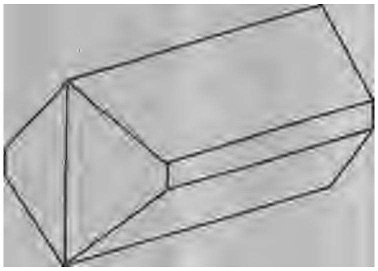
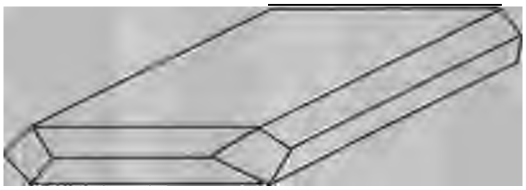
Circular 116 *1971*



SOLUBILITY AND ENTHALPY OF THE BARIUM-STRONTIUM SULFATE SOLID SOLUTION SERIES



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Circular 116

SOLUBILITY AND ENTHALPY OF THE BARIUM - STRONTIUM SULFATE SOLID SOLUTION SERIES

by Elise Brower and Jacques Renault

Socorro
1971

New Mexico Bureau of Mines and Mineral Resources
Don H. Baker, Jr., *Director*

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ABSTRACT

Strontium sulfate in equilibrium with aqueous solution leaches selectively from barium-strontium sulfate solid solutions at 25 degrees centigrade and at 1 atmosphere. Equilibrium concentrations of Sr^{++} and Ba^{++} in aqueous solution are not significantly different from values calulated on the assumption that the chemical activity of each component is proportional to its mole fraction in the solid.

The enthalpy of mixing for barium-strontium sulfate $(Ba,Sr)SO_4$ solid solutions was determined by calorimetry to be approximately zero at 25° and 61°C. The thermodynamic properties are, therefore, characteristic of an ideal mixture.

Nearly pure barite occurs frequently in hydrothermal deposits, whereas celestite and barium-strontium sulfate solid solutions of intermediate composition are scarce. Separation of the two sulfates could be the result of fractional precipitation in the presence of low sulfate concentrations or by leaching of an antecedent solid solution.

INTRODUCTION

The concentration of barium in the earth's crust is slightly greater than strontium in a ratio of 1.13 to 1, and the two elements exhibit a similar geochemistry in igneous rocks (Mason, 1966; Rankama and Sahama, 1950; and Hanor, 1966). However, barite is a common mineral in hydrothermal deposits, whereas celestite and $(Ba,Sr)SO_4$ solid solutions of intermediate composition are rare (Deer et al., 1962; Palache et al., 1951). Both celestite and barite are commonly found in sedimentary deposits, but intermediate $(Ba,Sr)SO_4$ is apparently rare in these rocks. Although the $BaSO_4$-$SrSO_4$ system has been studied by others, some of the factors which may govern the geochemical distribution of barite and celestite are not well understood. We have studied certain physicochemical properties which are pertinent to the precipitation and dissolution of $(Ba,Sr)SO_4$ in order to understand the conditions in which hydrothermal sulfates are deposited and recrystallized.

This report describes experimental studies of solubility and enthalpy of precipitation in the $BaSO_4$-$SrSO_4$ system between zero and 100°C at atmospheric pressure. Tentative conclusions are made regarding the deposition of barite and celestite in hydrothermal veins.

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PREVIOUS STUDIES

Previous workers have shown by x-ray analysis that a complete series of synthetic solid solutions exist between barite and celestite in which Ba^{++} and Sr^{++} substitute one for another in the orthorhombic crystal lattice (Bostrom et al., 1968). Some investigators have suggested, however, that it is not experimentally feasible to establish equilibrium between the solid solution and the aqueous solution of $(Ba,Sr)SO_4$ (Gordon et al., 1954; Cohen and Gordon, 1961; and Starke, 1964).

It should be mentioned, however, that their conclusions are based solely on data obtained by precipitation from aqueous solution. One purpose of this study is to remove all doubt concerning the establishment of equilibrium between the solid and aqueous solutions of $(Ba,Sr)SO_4$ by an approach from the opposite end-point, namely by dissolving solid $(Ba,Sr)SO_4$.

Because of the difference in solubility products of the two end-members, $\mathbf{K}_{BaSO4} = \mathbf{10^{-10}}$ and $K_{SrSO4} = \mathbf{10^{-6.4}}$, Ba^{++} preferentially concentrated in the solid phase and Sr^{++} in the aqueous phase in the precipitation of $(Ba,Sr)SO_4$ as shown by the experimental work of Gordon et al. (1954), Cohen and Gordon (1961), and Starke (1964). Gordon et al. (1954) slowly precipitated a solid solution of $(Ba,Sr)SO_4$ and analyzed the aqueous solution at intervals during the precipitation. The results suggested that strontium is heterogeneously distributed throughout the $(Ba,Sr)SO_4$ solid solution.

This heterogeneity is presumed to result from each successive surface layer growing in response to an aqueous phase of progressively increasing strontium content.

Hanor (1968) interpreted the data of Gordon et al. (1954) and Cohen and Gordon (1961) to mean that $(Ba,Sr)SO_4$ is an inert substance which fails to re-equilibrate in response to changes in the composition of the liquid, and he constructed a precipitation model that agrees with the observed frequency distribution in nature.

During the course of a contract research project to develop a commercial process for the chemical separation for barium and strontium in the Mountain Pass, California deposit, we discovered that finely divided $(Ba,Sr)SO_4$ is not chemically inert to aqueous barium ion (Brower and Bhappu, 1969). This study showed that when either fine-grained solid $(Ba,Sr)SO_4$ or pure $SrSO_4$ is equilibrated with an amount of barium chloride in aqueous solution equivalent to the $SrSO_4$ in the solid phase, nearly all the barium is in the solid phase and approximately 98 percent of the strontium is in solution at the end of 24 hours. The metatheses are illustrated by the following equations:

$$\underset{\text{(solid)}}{(Ba,Sr)SO_4} + \underset{\text{(aqueous)}}{BaCl_2} \rightarrow \underset{\text{(solid)}}{BaSO_4} + \underset{\text{(aqueous)}}{SrCl_2} \tag{1}$$

$$\underset{\text{(solid)}}{SrSO_4} + \underset{\text{(aqueous)}}{BaC1_2} \rightarrow \underset{\text{(solid)}}{BaSO_4} + \underset{\text{(aqueous)}}{SrC1_2} \tag{2}$$

