

Barite solubilities and thermodynamic quantities up to 300°C and 1400 bars

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Abstract

Solubilities of specially synthesized coarse-grained barite were determined in H₂O solutions from 22 to 280°C and 1 to 1400 bars, and in 0.2 and 4 molal NaCl solutions from 100 to 250°C and 1 to 500 bars. Barite solubilities are low, ranging between 10⁻⁶ and 10⁻⁸ molal. Isobaric solubilities are maximum near 100°C in H₂O solutions; the maxima migrate to progressively higher temperatures in solutions of increasing NaCl concentrations. Isothermal solubilities increase with rising NaCl concentration and pressure. The effect of NaCl on increasing solubilities becomes greater with rising temperature.

Changing temperatures cause different responses, depending on the composition of the solution and the temperature range. Initially-saturated dilute natural waters would precipitate barite with either increasing temperature or decreasing temperature, depending on the circumstances. Saline solutions are capable of behaving much like dilute solutions below 1 molal NaCl, but at higher NaCl concentrations the temperature effect on isobaric solubilities is monotonically positive. Barite solubility in sufficiently saline solutions in nature would increase with depth, due to increasing temperature and pressure. Precipitation would tend to occur during migration of solutions toward the surface. Because the low solubility of barite precludes effective transport of BaSO₄ in large quantities, precipitation of barite by the reaction of Ba²⁺ with sulfate derived from the oxidation of S²⁻ may be more important as a depositional mechanism than changes in the temperature–pressure environment.

Thermodynamic equilibrium constants (*K*) and the free-energy changes for the reaction (ΔG) for the dissolution of barite were calculated from the solubility data. ΔG values in kcal/mole at 1 bar are closely reproduced by the equation $\Delta G = 1.15046 \times 10^{-4}T^2 - 4.02952 \times 10^{-2}T + 15.386$ (*T* in °K). Enthalpies, entropies, and volumes of reaction obtained from the solubility data are in accord with published thermodynamic data. Activity coefficients calculated using barite solubilities in NaCl solutions and log *K* data are accurately modeled by an extended form of the Debye-Hückel equation.

Introduction

This paper presents experimental determinations of the solubility of pure, coarsely-crystalline barite in water and NaCl–water solutions over a range of temperature and pressure conditions. The solubility studies provide necessary basic physical-chemical data needed to understand the causes of precipitation, dissolution, or decomposition of barite in nature. They also provide data needed for evaluating thermodynamic quantities of BaSO₄ in aqueous solutions.

Barite occurs in a wide variety of geologic environments. Most economically-important barite deposits are found in sedimentary rocks as bedded barite (Brobst, 1970). Barite also occurs in sedimentary

rocks as rosettes and nodules, as a cementing mineral, and as residual accumulations. Many occurrences of barite are of hydrothermal origin. Sulfide mineral deposits commonly contain barite as a gangue mineral. Some gold deposits in the western U.S. contain frankdicksonite (BaF₂) as well as barite (Radtke and Brown, 1974). Barite is also associated with some carbonatites (Heinrich, 1966). The extreme diversity of barite occurrences suggests that barite is deposited under diverse geochemical conditions.

Many measurements of barite or BaSO₄ solubility have been made. In most studies, the solid utilized was either a sample of natural barite or precipitated

BaSO₄. The use of either of these solids can introduce error. Natural barites may contain minor amounts of other elements, such as Sr, Ca, and Pb, as substitutes for Ba in the crystal structure. The presence of small amounts of impurities may affect Ba concentrations in aqueous solutions (Gundlach *et al.*, 1972). Barites with strontium showed an incongruent solubility. Natural barites may also contain small inclusions of other minerals capable of dissolving and increasing the ionic strength. The very low solubility of barite, of the order of 10⁻⁵ moles BaSO₄ per kilogram of solvent causes similar levels of other ions to have much greater relative effect on solution properties than they would if concentrations were higher. Ionic substitution and the contamination of samples with other minerals can be avoided by using precipitated barium sulfate. However, these precipitates may be poorly crystalline, have a very fine grain size, and contain occluded barium chloride, sodium sulfate, or other salts, depending upon the conditions of precipitation. Balarew (1925) pointed out that BaSO₄ precipitates contain up to as much as 1 percent of occluded BaCl₂. Even the precipitates washed until negative tests were obtained for chloride released more Cl⁻ on prolonged grinding. In a recent study of SrSO₄ precipitates, Mager and Lieser (1972) showed that recrystallization caused the slow release of occluded Na₂SO₄.

Particle size and crystallinity also affect measured solubilities. Lemarchands (1928) found that particles smaller than 1.7 microns had solubilities as much as three times that of larger particles. Herovsky and Berezicky (1929) found that freshly-precipitated BaSO₄ was about 8 times more soluble than a precipitate 30 hours old. In studies of SrSO₄ solubility, Gallo (1935) showed that a calcined precipitate had a lower solubility than a newly-formed precipitate. Measurements of celestite solubility by Strübel (1966) and by Blount and Dickson (1967) were significantly lower than were obtained by Gallo on calcined material. If synthetic solids are to be used, they must be as free as possible of occluded ions, consist of grains larger than 2 microns, and be highly crystalline.

Solubilities of barite and precipitated BaSO₄ in water and in salt solutions made by many investigators have been summarized by Strübel (1967) and Gundlach *et al.* (1972). Results of the more consistent studies of later researchers are illustrated in Figure 1. Table 1 summarizes previous studies of BaSO₄ and barite solubility in various kinds of salt solutions.

A wide variety of analytical procedures were used

by different investigators for the solubility measurements. Templeton (1960) used emission spectroscopy for barium and a reduction-colorimetric procedure for sulfur. Radioisotope methods using precipitated BaSO₄ with barium 140 and 133 as a tracer were employed by Puchelt (1967). Strübel (1967) employed crystal weight-loss and X-ray fluorescence to determine barium. Uchameyshvili *et al.* (1966) used crystal weight-loss measurements on barite crystals. Some of the scatter in experimental results reflects analytical problems and uncertainties as well as significant solubility differences.

Present study

Experimental materials

Samples of coarse-grained synthetic barite were prepared by slow precipitation from a hot, acidic, dilute (0.01 molal) BaCl₂ solutions by adding dilute Na₂SO₄ solution, following procedures described by Blount (1971, 1974). The synthetic barite consisted of 0.5 g quantities of crystals ranging from 0.01 to 0.1 mm thick. No amorphous or submicron material was present. Except for the growth of some crystals to form aggregates, barite was unchanged after a year of exposure to solutions at elevated temperatures and pressures. All experimental solutions were made from redistilled water and reagent-grade chemicals.

Analytical procedures

Barium determinations on experimental solutions were made by X-ray fluorescence analysis of ion-exchange resin pellets after the barium had been taken up by the resin, as described by Blount *et al.* (1971, 1973). Pre-weighed quantities of a chelating ion-exchange resin (Chelex 100) were equilibrated with weighed quantities of experimental solutions at a pH near 10. Strongly saline solutions were diluted 10-fold to eliminate interference by sodium ion. The resin was recovered by filtration, dried, and pelletized in a 0.5" diameter die. Standard pellets were prepared by equilibrating solutions with known quantities of barium with resin samples. Barium recovery was around 99 percent from test solutions. A Phillips model 1410 vacuum spectrograph equipped with a 100 kV tungsten target tube was used to measure the intensity of the BaK α peak. The accuracy of the analytical procedure was better than ± 5 percent. The K α peak, in spite of high background, showed better linearity and reproducibility for the resin sample analysis procedure than the L α line.

