.998	6.028	-8.572	70.0	0.6891	4.374	6.171	-8.746
15.0	0.9826	9.035	5.949	-8.629	40.3	0.9242	7.015	6.024	-8.573	74.9	0.6042	3.878	6.216	-8.797
15.0	0.9851	9.069	5.949	-8.626	40.3	0.9163	7.017	6.028	-8.569	75.3	0.6075	3.840	6.213	-8.808
15.0	0.9851	9.092	5.950	-8.623	40.3	0.9142	7.002	6.028	-8.571	75.3	0.6075	3.891	6.218	-8.794
15.0	0.9784	9.093	5.953	-8.620	40.3	0.9286	7.045	6.024	-8.571	75.6	0.6071	3.864	6.218	-8.800
20.2	0.9650	8.838	5.976	-8.572	44.9	0.9025	6.623	6.042	-8.583	75.6	0.6136	3.889	6.216	-8.798
20.2	0.9661	8.849	5.976	-8.571	44.9	0.8989	6.525	6.038	-8.598	75.6	0.6091	3.868	6.217	-8.801
20.2	0.9747	8.897	5.974	-8.569	44.9	0.8996	6.478	6.035	-8.606	75.7	0.6003	3.829	6.220	-8.805
20.2	0.9668	8.864	5.976	-8.570	44.9	0.9000	6.531	6.038	-8.597	75.7	0.5953	3.841	6.225	-8.798
20.2	0.9784	8.865	5.971	-8.575	44.9	0.8957	6.538	6.041	-8.594	75.7	0.5867	3.854	6.232	-8.788
20.2	0.9674	8.850	5.975	-8.572	45.0	0.8951	6.518	6.040	-8.596	80.2	0.5155	3.459	6.279	-8.832
25.0	0.9636	8.37	5.982	-8.569	45.0	0.0101	6.541	6.034	-8.599	80.2	0.5187	3.436	6.273	-8.842
25.0	0.9646	8.32	5.983	-8.571	45.0	0.9076	6.530	6.035	-8.600	80.2	0.5324	3.483	6.267	-8.838
25.0	0.9636	8.37	5.986	-8.564	45.0	0.9063	6.543	6.036	-8.597	80.2	0.5312	3.474	6.267	-8.840
25.0	0.9637	8.456	5.986	-8.557	45.1	0.9083	6.532	6.035	-8.599	80.2	0.5255	3.477	6.272	-8.835
25.0	0.9618	8.438	5.986	-8.559	50.3	0.8647	6.094	6.064	-8.610	80.3	0.5308	3.475	6.269	-8.839
25.0	0.9607	8.420	5.985	-8.561	50.3	0.8658	6.062	6.062	-8.616	80.4	0.5232	3.440	6.272	-8.843
25.0	0.9542	8.441	5.989	-8.555	50.3	0.8745	6.078	6.059	-8.618	80.5	0.5279	3.457	6.270	-8.842
25.0	0.9641	8.471	5.986	-8.555	50.3	0.8666	6.077	6.062	-8.614	89.8	0.2967	2.463	6.456	-8.932
25.0	0.9671	8.471	5.985	-8.557	50.3	0.8645	6.049	6.062	-8.618	89.9	0.2942	2.465	6.461	-8.927
25.0	0.9670	8.447	5.984	-8.560	50.3	0.8788	6.092	6.057	-8.617	90.0	0.3004	2.459	6.452	-8.939
25.0	0.2832	5.357	6.333	-8.540	50.3	0.8782	6.091	6.058	-8.617	90.0	0.3095	2.527	6.449	-8.922
25.0	0.09439	3.560	6.644	-8.533	54.8	0.8509	5.699	6.076	-8.642	90.0	0.3072	2.510	6.450	-8.926
25.0	0.09439	3.565	6.645	-8.531	54.9	0.8332	5.641	6.082	-8.643	90.0	0.2912	2.449	6.464	-8.930
25.0	0.0287	2.232	6.969	-8.565	54.9	0.8441	5.684	6.079	-8.640	90.0	0.2864	2.437	6.469	-8.928
25.0	0.000303	0.4576	8.270	-8.544	54.9	0.8441	5.712	6.081	-8.635	90.1	0.2974	2.457	6.456	-8.935