The process goes nearly to completion because $BaSO_4$ is more insoluble than $SrSO_4$, and the system is sulfate-deficient: the molar quantity of sulfate ion in the solid and aqueous phases is less than the sum of the molar quantities of barium and strontium ion in the two phases. If the law of mass action determines the outcome of the competition of Ba^{++} and Sr^{++} for $SO_4^{=}$, the partitioning of barium and strontium between aqueous and solid solutions will be determined by the ratio of the equilibrium constants:

$$\frac{[Sr^{++}] / [Ba++]}{N_S \ / N_B} = \frac{{}^{K}SrSO_4}{{}^{K}BaSO_4} \approx 4{,}000\ (25^{\circ}C)$$

where N is the mole fraction of strontium in the solid and N_B is the mole fraction of barium in the solid.

THEORETICAL CONSIDERATIONS

Three hypotheses that might explain the scarcity of natural $(Ba,Sr)SO_4$ of intermediate composition are (1) a deficiency of any one of the component ions, (2) a removal of strontium by the process shown in equation (3)

$$\underset{\text{(solid)}}{(Ba,Sr)SO_4} + \underset{\text{(aqueous)}}{CO_3^{=}} \longrightarrow \underset{\text{(solid)}}{BaSO_4} + \underset{\text{(solid)}}{SrCO_3} + \underset{\text{(aqueous)}}{SO_4^{=}} \qquad (3)$$

or (3) the thermodynamic instability of intermediate $(Ba,Sr)SO_4$ relative to the end-members. Since the first two hypotheses could occur under particular geological circumstances, this investigation attempts to evaluate to hypothesis (3). Is the formation of intermediate $(Ba,Sr)SO_4$ from barite and celestite a spontaneous process, and, if so, how closely does the solid solution approach ideality?

The free energy of mixing pure barite and celestite to form one mole of solid solution is given by the following expression:

$$\Delta F_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (4)$$

If the process is spontaneous, then ΔF_{mix} must have a negative value. For an ideal solution there is no difference in the interaction energy between like and unlike molecules; therefore, the heat of mixing is zero. If the heat of mixing is zero for the $(Ba,Sr)SO_4$ solid solution, then the heat evolved in the precipitation of one mole of $(Ba,Sr)SO_4$ should be the sum of the molar heats for precipitating the individual components multiplied by their mole fractions, as illustrated in (5) and (6) where N_B and N_S are the mole-fractions of $BaSO_4$ and $SrSO_4$ in the solid solution respectively.

$$\Delta H_{mix} = O \qquad (5)$$

$$\Delta H_{ppt(Ba_{N_B},Sr_{N_S})SO_4} = N_B\Delta H_{ppt(BaSO_4)} + N_S\Delta H_{ppt(SrSO_4)} \qquad (6)$$

When the enthalpy of mixing is zero, the only contribution to the free energy of mixing is the entropy term, $-T\Delta S_{mix}$. The entropy of mixing one mole of solid solution is given in (7), and the free energy of mixing in (8).

$$\Delta S_{mix} = -R(N_B \ln N_B + N_S \ln N_S) \qquad (7)$$

$$\Delta F_{mix} = RT(N_B \ln N_B + N_S \ln N_S) \qquad (8)$$

Therefore, when $\Delta H = O$, regardless of the values of the respective mole fractions, the value of ΔF_{mix} is always negative, and the formation of an ideal solid solution is a spontaneous process. A more extensive treatment of the thermodynamics of mixing is given in Hildebrand and Scott (1950).

To determine how closely the $(Ba,Sr)SO_4$ solid solution approaches ideality, an expression for equilibrium between a solid solution and an aqueous solution was derived as follows: where

ΔF_S = standard free energy of pure $SrSO_4$

K_S = equilibrium constant for pure $SrSO_4$ in equilibrium with its aqueous solution

$\Delta F_S'$ = standard free energy of one mole of $SrSO_4$ as a component of $(Ba,Sr)SO_4$ with mole-fraction N_S

K_S' = equilibrium constant for $SrSO_4$ as a component of a solid solution in equilibrium with its aqueous solution

$\Delta F_S^{(mix)}$ = change in ΔF_S when one mole of $SrSO_4$ is mixed in a solid solution of mole fraction N_S.

The free energy of mixing per mole of $SrSO_4$ is the difference between the standard free energy of pure $SrSO_4$ and $SrSO_4$ as a component in $(Ba,Sr)SO_4$ as given in (9).

$$\Delta F_S^{mix} = \Delta F_S - \Delta F_S' \tag{9}$$

For an ideal solution ΔH^{mix} is zero and ΔS^{mix} is $-R\ln N_S$, therefore, ΔF_S^{mix} is given by equation (10).

$$\Delta F_S^{mix} = RT\ln N_S \tag{10}$$

Combining equations (9) and (10) with (11) and (12), which relate the equilibrium constants to the standard free energies, gives equation (13), which relates the equilibrium constant of $SrSO_4$ in solid solution to that of the pure substance.

$$\Delta F_S = -RT\ln K_S \tag{11}$$

$$\Delta F_S' = -RT\ln K_S' \tag{12}$$

$$K_S' = N_S K_S \tag{13}$$

The derivation of an equilibrium expression for $BaSO_4$ is analogous to that for $SrSO_4$.

Equilibrium expressions (14) and (15) apply to the dissolution of $(Ba_{N_B},Sr_{N_S})SO_4$ in water if the solid solution is ideal.

$$[Sr^{++}][SO_4^{=}] = N_S K_S \tag{14}$$

$$[Ba^{++}][SO_4^{=}] = N_B K_B \tag{15}$$

EXPERIMENTAL INVESTIGATIONS

Enthalpy Measurements

The enthalpies of mixing were evaluated in this study by direct calorimetric measurements of the heat of precipitation of solid solutions of $SrSO_4$ and $BaSO_4$ at 25° and 61°C.