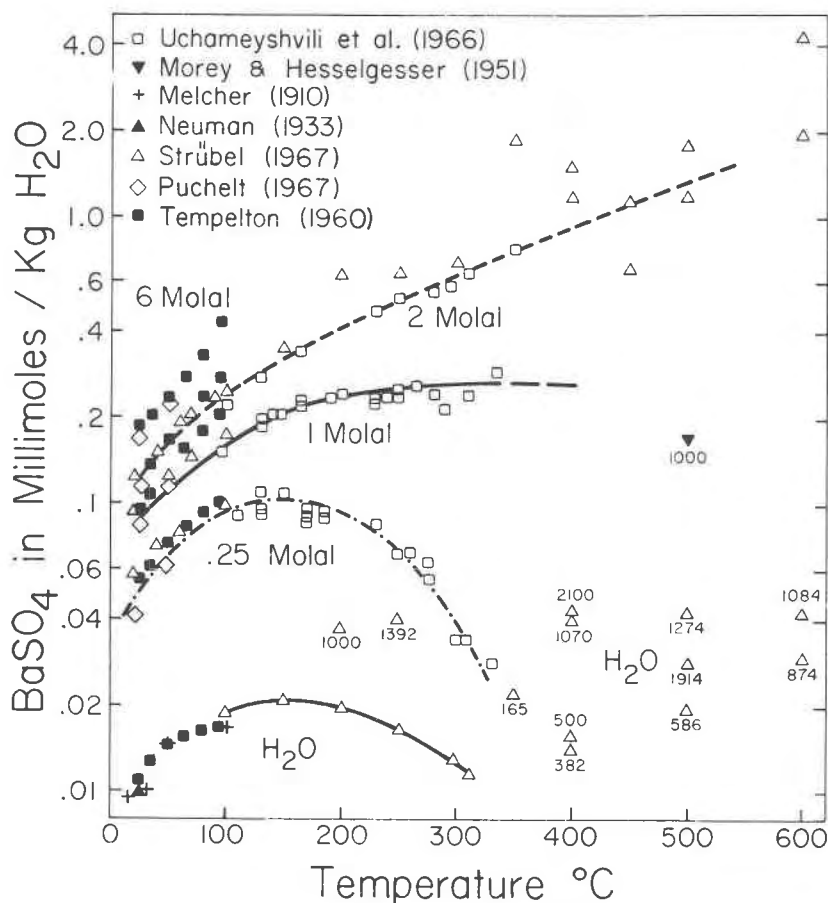


Fig. 1. Results of previous determinations of BaSO₄ or barite solubility in H₂O and some NaCl-H₂O solutions. Where necessary, short interpolations or extrapolations were used to obtain values at the indicated NaCl concentrations. The numbers next to data points are the pressures in bars.

Experimental equipment

Solubility measurements were made using the hydrothermal solution equipment (HSE) described by Dickson *et al.* (1963). A 400 ml capacity collapsible teflon sample cell, containing 0.5 g synthetic barite, and filled with boiled, CO₂-free distilled water or NaCl-water solution, was connected to a teflon-lined stainless steel tube and installed in a large stainless steel pressure vessel. Pressure was controlled by pumping CO₂-free water into or out of the space in the pressure vessel surrounding the sample cell. Heating was provided by a large muffle furnace. The HSE-furnace assembly was rocked through an angle of 170° to provide mixing of solution and barite. Samples of this solution were taken from the sample cell at intervals of time (2 to 12 days) by opening a valve located at the other end of the teflon-lined tubing connected to the sample cell. Pressure was maintained by simultaneously pumping water into the

pressure vessel. Experimental conditions were maintained until analyses of successive samples agreed within the uncertainty of the analytical procedure. Uncertainties in temperature, measured with a chromel-alumel thermocouple, were 1.5 percent. Pressures were measured with a calibrated precision-type Heise pressure gauge with an uncertainty of ± 3 bars.

System BaSO₄-H₂O

Experimental determinations of barite solubility in water are presented in Table 2 and illustrated in Figure 2, which includes data by other workers for comparison. Solubilities were measured from both undersaturated ("U") and supersaturated ("S") conditions. Table 3 gives solubilities at selected constant temperature and pressure conditions. The isobaric solubility curves in Figure 2 show maxima between 100 and 150°C. Pressure and temperature effects on barite solubility above 150°C are similar to solubility

Table 1. Summary of experimental conditions used for previous studies of the solubility of barite and precipitated BaSO₄ in salt solutions

Authors and Experimental Solid	Salt solutions studied	Range of Concentration	Temperature
Fresenius & Hintz (1896) ppt. BaSO ₄	NH ₄ Cl, NaCl, HNO ₃ , HCl	0 - 10 wt.%	Not Given room temp.
Fraps (1902) ppt. BaSO ₄	FeCl ₃ , AlCl ₃ MgCl ₂	1-100 g/liter	Not given room temp.
Neuman (1933) ppt. BaSO ₄	KCl, KNO ₃ , MgCl ₂ , Mg(NO ₃) ₂ LaCl ₃ , La(NO ₃) ₃	0.00001 to 0.036 molar	25°C
Templeton (1960) ppt. BaSO ₄	NaCl	0.2 to 20 weight percent	25 - 95°C
Lieser (1965) ppt. BaSO ₄	Na ₂ SO ₄	0.0001 to 1 molar	20°C
Uchameyshvili et al. (1966) barite	NaCl, KCl, MgCl ₂ , CaCl ₂	0.1-2 moles/kg	95 - 370°C
Puchelt (1967) ppt. BaSO ₄	NaCl, KCl MgCl ₂ , CaCl ₂	0 to 26 weight percent	25 & 50°C
Strübel (1967) ppt. BaSO ₄ & barite	NaCl	0-2 moles/kg	20 - 600°C

trends of anhydrite and celestite (Blount and Dickson, 1967, 1969; Blount and Dickson, in preparation), both of which show considerably greater solubility. Isothermal solubilities of all the minerals increase at increasing rates with pressure rise. Plots of logarithms of solubilities *vs.* pressure at constant temperature, and *vs.* temperature at constant pressure (above 150°C), are nearly straight lines.

System BaSO₄-NaCl-H₂O

Table 4 gives experimentally-determined barite solubilities in 0.2 and 4.0 molal (moles/kg H₂O) NaCl solutions, at temperatures from 94 to 253°C and pressures close to the vapor pressure and near 500 bars. The uncertainty of barium analyses in the 4-molal solutions is greater (±7%) than in water or in more dilute NaCl solutions. A large excess of sodium can result in less than a 100 percent recovery of barium by the ion-exchange resin. High results could be produced by contamination of sample solutions during sampling. Under these experimental conditions, BaSO₄ could precipitate in the cooler teflon-

lined sampling tube and be subsequently swept out during sampling. The first few milliliters of sample solution were discarded in an effort to reduce the possibility of sample contamination.

Smoothed data corrected to regular intervals of temperature, pressure, and NaCl concentration were used in the construction of Figure 3. Vapor-pressure data for NaCl solutions were from Haas (1971). The presence of millimolar concentrations of BaSO₄ have only trivial effects upon solution vapor pressures. Barite solubility in NaCl solutions is greater than the solubility in water at all conditions studied. Increasing pressure invariably increases solubility.