Table 4. Summary of the average experimental and calculated values of log K witherite.

t°C	No.[1]	Obs. Log K	Stand. Dev.	Calc.[2] Log K
-0.2	5	-8.739	0.004	-8.740
5.0	7	-8.680	0.010	-8.678
10.0	5	-8.635	0.005	-8.632
15.0	12	-8.607	0.014	-8.598
20.2	6	-8.572	0.002	-8.574
25.0[3]	10	-8.561	0.006	-8.562
25.0[4]	5	-8.555	0.012	-8.562
27.2	2	-8.563	0.005	-8.559
27.6	6	-8.556	0.004	-8.558
29.8	7	-8.557	0.010	-8.557
35.0	8	-8.563	0.006	-8.561
40.3	6	-8.571	0.002	-8.573
45.0	10	-8.597	0.006	-8.589
50.3	7	-8.616	0.003	-8.613
54.9	9	-8.640	0.005	-8.639
60.1	5	-8.669	0.006	-8.680
64.8	9	-8.706	0.004	-8.707
65.0	1	-8.705	---	-8.709
69.9	5	-8.747	0.003	-8.748
74.9	1	-8.797	---	-8.790
75.3	2	-8.801	0.010	-8.794
75.7	6	-8.798	0.006	-8.797
80.2	5	-8.837	0.004	-8.838
80.4	2	-8.841	0.002	-8.841
89.8	1	-8.932	---	-8.932
90.0	7	-8.930	0.006	-8.933

[1] Number of determinations.
[2] Calculated value using eqn. 13.
[3] Mean of the ~0.96 atm. CO_2 partial pressure.
[4] Mean of the average values of five CO_2 partial pressures.

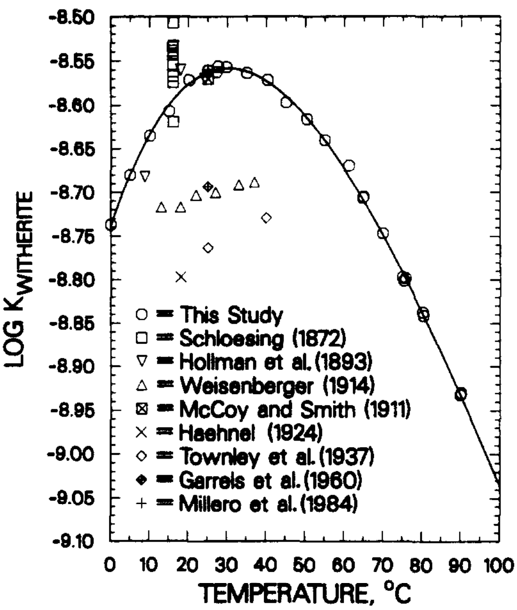

FIG. 5. The temperature dependence of the log equilibrium constant of witherite. The recalculated literature data that fall within the boundaries of this figure are shown.

Preliminary evaluation of $\Delta_f G°$, $\Delta_f H°$ and $S°$ of $Ba^{2+}(aq)$

Many of the thermodynamic data selections for Ba depend on the thermodynamic values for the key compounds BaO(cr) and $BaCl_2$(cr). The NBS analysis and documentation of the thermodynamic information on Ba compounds was published by PARKER (1969) and the selections by PARKER *et al.* (1971). The selections were later republished in a combined NBS publication (WAGMAN *et al.*, 1982). These selections for Ba compounds were made prior to the determination of $\Delta_f H°$ of BaO(cr) by FITZGIBBON *et al.* (1973) and, therefore, the thermodynamic data for Ba compounds are in need of major revision (PARKER, written commun.).

The status of the Ba selections and the reasons for some of the inconsistencies will be briefly explained with the aid of Table 6 which summarizes data from three major thermodynamic complications and presents our provisional values for various aqueous Ba species.