The calorimeter and experimental procedure are modeled after that of O'Hara, Wu, and Hepler (1961), but the water bath has been replaced by an ingot of aluminum 8x8x12 inches. A 3.5-inch hole bored through the long dimension contains the Dewar flask, and the ends of the hole are closed by removable 2-inch-thick aluminum plugs. The upper plug has holes for the stirrer and electrical leads to the thermistor bridge and heater.

Barium and strontium chloride solutions were pipetted into the Dewar flask, and a 15-ml sample of 1.0 M Na_2SO_4 was introduced in a sealed glass ampoule. After thermal equilibrium had been established, the ampoule was broken and the change of enthalpy was measured. The heat of dilution of 1.0 M Na_2SO_4 was also measured, and the result used to calculate enthalpies of precipitation at infinite dilution. Experimental error in repeated runs was ± 0.2 kcal/mole.

The chemical reaction that takes place in the calorimeter is given in equation (16).

$$\underset{\text{(aqueous)}}{N_B\,BaCl_2} + \underset{\text{(aqueous)}}{N_S\,SrCl_2} + \underset{\text{(aqueous)}}{Na_2SO_4} \longrightarrow \underset{\text{(solid)}}{(Ba_{N_B},Sr_{N_S})SO_4} + \underset{\text{(aqueous)}}{2NaCl} \tag{16}$$

That the precipitates formed in the calorimetry experiments were true solid solutions and not mechanical mixtures of $BaSO_4$ and $SrSO_4$ was determined by X-ray diffraction.

X-ray powder diffraction patterns were obtained using K_a radiation from a copper target. The Norelco diffractometer was run at 1/8° min^{-1} and the recorder at 0.25°/inch. Ultrapure rubidium iodide was used as an internal standard, since the 200 peak at 20 = 24.22 is well defined and located between the 111 and 002 peaks of $BaSO_4$ and $SrSO_4$. Each 111 diffraction peak was scanned twice in both directions, and the d-spacing of this peak vs mole percent $BaSO_4$ is plotted in fig. 1. The angle 20 was measured to ± 0.01°, which gives a relative error of 1 percent in composition between the barium and strontium end-members of the system. The $(Ba,Sr)SO_4$ precipitates gave single-phase patterns whose diffraction peaks were shifted in proportion to the change in mole composition as the series progressed from one end-member to the other.

The data obtained from the calorimetry experiments are summarized in figs. 2 and 3. A plot of enthalpy of precipitation versus mole fraction of either component should give a straight line for an ideal solution. The theoretical lines representing $\Delta H_{mix} = 0$ are shown for comparison with the analytical results. The mean H of precipitation for $BaSO_4$ and $SrSO_4$ is -3.7 and +0.45 kcal/mole at 25°C and -2.0 and +3.1 kcal/mole at 61°C. The values of H for intermediate composition have a mean deviation of 0.2 kcal/mole from the theoretical lines. Ludd and Lee (1961) give the lattice energies of $BaSO_4$ and $SrSO_4$ as 578 and 591 kcal/mole. Thus, the deviation of the experimental values of H from the theoretical line representing $H_{mix} = 0$ are less than 0.04 percent of the crystal lattice energy, and consequently the $(Ba,Sr)SO_4$ solid solution is nearly ideal.

DISSOLUTION OF $(Ba,Sr)SO_4$

Equilibration Experiments

The ideality of the $(Ba,Sr)SO_4$ solid solution was further tested by determining the concentrations of Sr^{++} ion in solution in equilibrium with solid $(Ba,Sr)SO_4$ of various compositions.

Solid solutions were prepared at 25°C by instantaneous precipitation from solutions containing barium and strontium chloride on addition of excess $Na_t SO_4$ solution. Digestion time was less than 30 minutes. X-ray diffraction patterns showed that the precipitates were composed of single phase for each $(Ba,Sr)SO_4$ composition.

Four grams of each $(Ba,Sr)SO_4$ precipitate were equilibrated in 2 liters of distilled water for one week. During equilibration the vessels were continuously rotated.

Concentrations of Ba^{++} and Sr^{++} in solution were determined by atomic absorption with a model 303 Perkin-Elmer spectrometer. Wherever possible, analyses were checked by the conductimetric method. The maximum relative error for the atomic absorption analysis was ± 10 percent. Analyses by the two methods agreed within 5 percent.

To analyze for sulfate and for barium in solutions containing less than 1 ppm, 2 liters of the solution were dried by evaporation and the residue fused with Na_2CO_3. The sulfate was determined gravimetrically as $BaSO_4$ and the barium determined by atomic absorption.

The data for barium concentrations in solutions saturated with $(Ba,Sr)SO_4$ or mixtures of pure $BaSO_4$ and $SrSO_4$ are relatively inaccurate, because the high sulfate concentrations depress the barium to levels below the limits of detection with the atomic absorption spectrophotometer. The data for Ba^{++}, however, are all within an order of magnitude of the values predicted by equation (15).

For an ideal solid solution in which $N_s \geq 0.1$ the Sr^{++} concentration should be approximately equal to that of sulfate since $K_S >> K_B$. For aqueous solutions saturated with respect to solid solutions having compositions clustered about $(Ba_{0.75}, Sr_{0.25})SO_4$, the strontium ion concentration was found to be nearly equal to the sulfate as predicted by the solubility products. Strontium ion concentration versus $\sqrt{N}$ is plotted for a series of solid solutions in fig. 4.

For an ideal solid solution the activity of the solute in the aqueous phase is equal to its concentration, and the activity in the solid is equal to its mole fraction. A plot of Sr^{++} concentration versus the square root of the mole fraction in the solid should give a straight line for an ideal solid solution. The graph in fig. 4 shows that ideality is closely approached for strontium mole fractions above 0.30. The mean deviation for the cluster of points at $\sqrt{N}=0.45$ from the line representing the ideal solution is approximately 33 percent and corresponds to an activity coefficient of 0.5 for the solid in the solid solution or 1.5 for the ions in solution.