Barite solubilities of Figure 3 were graphically interpolated or extrapolated to obtain solubility values at 100, 150, 200, and 250°C at the vapor pressure and at 500 bars. These values were used to prepare Figure 4, in which logarithms of barite solubility are plotted against a function involving the square root of NaCl concentration. The curves were positioned on the basis of an extended Debye-Hückel equation. Solubilities plotted in this way change almost linearly with

the NaCl concentration function. Figure 9 presents 25°C data of other workers plotted in the same way. Solubility measurements by previous workers are shown for comparison in Figures 3 and 4. There is

rather good agreement between the solubilities obtained during the present study and those obtained by Uchameyshvili *et al.* (1966). Results obtained by Strübel (1967) and Templeton (1960) are generally

Table 2. Experimental determinations of barite solubility in H₂O solutions

Experimental condition	Sample Number	Temperature in °C	Pressure in bars	Approach Direction Equilib. Time Days.	BaSO ₄ in millimoles/kg H ₂ O
1	B 1	96	36	U 2	0.0174
	B 2	97	41	U 12	0.0176
	B 3	99	46	U 37	0.0171
2	B 4	96.5	496	U 5	0.0258
	B 5	95	460	U 11	0.0242
3	B 6	97	882	U 3	0.0375
	B 7	96.5	862	U 6	0.0342
2R	B 8	97	466	U 8	0.0253
4	B 9	189	402	S 4	0.0150
	B 10	189	404	S 9	0.0146
5	B11	189	100	S 4	0.0100
	B12	189	100	U 3	0.0104
	B13	188	106	U 5	0.0105
6	B14	190	904	U 6	0.0237
	B15	189	902	U 11	0.0239
7	B16	248	522	S 2	0.0083
7R	B17	249	484	U 5	0.0079
8	B18	247	956	U 4	0.0140
	B19	249	1010	U 8	0.0147
9	B20	247	92	S 3	0.0048
	B21	249	104	S 6	0.0048
10	B22	279	994	U 5	0.0120
	B23	279	996	U 7	0.0125
11	B24	219	492	S 3	0.0124
	B25	218.5	468	S 10	0.0118
11R	B26	217	472	U 5	0.0115
	B27	217	456	U 8	0.0117
12	B28	217	106	S 3	0.0075
	B29	224	176	S 14	0.0066
13	Y1	24	1002	U 2	0.0289
	Y2	24	1008	U 8	0.0288
14	Y3	23	500	S 3	0.0182
	Y4	23	518	S 6	0.0177
	Y5	22	508	S 10	0.0187
15	Y6	157	1406	U 7	0.0546
	Y7	156	1392	U 10	0.0552
	Y8	158	1410	U 11	0.0518
16	Y9	155	102	S 3	0.0179
	Y10	155	102	S 6	0.0156
	Y11	157	110	S 9	0.0160

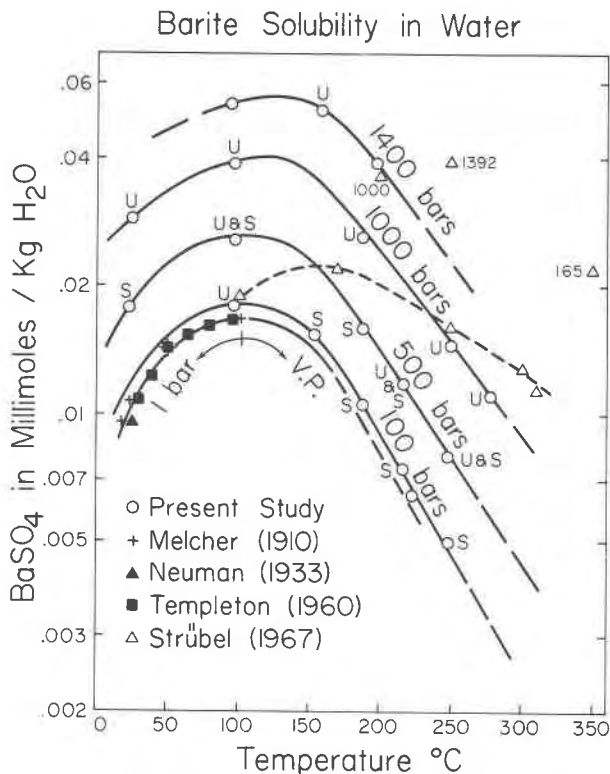


Fig. 2. Solubility of barite in H₂O as a function of temperature at several pressures. Results by previous workers are shown for comparison. The letters "U" and "S" indicate whether the data point was approached from undersaturated or supersaturated solutions.

higher than those obtained in the present study. Barite solubility determinations of this study and by Uchameyshvili *et al.* (1966) give internally-consistent data over the ranges of temperature, pressure, and

Table 3. Barite solubilities in millimoles/kg H₂O in H₂O solution at various temperatures and pressures

T°C	Low* Pressure	100 bars	Pressure 500 bars	1000 bars	1400 bars
25	0.0106**	0.0117	0.0184	0.0290	
60	0.0152**	0.0163	0.0236	0.0350	0.0480
80	0.0160**	0.0175	0.0251	0.0380	0.0510
100	0.0168	0.0180	0.0260	0.0390	0.0535
125	0.0166	0.0180	0.0261	0.0405	0.0560
150	0.0146	0.0158	0.0232	0.0375	0.0540
175	0.0113	0.0124	0.0187	0.0307	0.0465
200	0.0084	0.00920	0.0141	0.0240	0.0360
225	0.00620	0.00675	0.0107	0.0190	0.0301
250	0.00445	0.00470	0.00790	0.0147	0.0243
300†	0.00248	0.00250	0.0044	0.0089	

*Pressure equals 1 bar up to 100°C, the vapor pressure above 100°C.

**Solubilities based on studies by Melcher (1910) and Templeton (1960).

†Values obtained by short extrapolation.

Table 4. Experimental determinations of barite solubility in NaCl-H₂O solutions

Sample Number	Temperature in °C	Pressure in bars	Equilib. Time in days	NaCl in moles KgH ₂ O	BaSO ₄ in millimoles kg H ₂ O
Z 1	224	134	3	0.20	0.071
Z 2	223	126	5	"	0.069
Z 3	253	124	3	"	0.058
Z 4	253	128	9	"	0.057
Z 5	171	12	3	"	0.077
Z 6	167	8	10	"	0.076
Z 7	118	5	2	"	0.084
Z 8	98	478	13	"	0.106
Z 9	98.5	492	20	"	0.108
Z10	100	492	49	"	0.113
Z11	149	500	12	"	0.115
Z12	150	500	14	"	0.121
Z13	245	502	9	"	0.088
Z14	245	482	19	"	0.092
Z15	246	106	2	"	0.058
Z16	245	103	3	"	0.062
Y 1	96.5	520	3	4.00	0.324
Y 2	94.5	480	7	"	0.311
Y 3	95.5	500	14	"	0.307
Y 4	94	106	3	"	0.260
Y 5	96	106	5	"	0.265
Y 6	95	92	8	"	0.255
Y 7	153	560	2	"	0.53
Y 8	153	512	4	"	0.51
Y 9	152.5	492	6	"	0.50
Y10	152.5	500	33	"	0.53
Y11	151	500	39	"	0.52
Y12	152	505	42	"	0.49
Y13	202	456	5	"	0.69
Y14	202	500	14	"	0.73
Y15	203	507	17	"	0.76
Y16	203	498	21	"	0.69
Y17	202.5	499	73	"	0.74
Y18	200	470	79	"	0.73
Y19	200	492	87	"	0.64

NaCl concentration conditions covered. Table 5 presents a summary of barite solubilities at even values of temperature, pressure, and NaCl concentration.

Geological applications

The behavior of barite solubility below the Earth's surface is a function of many factors besides temperature and pressure. Such factors could include the presence of other dissolved substances in solution, ion exchange with clay minerals and other substances, and the possible instability of barite under sulfate-reducing conditions or under conditions that favor the formation of witherite, Ba CO₃. The experimental measurements give the chemical tendencies for idealized circumstances, which may not be approximated in nature. Strübel (1968) suggested that barite could precipitate from natural saline waters by

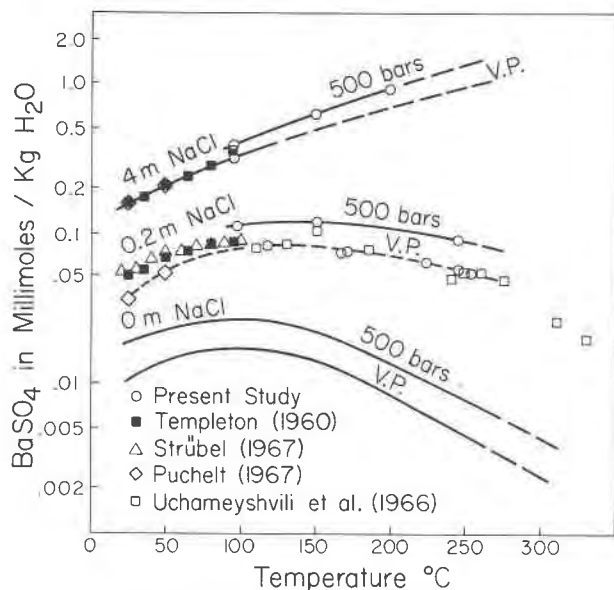


Fig. 3. Solubility of barite in H_2O and 0.2 and 4 molal $\text{NaCl-H}_2\text{O}$ solutions as a function of temperature at the vapor pressure and 500 bars. Previous results are shown for comparison.

cooling, or by reaction of Ba-containing solutions with sulfate produced by oxidation of sulfide ion; conclusions of this study are in agreement.