The selection for the Ba compounds by NBS are based on the heats of solution of Ba(cr) and $BaCl_2$(cr) in dilute HCl (EHRLICH *et al.*, 1963). The only enthalpy value for BaO(cr) then available was that of MAH (1963); this value of $\Delta_f H°$ of -582.0 kJ · mol^{-1} was recognized as inconsistent with the other data and was rejected (PARKER, 1969; PARKER *et al.*, 1971; PARKER, written commun.).

Because of the serious experimental difficulties in the direct determination of $\Delta_f H°$ of BaO(cr) from the combustion of Ba(cr) with O_2(g) (MAH, 1963; FITZGIBBON *et al.*, 1973), the Russian Ba compilations (NAUMOV *et al.*, 1971; GLUSHKO *et al.*, 1979) are based on the heat of solution of Ba(cr) and BaH_2(cr) in HCl and the direct hydrogenation of Ba(cr) (VOROB'EV *et al.*, 1968). The $\Delta_f H°$ value for Ba^{2+}(aq) obtained is significantly different from that of NBS (Table 6). Reasonable values for log K and $\Delta_r G°$ for witherite (Eqn. 11) can be obtained using the data of NAUMOV *et al.* (1971). The later Russian thermodynamic compilations have changed the thermodynamic selections for $BaCO_3$(cr) (GLUSHKO *et al.*, 1979) to reflect a newer determination of $\Delta_f H°$ of BaO(cr) (FITZGIBBON *et al.*, 1973). This was done without any adjustments of the thermodynamic selections for Ba^{2+}(aq), the consequence is an extremely low value of -10.1 for log K_{BaCO_3}(cr) (Eqn. 11) calculated from the compilation of GLUSHKO *et al.* (1979).

A similar problem exists in the compilation of ROBIE *et al.* (1979). The earlier thermodynamic selections for BaO(cr) were based on the data of MAH (1963) in ROBIE

Table 5. Summary of thermodynamic data at 298.15 K.

Reaction Number	log K 298.15°K	$\Delta_r G°$ KJ.mol^{-1}	$\Delta_r H°$ KJ.mol^{-1}	$\Delta_r S°$ J.mol^{-1}.K^{-1}
3	0.982	-5.606	23.262	96.8
8	2.71	-15.486	14.841	101.7
11	-8.562	48.869	2.940	-154.0

Table 6. Summary of recommended values and comparison with other thermodynamic data. See text for details. Units of enthalpy, Gibbs energy and entropy are $kJ.mol^{-1}$, $kJ.mol^{-1}$, and $J.mol^{-1}.K^{-1}$. Temperature of all data is 298.15K.

Substance and State	Wagman et al. (1982)			Glushko et al. (1979)			Robie et al. (1979)			This study		
	$\Delta_f H°$	$\Delta_f G°$	S°	$\Delta_f H°$	$\Delta_f G°$	S°	$\Delta_f H°$	$\Delta_f G°$	S°	$\Delta_f H°$	$\Delta_f G°$	S°
Ba(cr)	0	0	62.8	0	0	62.47	0	0	62.42	0	0	62.42[1]
BaO(cr)	-553.5	-525.1	70.42	-548.1	-520.37	72.1	-548.1	-520.368	72.1	-548.1	-520.394	72.1[2]
$BaCO_3$(cr)	-1216.3	-1137.6	112.1	-1210.85	-1132.25	112.13	-1210.85	-1132.25	112.13	-1210.85	-1132.21	112.13[2]
Ba^{2+}(aq)	-537.64	-560.77	9.6	-524.05	-546.832	8.4	-537.64	-560.74	9.6	-532.5	-555.36	8.4[3]
$BaHCO_3^+$(aq)	--	--	--	--	--	--	--	--	--	-1245.7	-1136.68	10.0
$BaCO_3^0$(aq)	--	--	--	--	--	--	--	--	--	-1222.6	-1067.85	-143.[illegible]

[1] Hultgren et al. (1973)

[2] Robie et al. (1979), Glushko et al. (1979)

[3] S° of Glushko et al. (1979) was used. A value of 8.13 $J.mol^{-1}.K^{-1}$ is calculated using the second law method and eqn. 13.

and WALDBAUM (1968). These were replaced with the data of FITZGIBBON *et al.* (1973) with adjustments in the thermodynamic selections of $BaCO_3$(cr) but, without any approximate changes in the NBS thermodynamic selections for Ba^{2+}(aq). The incompatibility between the aqueous Ba^{2+} data and revised data for $BaCO_3$(cr) results in a high value for the calculated log equilibrium constant (−7.64) for the dissolution of witherite from the tables of ROBIE *et al.* (1979).