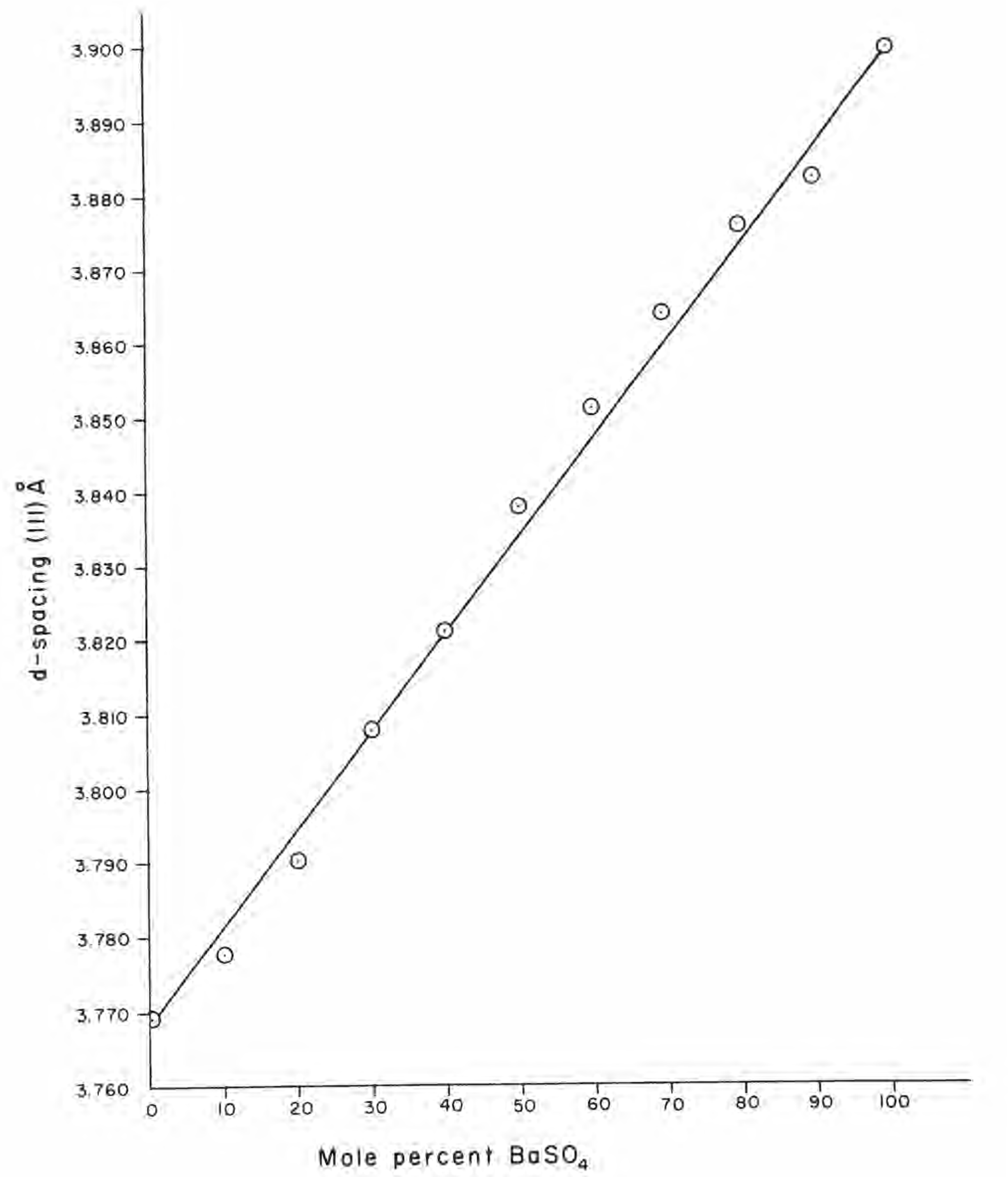

Figure 1. d-spacing (11 1)A versus mole percent $BaSO_4$ in (Ba, Sr)SO4

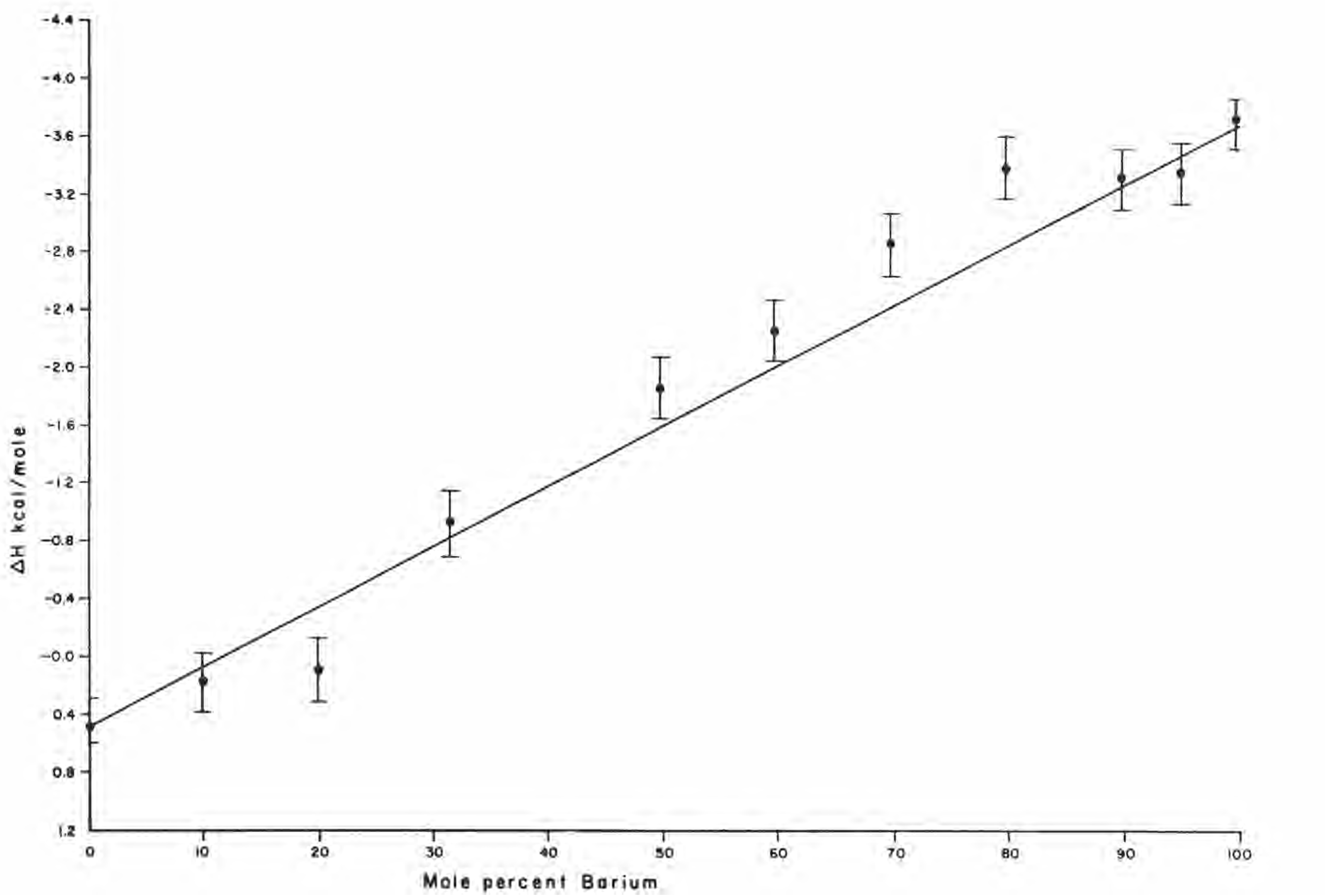

Figure 2. Enthalpy of precipitation of (Ba, Sr)SO_4 in kcal/mole at 25°C.

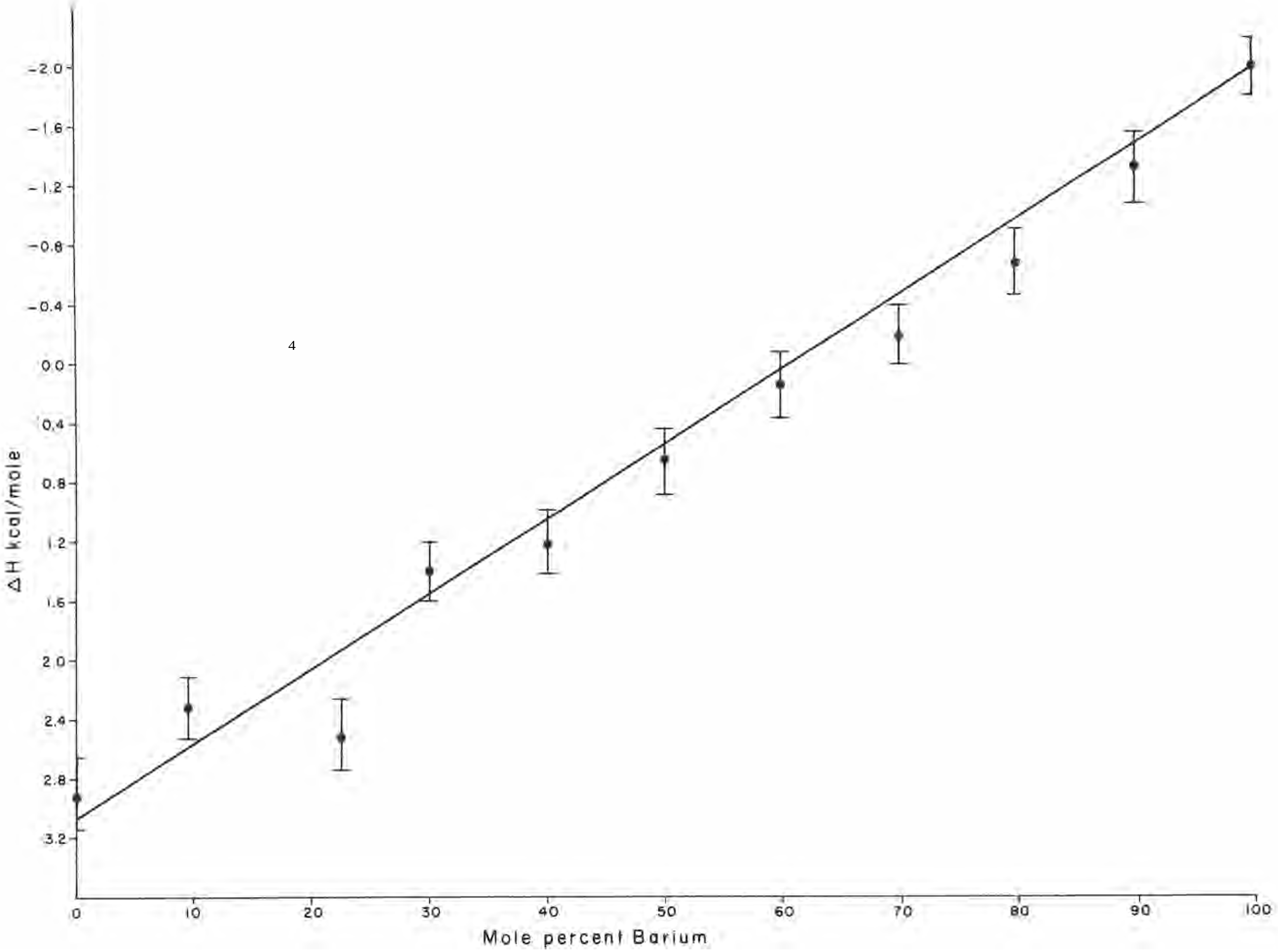

Figure 3. Enthalpy of precipitation of (Ba, Sr)SO$_4$ in kcal/mole at 61°C.

Assuming the discrepancy is real and not the result of imperfect equilibration, there would be a difference of only 0.4 kcal/mole between the real and ideal chemical potentials as calculated from equation (17).

$$\Delta F'_{real} - \Delta F'_{ideal} = -RT\ln\frac{(Sr^{++}ideal)^2}{(Sr^{++}\ meas.)^2} \qquad (17)$$

Serial Leaching Experiments

The solubility of intermediate $(Ba,Sr)SO_4$ is pertinent to the problems of barite-celestite deposition in hydrothermal veins and marine environments. If $(Ba,Sr)SO_4$ remains inert after being precipitated, its composition is an indicator of initial depositional conditions, but if it equilibrates freely with its environment its composition is determined by the post-depositional history. This problem was investigated by following the change in composition of a Sr-rich solid solution as it progressively leaches in successive portions of distilled water.