The solubility data can be used to construct diagrams depicting saturation conditions in the Earth's crust. Such diagrams are generally for simplified and essentially artificial conditions. Curves in Figure 5a depict constant-composition sections through the barite saturation surface projected onto the temperature-pressure plane. The saturation surface is terminated at low pressure by the curve representing the vapor pressure of saturated solutions (which is indistinguishable from the vapor pressure curve of pure water at the scale of the figure). The dashed lines represent two possible temperature-pressure conditions for an assumed geothermal gradient of $30^\circ\text{C}/\text{km}$. The first is for a pressure gradient of 100 bars/km, as a simple approximation to that of a column of water (hydrostatic). The second is for a pressure gradient of 250 bars/km, as a simple approximation to that produced by a column of rock (lithostatic). Solubilities under these two conditions are illustrated in Figure 5b. At a given depth, barite solubility is invariably greater at the higher-pressure conditions. Barite crystals would therefore tend to dissolve at points of pressure and precipitate between detrital grains where the pressure is lower. Barite could also precipitate at constant temperature by migration of solutions along pressure gradients as, for example, from places at high pressure to fissures with

lower pressures. For the models used here, barite solubility under the low-pressure conditions passes a maximum at about 4 km. Under the high-pressure conditions, solubilities remain nearly constant below 4 km. Therefore, barite-saturated ground waters moving in the Earth's crust could either dissolve or precipitate barite according to the direction of flow and the nature of pressure gradient. An important possibility is that barite could be precipitated from barite-saturated ground waters migrating toward hot regions in the crust.

The importance of NaCl solutions in barite deposi-

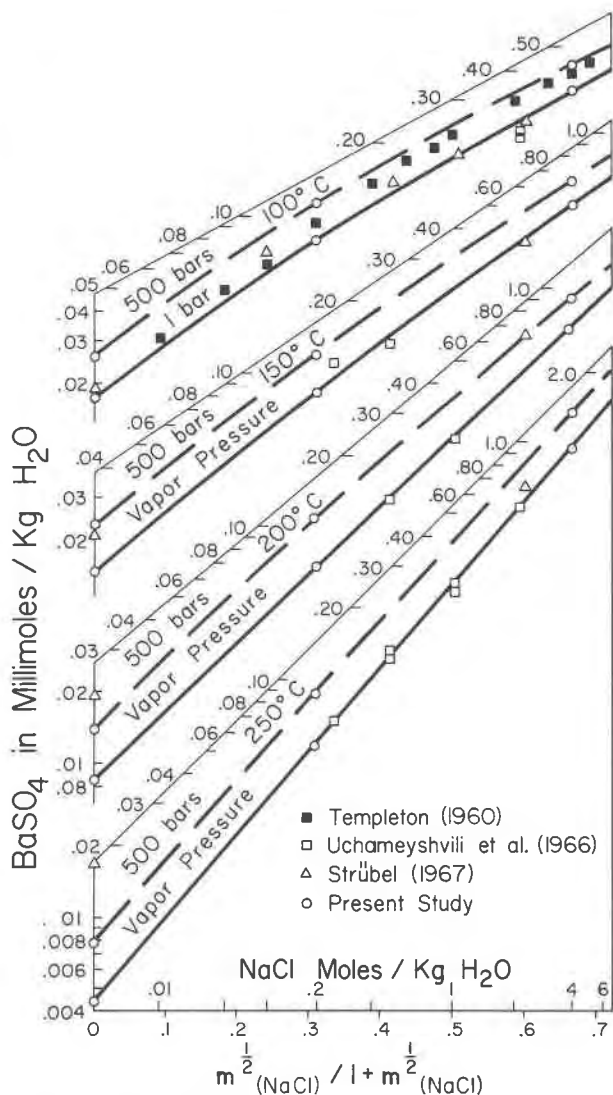


Fig. 4. Barite solubility in $\text{NaCl-H}_2\text{O}$ solutions as a function of the NaCl concentration. Previous results are shown for comparison. The curves represent solubilities calculated from equilibrium constants and an extended Debye-Hückel equation (Equation 12 in text).

Table 5. Barite solubilities in NaCl-H₂O solutions at even values of temperature, pressure, and NaCl concentration

Temp. °C	Press. bars	NaCl in moles/kg H ₂ O								
		0.0	0.1*	0.2	0.5*	1*	2*	3*	4	6**
(BaSO ₄ in millimoles/kg H ₂ O)										
100	1	0.0168	0.058	0.079	0.123	0.172	0.240	0.290	0.333	0.38
	500	0.0260	0.084	0.112	0.147	0.233	0.330	0.38	0.415	0.48
150	4-5†	0.0145	0.056	0.080	0.143	0.220	0.337	0.425	0.50	0.61
	500	0.0232	0.078	0.118	0.188	0.297	0.44	0.52	0.63	0.74
200	13-15†	0.0084	0.0415	0.067	0.130	0.232	0.43	0.555	0.68	0.90
	500	0.0141	0.070	0.108	0.208	0.340	0.562	0.74	0.90	1.15
250	36-39†	0.0044	0.0305	0.053	0.125	0.247	0.495	0.725	0.94	1.30
	500	0.0079	0.0505	0.087	0.195	0.350	0.72	1.03	1.32	1.77

*interpolated solubility
 **extrapolated solubility
 †range of vapor pressures

tion is attested to by the occurrence of concentrated salt solutions in barite fluid inclusions (Roedder, 1972). In solutions with NaCl concentrations above 1 mole/kg H₂O, barite solubility shows no maximum but increases continuously with increasing temperature. Barite solubility in NaCl solutions would increase with depth because of increased temperature and pressure. Therefore, constant-NaCl barite-saturated solutions that migrate upward from depth toward the surface could deposit some barite. The dilution of barite-saturated NaCl solutions with H₂O at constant temperature and pressure would produce

undersaturated solutions. Barite solubility in H₂O and in NaCl-H₂O solutions is quite low. The presence of MgCl₂ and CaCl₂ (Uchameyshvili *et al.*, 1966) increases barite solubilities, but only to a minor extent. Oxidation and reduction of sulfur species in solution probably have a more important role in the precipitation or dissolution of barite in nature than solubility. Barite solubilities are so low that the transport of large amounts of BaSO₄ in simple H₂O or NaCl-H₂O solutions seems highly improbable. Therefore, the deposition of barite in nature most likely requires the mixing of two different ground-

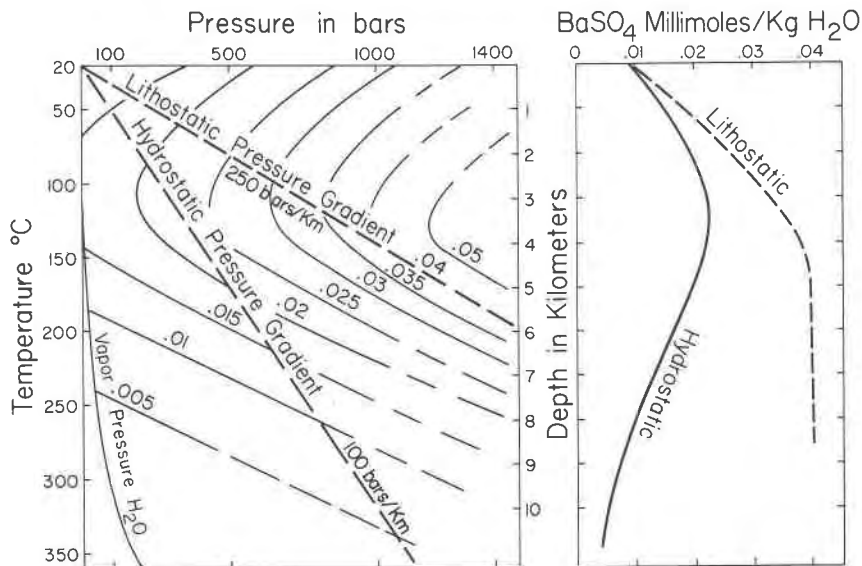


Fig. 5. Barite solubility in H₂O solutions at depth under specified geothermal pressure-gradient conditions. (5a) Constant-composition curves (millimoles/kg H₂O) on the barite saturation surface projected on the *T,P* plane. (5b) Barite solubility at depth in km, obtained from 5a assuming a geothermal gradient of 30°C/km at conditions approximating hydrostatic and lithostatic pressures.