A log K_{BaCO_3}(cr) of −8.560 and $\Delta_{soln.}H°$ of 1.52 $kJ \cdot mol^{-1}$ is calculated from the internally consistent data of NBS (PARKER, 1969; PARKER *et al.*, 1971; WAGMAN *et al.*, 1982) for Eqn. 11. The log K is in excellent agreement with our experimentally determined log K of −8.562, but a value of 2.94 $kJ \cdot mol^{-1}$ is obtained for $\Delta_{soln.}H°$ from our data. The NBS data need significant revisions for the thermodynamic formation property selections of BaO(cr) and $BaCO_3$(cr); therefore, significant revisions in the thermodynamic formation selections of Ba^{2+}(aq) are required to preserve the internal consistency of the tables.

Our experimental data provide a different pathway for the determination of thermodynamic values for Ba^{2+}(aq). From the temperature dependence of the equilibrium constant and using the second law method, the various thermodynamic properties can be determined. Combining these results with the thermodynamic selections for $BaCO_3$(cr) (Table 6) and the final recommended selections of CODATA (WAGMAN, private commun., cited in BUSENBERG *et al.*, 1984) for CO_3^{2-}(aq) and HCO_3^-(aq), the $\Delta_f G°$, $\Delta_f H°$, and S° for Ba^{2+}(aq), $BaCO_3^0$ (aq) and $BaHCO_3^+$ (aq) were evaluated.

PARKER (1969) fixed the value of the difference between the enthalpies of formation of BaO(cr) and $BaCl_2$(cr) at 305.0 $kJ \cdot mol^{-1}$. Accepting the value of FITZGIBBON *et al.* (1973) for $\Delta_f H°$ of BaO(cr), requires a value of $\Delta_f H°$ of −853.1 $kJ \cdot mol^{-1}$ for $BaCl_2$(cr). These values for Ba^{2+}(aq), $BaCO_3$(cr), and $BaCl_2$(cr) are in agreement with PARKER's (written commun.) suggested preliminary values.

CONCLUSIONS

(1) The association reaction for the formation of $BaHCO_3^+$(aq) (Eqn. 3) was evaluated between 5 and 80°C. The temperature dependence of the equilibrium constant is given by the expression

$$\log K_{BaHCO_3^+} = -3.0938 + 0.013669T,$$

where T is in degrees Kelvin.

(2) The association reaction for the formation of $BaCO_3^0$(aq) (Eqn. 8) was evaluated in the temperature range of 5 to 80°C. The temperature dependence of the association constant is given by the equation

$$\log K_{BaCO_3^0} = 0.113 + 0.008721T.$$

(3) One hundred and fifty new measurements were made of the solubility of $BaCO_3$(cr) between 0 and 90°C. The temperature dependence of the equilibrium constant (Eqn. 12) is given by the equation

$$\log K_{BaCO_3}(cr) = 607.642 + 0.121098T - 20011.25/T - 236.4948 \log T.$$

(4) Our calculated equilibrium constant for $BaCO_3$(cr) is identical to the value found by MILLERO *et al.* (1984) and in very good agreement with the recalculated values from the data of MCCOY and SMITH (1911), HOLLMAN (1893), and SCHOESING (1872). We define for the first time the temperature dependence of the witherite equilibrium constant.

(5) Three different methods were used at 298.15 K to evaluate the association constant of $BaHCO_3^+$(aq). The results are similar and demonstrate that careful pH measurements can yield association constants as accurate as those obtained by conductivity measurements and the solubility method.

(6) Provisional values for the enthalpy and Gibbs energies of formation for Ba^{2+}(aq), $BaHCO_3^+$(aq) and $BaCO_3^0$(aq) at 298.15 K and 1 atm total pressure are given in Table 6.

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