A 12-gram sample of $(Ba_{.20},Sr_{.80})SO_4$ and 15 liters of distilled water were placed in a 20-liter bottle which was rotated for a month. A 0.5-gram sample of solid and most of the liquid were then removed for analysis. A fresh portion of distilled water was added to the bulk of the solid and the extraction repeated seven times. Since the amount of solid removed represented a significant fraction of the total, the volume of fresh water added was also reduced for subsequent leachings by an appropriate amount.

Particle size of the starting material as well as the leached solid was below the limits of resolution with an optical microscope at 500x.

The composition of the solid phase was determined by a shift in the 111 X-ray diffraction peak, and Sr^{++} concentration in the aqueous phase was determined by atomic absorption spectrometry. Data at 25°C for serial leaching are summarized in fig. 4.

The experimental values of the strontium concentration in aqueous solution in the series of leaching of a strontium-rich $(Ba,Sr)SO_4$ sample are in close agreement with the theoretical values calculated from equation (1 4). Although the Sr^{++} concentrations for leaching a barium-rich solid solution were lower than the theoretical values, the change in concentration from one leach solution to the next in the series was in agreement with that predicted by theory.

The X-ray diffraction patterns of solid $(Ba,Sr)SO_4$ obtained after each equilibration, show that the mole fraction of barium sulfate increased systematically and that finely powdered strontium-rich $(Ba,Sr)SO_4$ can be converted to a single phase homogeneous solid solution of higher barium composition by leaching.

The diffraction peaks of all the solid solutions of intermediate composition were broadened relative to the end-members as shown in fig. 5, and the broadening was most extreme for equimolar $(Ba,Sr)SO_4$. The diffraction peaks of the leached series were also broadened and appeared nearly identical to the peaks of the freshly precipitated $(Ba,Sr)SO_4$ of the same molar composition. The cause of this broadening will be analyzed in a subsequent study.

The results of the serial leaching experiment show clearly that fine-grained $(Ba,Sr)SO_4$ solid solutions of intermediate composition are not chemically inert with respect to distilled water. Consequently, under the conditions of the experiment, the composition of the solid phase reflects the final rather than the initial environmental conditions.

Solubility Measurements

As recently as the last decade several authors have reported widely different results for the temperature dependence of the solubility of $SrSO_4$ in water (Holland, 1967). The disagreement may be due to difficulty in achieving saturation; and we have, therefore, repeated the measurements in the temperature range 2-95°C, being careful to verify the attainment of equilibrium by approach from both higher and lower concentrations. Monitoring conductivity as a function of time, we have found that equilibrium is reached in less than one minute by dissolution, but may be much slower by precipitation. Because the solubility of $SrSO_4$ is greater at lower temperatures, accurate solubility values were obtained rapidly by saturating first at high temperatures, measuring conductivity, and then gradually cooling to lower temperatures and higher concentrations of Sr^{++}.

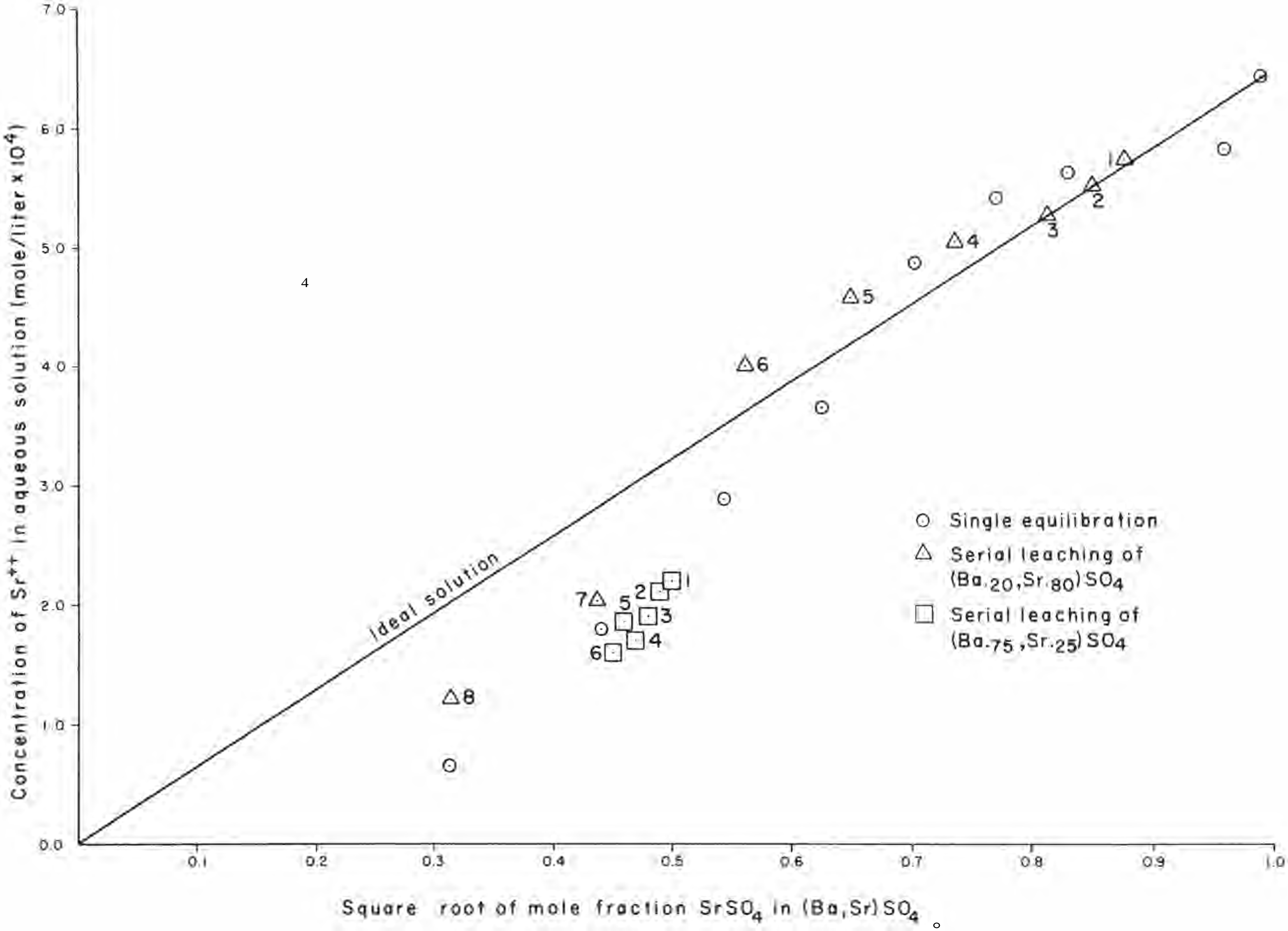

Figure 4. Equilibration of $SrSO_4$ between solid solution (Ba, Sr)SO_4 and aqueous solution at 25 °C.