Table 6. Evaluation of log K for the solution of barite in water

$T^{\circ}\text{C}$	1 bar -log K	100 bars -log K	500 bars -log K	1000 bars -log K	1400 bars -log K
25	9.98	9.88	9.51	9.12	---
60	9.67	9.61	9.30	8.96	8.69
80	9.63	9.55	9.24	8.89	8.65
100	9.59	9.53	9.22	8.87	8.61
125	9.62	9.53	9.22	8.85	8.57
150	9.73	9.65	9.32	8.91	8.61
175	9.94	9.86	9.50	9.09	8.73
200	10.22	10.11	9.75	9.30	8.95
225	10.53	10.40	9.99	9.50	9.14
250	10.80	10.69	10.24	9.72	---
300	11.44	11.31	10.73	10.13	---

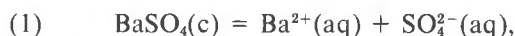
water solutions. For example, a Ba^{2+} solution could encounter a SO_4^{2-} solution, or a solution containing both Ba^{2+} and some sulfide ion could encounter oxygen-bearing ground waters that can oxidize sulfide to sulfate.

Thermodynamic quantities

Introduction

This section presents thermodynamic quantities calculated from barite solubility data and compares them with literature values. The calculated quantities for the reaction of barite with aqueous solutions in-

clude: logarithms of thermodynamic equilibrium constants, log K ; standard free energies ΔG ; enthalpies, ΔH ; entropies, ΔS ; volume changes, ΔV ; and heat capacities at constant pressure, ΔC_p ; and heat capacities at constant temperature, ΔC_T .¹ The reaction considered for these calculations was,



in which the reactant is barite (c) and the products are the ions in solution (aq) at the hypothetical standard state of unit molality ($m = 1$).

Evaluation log K and ΔG

The first step in the treatment of the solubility data was to calculate values for log K using the relationship,

$$(2) \quad \log K = 2 \log m + 2 \log \gamma_m$$

in which m represents the molality of saturated solutions and γ_m is the mean activity coefficient on the molality scale. Activity coefficients were calculated using an extended form of the Debye-Hückel equa-

¹ The superscripts and subscripts commonly used in thermodynamic expressions, as in the tables and figures, have been omitted from the text to reduce the time and cost of typesetting.

Table 7. Values for -log K for barite solubility at 1 bar

Temp. $^{\circ}\text{C}$	Present Study	MeIcher (1910)	Templeton (1960)	Malinin et. al. (1969)	Helgeson (1969)	Strübel (1967)	Calculated* (ion data)	Equation 5 Table 10	Equation 3 Table 10
25	9.98	9.96	9.96	9.72	9.70		9.97	9.97	9.97
35			9.83						
50		9.70	9.71	9.49	9.42				
60	9.67						9.56	9.60	9.66
65			9.66						
75				9.44					
80	9.63		9.62					9.53	9.59
95			9.59						
100	9.59	9.58		9.45	9.22	9.50	9.49	9.52	9.59
125	9.60			9.55				9.60	9.65
150	9.73			9.70	9.34	9.40	9.50	9.75	9.78
175	9.94			9.90				9.94	9.96
200	10.22			10.15	9.67	9.47	10.00	10.18	10.20
225	10.53			10.45				10.46	10.47
250	10.80			10.90	10.34	9.60	10.47	10.75	10.77
275	11.12			11.45					
300	11.44			12.15	11.05	9.83	11.10	11.40	11.47

*Calculated using Thermodynamic data in the literature. Refer to text.

tion

$$(3) \quad \log \gamma_m = \frac{-|Z_+Z_-| A_m \sqrt{I_m}}{(1 + B_m a_i \sqrt{I_m})}$$

in which $|Z_+Z_-|$ is the absolute value of the product of ionic charges (4 for BaSO_4), A_m and B_m are temperature and solution density dependent parameters that include the dielectric and several other physical constants, I_m is the ionic strength of solutions on the molality scale, and a_i is an ion-size parameter. The required physical constants were obtained from the *Revised List of Physical Constants* (National Bureau of Standards, 1971). The dielectric constant was calculated from equations 1, 2, and 3 given by Quist and Marshall (1965), which depend only upon temperature and solution density. Solution densities at the low concentrations considered were assumed to be the same as those for water at the same temperature and pressure. Water densities were obtained from Kennedy *et al.* (1958) and Holser and Kennedy (1958). An average value for the ion-size parameter was obtained from Kielland (1937). $\log \gamma_m$ values ranged from 0.013 to 0.036 for the experimental conditions covered in this study. As previously stated, uncertainties in the solubility data were about ± 5 percent or ± 0.02 in $\log m$. Since uncertainties in $\log \gamma_m$ are much less than the calculated values, the uncertainty in $\log K$ is essentially 2 times the uncertainty in $\log m$ or ± 0.04 . The 300°C values of $\log K$ have an uncertainty of ± 0.10 introduced by the short extrapolation needed to obtain $\log m$ values.

Calculated values for $\log K$ are presented in Tables 6 and 7 and plotted against $1/T$ in Figure 6. There is a maximum in $\log K$ near 100°C at all pressures. Increasing pressure causes $\log K$ values to increase almost linearly. The 1 bar $\log K$ values above 100°C were calculated from solubilities estimated by extrapolating downward from solubilities at the vapor pressures. Uncertainties introduced by the short extrapolation are small and therefore do not significantly affect the uncertainty in $\log K$ values. Many different values for $\log K$, most of which were at or near 25°C, but some at elevated conditions, have been cited by Sillen and Martell (1964, 1971). Values at 25°C and above, obtained from the studies by Melcher (1910), Templeton (1960), Strübel (1967), Malinin *et al.* (1969), and Helgeson (1969) are given in Table 7. The solubility data of Melcher and Templeton were in agreement with the present study, and their $\log K$ values naturally agree. Values reported by Malinin *et al.* are higher (less negative) below 150°C and lower above this temperature. Helgeson's $\log K$ values are

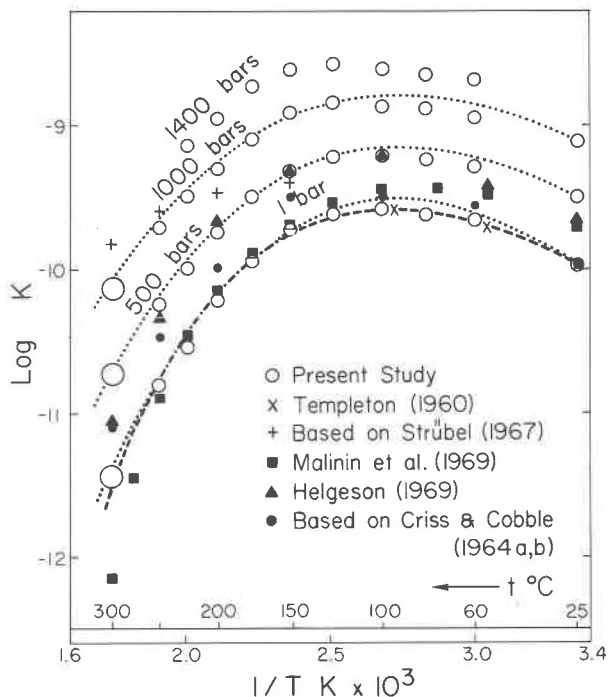


Fig. 6. Values for $\log K$ as a function of the reciprocal of the absolute temperature at 1, 500, 1000, and 1400 bars. $\log K$ values obtained in previous determinations or calculated from thermodynamic data are shown for comparison. Dotted curves represent values calculated from equation 5 in Table 10. Dashed curves represents values calculated from equation 3 in Table 10. Size of open circle represents the uncertainty.

higher at all temperatures. $\log K$ values calculated using thermal data for crystalline barite (Kelley, 1960), entropies for ions (Latimer, 1952), and entropy and heat capacity data for the ions in aqueous solution at higher temperatures (Criss and Cobble, 1964 a,b) differ from values obtained in other studies except at 25°C. The differences can be accounted for by changing ΔH by 300 calories or ΔS by 1 entropy unit.

ΔG values calculated from the equation,

$$(4) \quad \Delta G = -2.3025 RT \log K,$$

are listed in Table 9. Uncertainties in ΔG range from 60 to 250 calories, depending upon temperature and uncertainty in $\log K$. ΔG values are positive for all conditions, and steadily increase in value with increasing temperature. The value at 25°C and 1 bar agrees with Parker *et al.* (1971) but disagrees with Latimer *et al.* (1933) and Latimer (1952) (see Table 8).

Evaluation of ΔV , ΔH , and ΔS

The calculation of other thermodynamic quantities requires evaluation of the following relationships,

Table 8. Comparison of thermochemical data for dissolution of barite at 298.15°K and 1 bar

Source of data	ΔG_R° kcal/mole	ΔH_R° kcal/mole	ΔS_R° cal/mole K
Parker et al. (1971)*	+13.6 ± 0.2	+6.3 ± 0.25	-24.5 ± 0.45
Latimer et al. (1933)	+13.72	+5.46	-27.7
Latimer et al. (1952)	+12.06	+4.63	-24.5
Present study (Delta Process)	+13.6 ± 0.2	+6.35 ± 1.2	-24.3 ± 3.5
Equation 3 Table 10	+13.61	+5.03	-28.8

*Uncertainty from Parker as a personal communication

$$(5) \quad (\partial \Delta G / \partial P)_T = -RT(\partial \ln K / \partial P)_T = \Delta V$$

$$(6) \quad \{[\partial(\Delta G/T)]/[\partial(1/T)]\}_P = -R[\partial \ln K / \partial(1/T)]_P = \Delta H, \text{ and}$$

$$(7) \quad -(\partial \Delta G / \partial T)_P = R(\partial \ln K / \partial T)_P + R \ln K = \Delta S.$$

The data for $\log K$ and ΔG can be modeled by many different empirical equations (e.g. equations 3, 4, and 5 in Table 10). Values for ΔV , ΔH and ΔS are represented by the appropriate first derivatives of these equations. The values obtained, however, depend upon the type of model equation used. At present there is no theoretical basis for selecting a particular model equation over others.

Volume changes. ΔV values were obtained by differentiating both linear and quadratic equations that modelled isothermal variations of ΔG with pressure

with almost an equal degree of fitness. Calculated values for ΔV are illustrated in Figure 7. Values are markedly negative under all conditions. A maximum occurs near 75°C. Quadratic equation values are more negative than linear equation values. Also, values obtained from quadratic equations all showed that ΔV increased with pressure, as illustrated by the 1000 bar curve in Figure 7. Uncertainties in the ΔV values are estimated to be about ± 10 percent of the value.

For comparison, ΔV values were also calculated from the molar volumes of barite (Robie *et al.*, 1967), corrected for thermal expansion (Skinner, 1966) and the partial molal volumes for the ions (Ellis, 1967, 1968; and Millero, 1972) using the equation,

$$(8) \quad \Delta V = \bar{V}_{Ba^{++}} + \bar{V}_{SO_4} - V_{\text{barite}(c)}$$

Results of these calculations are shown by solid dots in Figure 7. Below 150°C, values obtained from linear equations are closer to those based on data for ions, whereas values obtained from quadratic equations are closer at higher temperatures. The solid curve in Figure 7 represents ΔV values calculated from an empirical equation (equation 1a in Table 10) based upon data for ions up to 200°C and the values obtained from quadratic equations above this temperature. The values obtained from this equation are within uncertainty estimates of Ellis (1967, 1968). ΔV values at 1000 bars were obtained by taking the difference between the 1- and 1000-bar values obtained from the quadratic equations, and adding this difference to the 1-bar values calculated from the empirical equation. Since most of the 1000-bar values of ΔV fall 15 percent above the 1-bar values, they differ

Table 9. Thermodynamic quantities for the solution of barite at 1 bar

Temperature K	ΔG_R° kcal mole	ΔH_R° kcal mole	ΔS_R° cal mole	ΔV_R° cal mole	ΔH_{-R}° * kcal mole	ΔH_{-R}° ** kcal mole	ΔS_R° * cal mole
298.15	13.61	6.35	-24.3	-1.24	6.3	5.0	-24.5
333.15	14.74	2.97	-35.3	-1.09	3.3	2.7	-34.0
353.15	15.56	1.04	-41.1	-1.11	---	1.0	---
373.15	16.37	- 0.89	-46.2	-1.18	0.0	- 0.5	-43.5
398.15	17.49	- 3.30	-52.2	-1.35	---	- 2.6	---
423.15	18.84	- 5.72	-58.0	-1.58	- 4.0	- 5.0	-53.0
448.15	20.39	- 8.13	-63.6	-1.87	---	- 7.7	---
473.15	22.12	-10.55	-69.0	-2.20	- 8.9	-10.5	-64.6
498.15	23.99	-12.96	-74.2	-2.58	---	-13.5	---
523.15	25.58	-15.37	-78.8	-2.98	-14.4	-16.7	-75.7
573.15	30.00	-20.20	-87.3	-3.87	-20.4	-23.8	-86.5

*Calculated using data for ions given by Criss and Cobble (1964a,b).

**Calculated by differentiation of equation 3 in Table 10.

significantly from ΔV at 1 bar. One calculation of ΔV at 1000 bars and 25°C, using partial molal ionic compressibilities and equations of Owen and Brinkley (1941), is 24 percent above the 1 bar value.

Heats of reaction. Differentiation of empirical equations such as 3 and 4 in Table 10 which model $\log K$ or ΔG variation with temperature (equations 6 and 7 in this section), produces ΔH and ΔS values at 25°C that do not agree with values calculated from standard-state data of Parker *et al.* (1971). ΔH values were therefore calculated using a delta process based upon text equation 6. Differences between values for $\Delta G/T$, $(-R \ln K)$, for successive data points listed in Table 6 were divided by the difference in $1/T$ values. The ΔH values at mean temperatures shown on Figure 8 do not fall along simple smooth curves. Uncertainties are large, and linear equations calculated for 1, 100, 500, and 1000 bars fit the data within the uncertainty limits shown. The terms of the four equations varied almost linearly with pressure, and the four equations were combined to produce equation 2 (Table 10), from which ΔH values may be calculated for desired temperatures and pressures. The solid lines of Figure 8 are based on values calculated from this equation. A closer reproduction of the data points in Figure 8 by higher-order equations is not

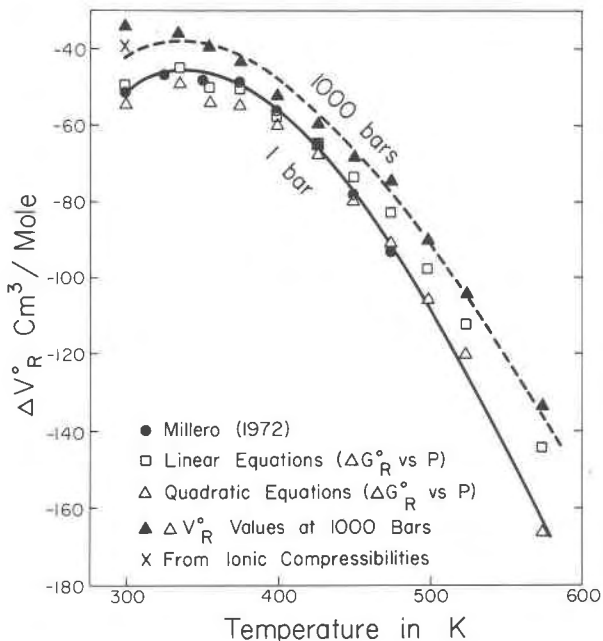


Fig. 7. Change in volume for reaction of barite with H₂O at infinite dilution, ΔV as a function of temperature at 1 and 1000 bars. ΔV value calculated from partial molar volumes of BaSO₄ in solution and molar values of barite are shown for comparison (see text).