The solubilities of $BaSO_4$ amd $SrSO_4$ were measured in a variety of electrolyte solutions. Although sodium chloride is the only uni-univalent salt that is geochemically important, ammonium chloride and nitrate were used to measure solubility at high ionic strengths because they caused much less interference with the atomic absorption analyses at high ionic strengths than did metallic salts.

The concentrations of $SrSO_4$ and $BaSO_4$ at the various temperatures were determined conductimetrically between 2° and 95°C. Solutions containing added electrolytes were analyzed for Sr^{++} and Ba^{++} by atomic absorption spectrometry. The solubility data at various ionic strengths are given in Tables 1 and 2.

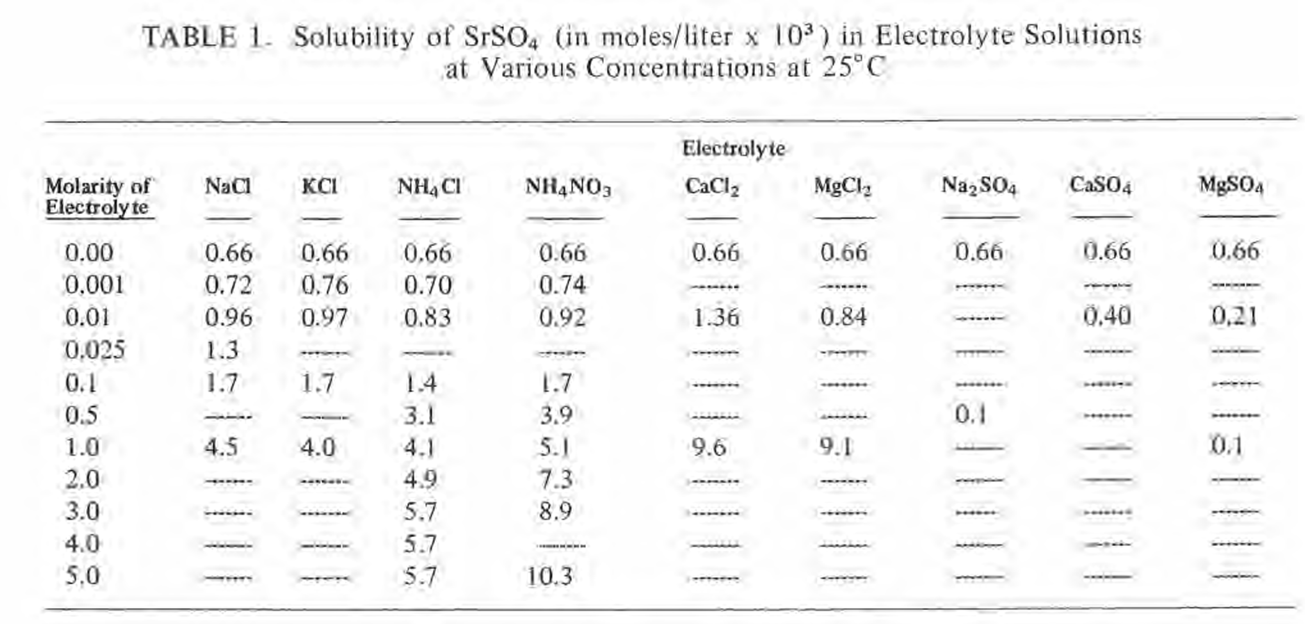

TABLE 1. Solubility of $SrSO_4$ (in moles/liter x 10^3) in Electrolyte Solutions at Various Concentrations at 25°C

	Electrolyte								
Molarity of Electrolyte	NaCl	KCl	NH_4Cl	NH_4NO_3	$CaCl_2$	$MgCl_2$	Na_2SO_4	$CaSO_4$	$MgSO_4$
0.00	0.66	0.66	0.66	0.66	0.66	0.66	0.66	0.66	0.66
0.001	0.72	0.76	0.70	0.74	------	------	------	------	------
0.01	0.96	0.97	0.83	0.92	1.36	0.84	------	0.40	0.21
0.025	1.3	------	------	------	------	------	------	------	------
0.1	1.7	1.7	1.4	1.7	------	------	------	------	------
0.5	------	------	3.1	3.9	------	------	0.1	------	------
1.0	4.5	4.0	4.1	5.1	9.6	9.1	------	------	0.1
2.0	------	------	4.9	7.3	------	------	------	------	------
3.0	------	------	5.7	8.9	------	------	------	------	------
4.0	------	------	5.7	------	------	------	------	------	------
5.0	------	------	5.7	10.3	------	------	------	------	------