Table 10. Equations for thermodynamic quantities and parameters for Debye-Hückel equation

(1a)	$\Delta V_R^\circ = -1.3722 \times 10^5 T^{-1} - 1.20391 T + 767.58$ ΔV_R° in cm ³ /mole
(1b)	$\Delta V_R^\circ = -3.281 \times 10^3 T^{-1} - 2.8788 \times 10^{-2} T + 18.35$ ΔV_R° in cal/moles bar
(2)	$\Delta H_R^\circ = 2.9674 \times 10^{-2} P T - 96.594 T - 10.7696 P + 35154$ ΔH_R° in cal/mole
(3)	$\Delta G_R^\circ = 1.15046 \times 10^{-4} T^2 - 4.02952 \times 10^{-2} T + 15.386$ ΔG_R° in kcal/mole
(4)	$\log K^\circ = -1.45823 \times 10^3 T^{-1} \log T + 3.55471 \log T - 9.036696$ $\times 10^{-3} T \log T$
(5)	$\log K^\circ = (1.49325 \times 10^{-2} P - 48.61) \log T$ $+ (2.35365 P - 7682.76) T^{-1} - 4.398 \times 10^{-2} P + 136.079$
(6)	$\alpha_i = 3.839 + 5.155 \times 10^{-3} T - 1.263 \times 10^{-5} T^2 + 1.401$ $\times 10^{-3} P - 3.02 \times 10^{-6} P T$ α_i in Angstroms; parameter in eq 12
(7)	$C = -0.484 + 2.376 \times 10^{-3} T - 3.338 \times 10^{-6} T^2 - 1.73$ $\times 10^{-5} P + 1.00 \times 10^{-7} P T$ parameter in eq 12

justified, because of the large uncertainties in the data. The average difference between the ΔH values calculated from the equation and the data points is ± 1.2 kcal/mole. The ΔH values at 25°C and 1 bar calculated in this study agree with ΔH values obtained using standard data cited by Parker *et al.* (1971) and Parker (personal communication, 1974), as shown in Table 8. Values obtained from Latimer *et al.* (1933) and Latimer (1952) do not agree with those from Parker or based on the present study.

Entropies and heat capacities of reaction. Values for ΔS were calculated from Gibbs-Helmholtz equation,

$$(9) \quad \Delta S = \Delta H/T + 2.3025 R \log K,$$

using $\log K$ data from Table 6 and ΔH values calculated from equation 2 (Table 10). Values for ΔS at 1 bar are given in Table 9. The value at 25°C agrees with that calculated from standard-state data (see Table 8).

As a further check on the calculation procedures, equations 1 and 2 in Table 10 were compared, using the following thermodynamic equations of state,

$$(10) \quad (\partial \Delta H / \partial P)_T = \Delta C_T = \Delta V - T(\partial \Delta V / \partial T)_P \text{ and}$$

$$(11) \quad (\partial \Delta V / \partial T)_P = -(\partial \Delta S / \partial P)_T.$$

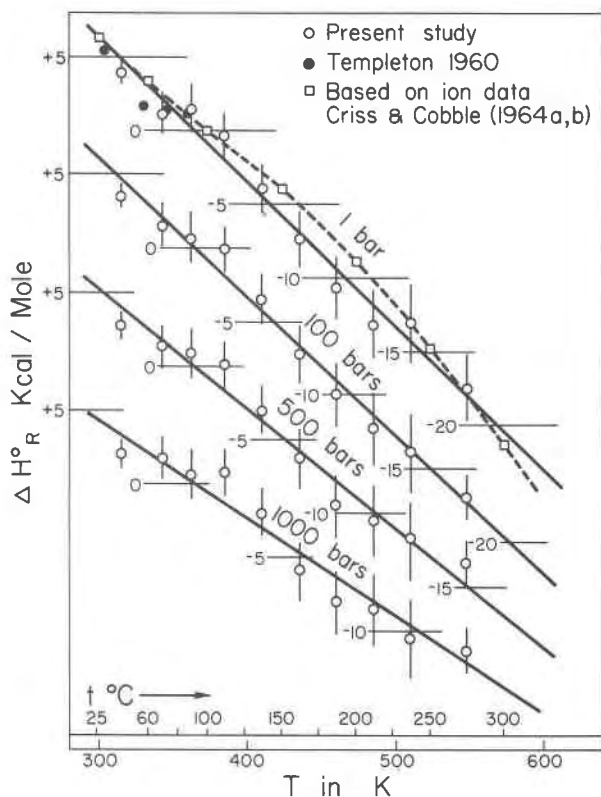


Fig. 8. Evaluation of the heat of reaction at infinite dilution, ΔH , as a function of temperature at constant pressures of 1, 100, 500, and 1000 bars. The open circles represent values obtained for successive temperature intervals of the function,

$$[\Delta G_{(T_2)}/T - \Delta G_{(T_1)}/T]/(1/T_2 - 1/T_1),$$

plotted at the average temperature. The length of vertical bar gives the uncertainty in the calculation. Refer to text for description of curves.

Values for ΔC_t calculated from equations 1 and 2 in Table 10 are in good agreement, considering the uncertainties in the data. The cross derivatives in equation 11 were also found to be within acceptable agreement.

Values for ΔH and ΔS from 25 to 300°C were also calculated, using data for ionic entropies and heat capacities given by Criss and Cobble (1964a, 1964b), data for barite given by Kelley (1960), standard data for ions given by Latimer (1952), and standard-state data given by Parker *et al.* (1971). The results of these calculations are given in Table 9. ΔH values at 1 bar are also shown in Figure 8. The agreement between the sets of ΔH and ΔS data in Table 9 is good. Most values are within estimated uncertainty ranges.

Values for ΔC_p obtained by differentiation of equation 2 in Table 10 are markedly negative (-96 cal/mole °K at 1 bar). Uncertainties are very large.

The linear equation used to represent ΔH data variation with temperature assumes that ΔC_p does not change with temperature. It is known that ΔC_p values vary with temperature (Criss and Cobble, 1964b; and Criss, personal communication, 1974). The values obtained from equation 2 at each pressure then represent an average value over the temperature range 25 to 300°C. The average value at 1 bar is fairly close to the average obtained from values given by Criss and Cobble. Pressure rise significantly increases ΔC_p values. Most of this change is due to changes in the ionic heat capacities. Details of both the temperature and pressure dependences of ΔC_p cannot be evaluated from the solubility based data.

Calculation of log K from ΔH data

Integration of equation 2 in Table 10 with respect to $1/T$ yields values for log K and ΔG . Integration constants were calculated from the log K values of Table 6 at 298°K. Since the integration constants varied almost linearly with pressure, a single equation of log K was obtained and is given in Table 10 as equation 5. Log K values obtained from this equation are given in Table 7 and illustrated by dotted curves in Figure 6. There is good agreement with log K values in Table 6 except at 60 to 100°C. The differences in this temperature interval are greater than the uncertainties in log K values. The model, equation 5 in Table 10, is too simplified. The closeness of the fit at most temperatures shows that log K calculations are not very sensitive to the values of ΔC_p . Values for ΔC_p obtained by successive differentiation of equations 3 or 4 in Table 10, which model the log K and ΔG data very well, differ markedly from those obtained from Criss and Cobble (1964b) and Criss (personal communication, 1974). However, values of ΔC_p obtained by such differentiations are generally little better than guesses.

Activity coefficients for $BaSO_4(aq)$

Barite solubilities in salt solutions and the previously-determined equilibrium constants were used to calculate logarithms of the mean activity coefficient, γ_m , for $BaSO_4$ in solution, using text equation 2. Barite solubilities in 0.2, 1, and 4 molal NaCl solutions from Table 5, the values of log K at the temperature and pressure specified, and the calculated log γ_m values are given in Table 11. Barite solubilities at 25°C were obtained from Puchelt (1967, Fig. 2). Log γ_m values become more negative with increasing temperature or increasing NaCl con-

Table 11. Measured and calculated activity coefficients for BaSO₄ in NaCl-H₂O solutions

T°C	P bars	NaCl Molal	BaSO ₄ Milli-Molal	ρ [†] gm/Cm ³	-log K ⁰ Eq (2)	log γ _m Eq (2)	log γ _m Eq (12)	a _i x10 ⁸ Cm	C
25	1	0.2	0.037*	1.010	9.98	-0.56	-0.57	4.25	-0.073
100	1	"	0.079	0.966	9.59	-0.69	-0.68	4.00	-0.062
"	500	"	0.112	0.988	9.22	-0.66	-0.65	4.14	-0.052
150	5	"	0.082	0.924	9.73	-0.78	-0.79	3.76	-0.076
"	500	"	0.118	0.951	9.32	-0.73	-0.75	3.82	-0.064
200	15	"	0.068	0.875	10.21	-0.94	-0.94	3.45	-0.107
"	500	"	0.108	0.905	9.75	-0.91	-0.89	3.44	-0.092
250	39	"	0.053	0.823	10.76	-1.10	-1.13	3.07	-0.153
"	500	"	0.087	0.858	10.24	-1.06	-1.06	2.99	-0.137
25	1	1.0	0.077*	1.036	9.98	-0.91	0.88	4.25	-0.073
100	1	"	0.172	0.997	9.59	-1.03	-1.04	4.00	-0.062
"	500	"	0.233	1.016	9.22	-0.98	-0.98	4.14	-0.052
150	5	"	0.220	0.957	9.73	-1.21	-1.20	3.76	-0.076
"	500	"	0.297	0.981	9.32	-1.13	-1.14	3.82	-0.064
200	15	"	0.232	0.909	10.21	-1.47	-1.45	3.45	-0.107
"	500	"	0.340	0.936	9.75	-1.41	-1.38	3.44	-0.092
250	38	"	0.240	0.849	10.76	-1.76	-1.80	3.07	-0.153
"	500	"	0.350	0.887	10.24	-1.66	-1.70	2.99	-0.137

centration. Increasing pressure causes values to become less negative.

The solubility-based log γ_m values were compared with values calculated from text equation 3, an extended form of the Debye-Hückel equation. Values obtained from equation 3 disagreed systematically with those obtained from equation 2. Equation 3 assumes that the mean ion-size parameter does not change with temperature and pressure. Malinin *et al.* (1969) varied the a_i values in their calculations of log K at high temperature. However, the use of their a_i values resulted in an overcorrection. Also, variation of the a_i parameter alone did not result in a satisfactory correction. In a study of the thermodynamics of CaSO₄·2H₂O in NaCl solutions, Marshall and Slusher (1966) varied the product B_ma_i and added terms to the Debye-Hückel equation that were proportional to the ionic strength and the square of the ionic strength. It was found necessary to add a term linear with respect to ionic strength to equation 3 to produce the equation,

$$(12) \quad \log \gamma_m = \frac{-|Z_+Z_-| A_m \sqrt{I_m}}{(1 + B_m a_i \sqrt{I_m}) + C I_m}$$

in which a_i and C are temperature- and pressure-dependent parameters. Log γ_m values calculated using equation 12 and the appropriate a_i- and C- parameter values are listed in Table 11. Equations for calculating a_i and C are given as equations 6 and 7 in Table 10.

Curves representing barite solubility variation with NaCl concentration in Figures 4 and 9 are based on solubility values calculated using equation 2, log γ_m from equation 12 and log K from Table 6. A marked discrepancy exists between solubility measurements at 25°C of Puchelt (1967) and those by Neuman (1933, in KCl solutions), Templeton (1960), and Strübel (1967). Puchelt's results agree with those calculated from equation 12. To fit the solubility data of

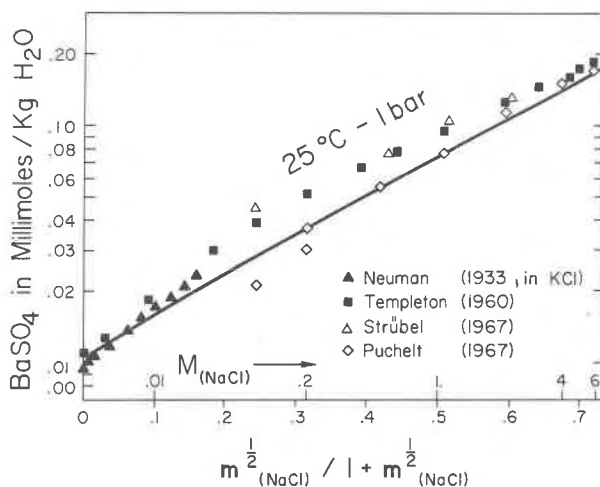


Fig. 9. Barite solubility in NaCl-H₂O solutions at 25°C, 1 bar, as a function of NaCl concentration. The curve represents solubilities based upon calculations using an extended Debye-Hückel equation (refer to text).

other workers, a_i in equation 12 would have to be near 2×10^{-8} cm, which does not agree with Kieland's value (1937). Furthermore, an abrupt change in the temperature-dependence of the ion-size parameter a_i would be required. Therefore, the solubility measurements by Neuman, Templeton, and Strübel in salt solutions are probably too large. Templeton's (1960) data were used to calculate $\log K$ and ΔG values at 25°C (Parker, personal communication), and this value is based upon extrapolation of data that may not represent the solubility of coarsely-crystalline barite. The ΔG value may still be correct within the uncertainty limit given by Parker (see Table 8).

Conclusions

Barite solubilities of this study have been compared with previous determinations and have also been used to calculate thermodynamic quantities for the dissolution of barite in aqueous solutions. There is considerable disagreement between the results of this study and most previous studies. Barite solubilities of this study were made using a pure, coarsely-crystalline barite under reproducible and reversible conditions. Present results show smoother variations with temperature, pressure, and NaCl concentration than do most previous results. An additional important observation that seems to confirm the greater accuracy of the present solubility measurements is the close agreement between thermodynamic quantities calculated from these solubilities and those calculated from thermal and solution density data. Barite solubilities of this study are compatible with the standard-state quantities reported for barite and BaSO₄ in solution (Parker *et al.*, 1971). Although uncertainties are rather large, thermodynamic quantities calculated from the solubility data at temperatures from 25 to 300°C agreed with those obtained from the literature for partial molal volumes, enthalpies, entropies, and heat capacities. Activity coefficients obtained from barite solubilities in NaCl solutions and solubility-based $\log K$ values were accurately modeled by an extended form of the Debye-Hückel equation up to high NaCl concentrations. Most of the previous solubility data produce calculated thermodynamic quantities that differ significantly from those based on thermal measurements. The results of those thermodynamic calculations support the accuracy of the solubilities of this study and those of the studies by Puchelt (1967) and Uchameyshvilli *et al.* (1966).

The solubility of barite is very low under all experi-

mental conditions examined in the present study. No mechanism can be predicted from solubility data or the thermodynamic calculations that would significantly alter the solubility relations so that appreciable BaSO₄ can be carried in hydrothermal solutions. The most probable cause of BaSO₄ deposition is the oxidation of reduced sulfur species to sulfate in solutions carrying barium.

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