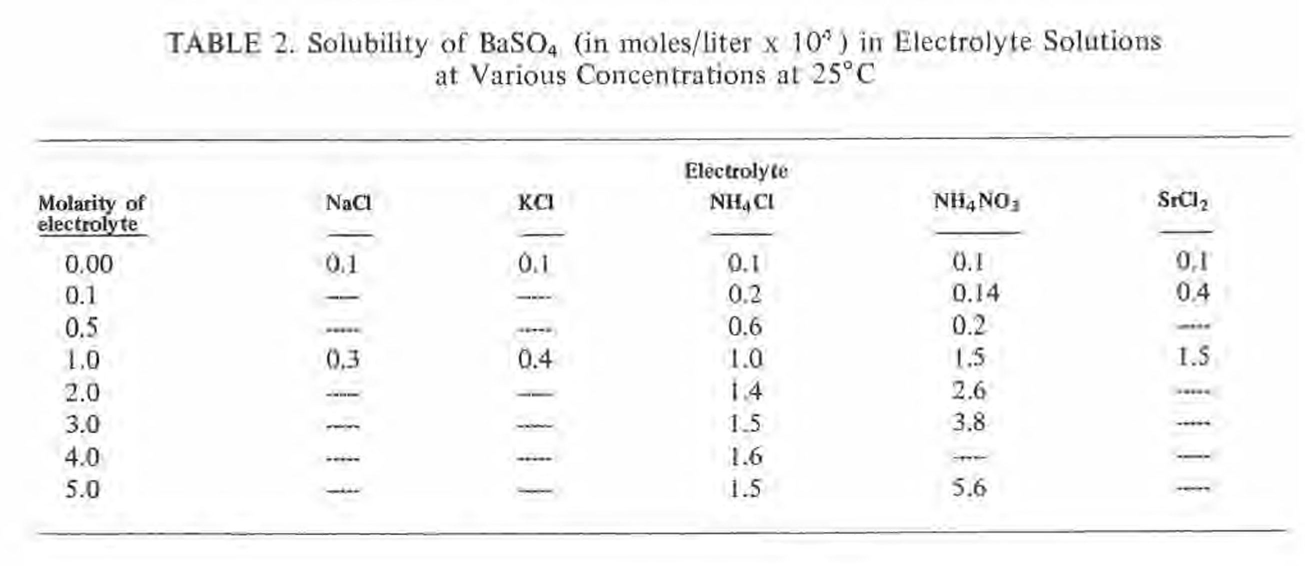

TABLE 2. Solubility of $BaSO_4$ (in moles/liter x 10^3) in Electrolyte Solutions at Various Concentrations at 25°C

	Electrolyte				
Molarity of electrolyte	NaCl	KCl	NH_4Cl	NH_4NO_3	$SrCl_2$
0.00	0.1	0.1	0.1	0.1	0.1
0.1	-----	-----	0.2	0.14	0.4
0.5	-----	-----	0.6	0.2	-----
1.0	0.3	0.4	1.0	1.5	1.5
2.0	-----	-----	1.4	2.6	-----
3.0	-----	-----	1.5	3.8	-----
4.0	-----	-----	1.6	-----	-----
5.0	-----	-----	1.5	5.6	-----

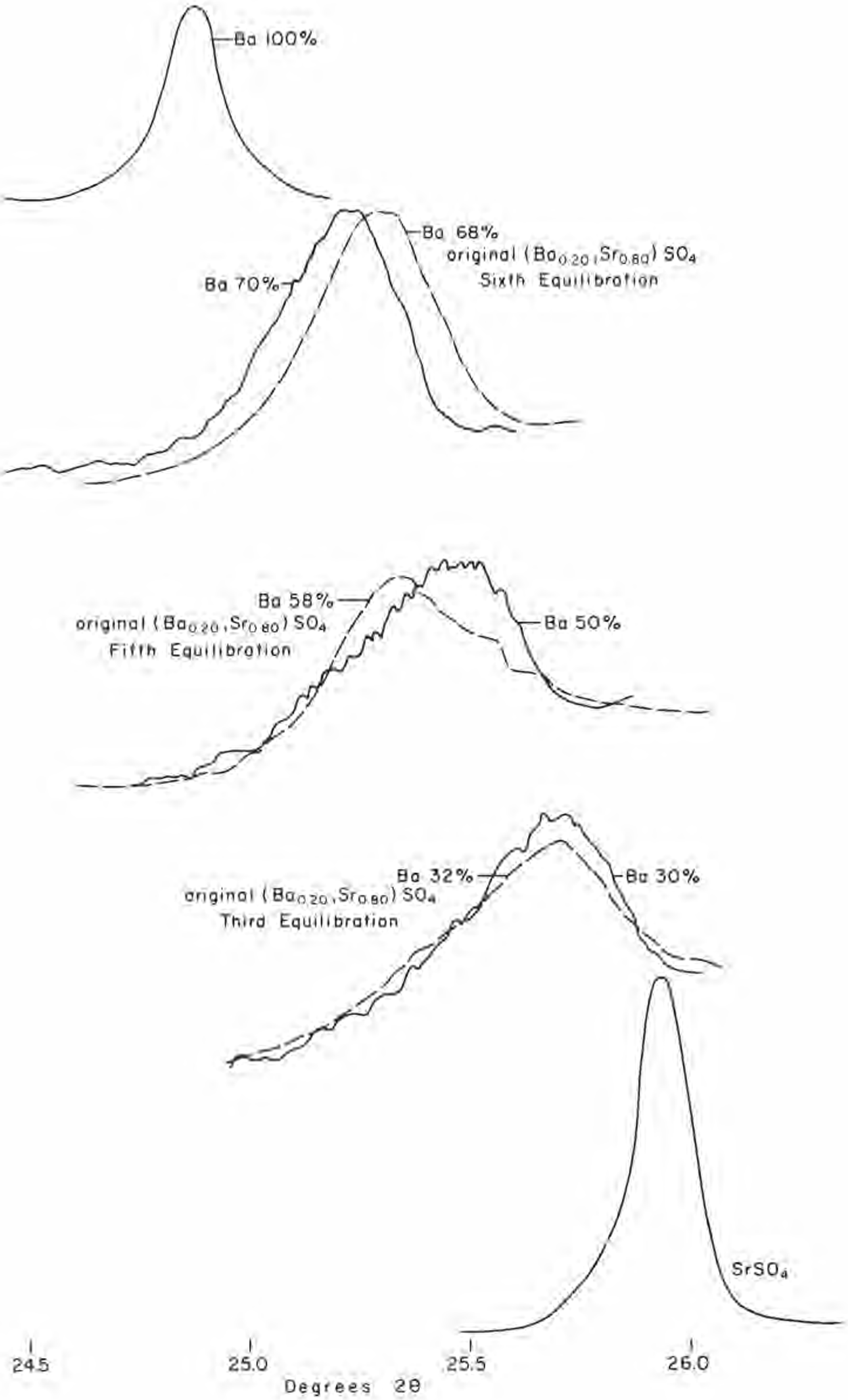

Figure 5A. Variation in shape of 111 diffraction peak with change in mole fraction.
—— freshly precipitated sample; ..... leached sample
$BaSO_4$ and $SrSO_4$, 500 cps = full scale
$(Ba, Sr)SO_4$, 200 cps = full scale.

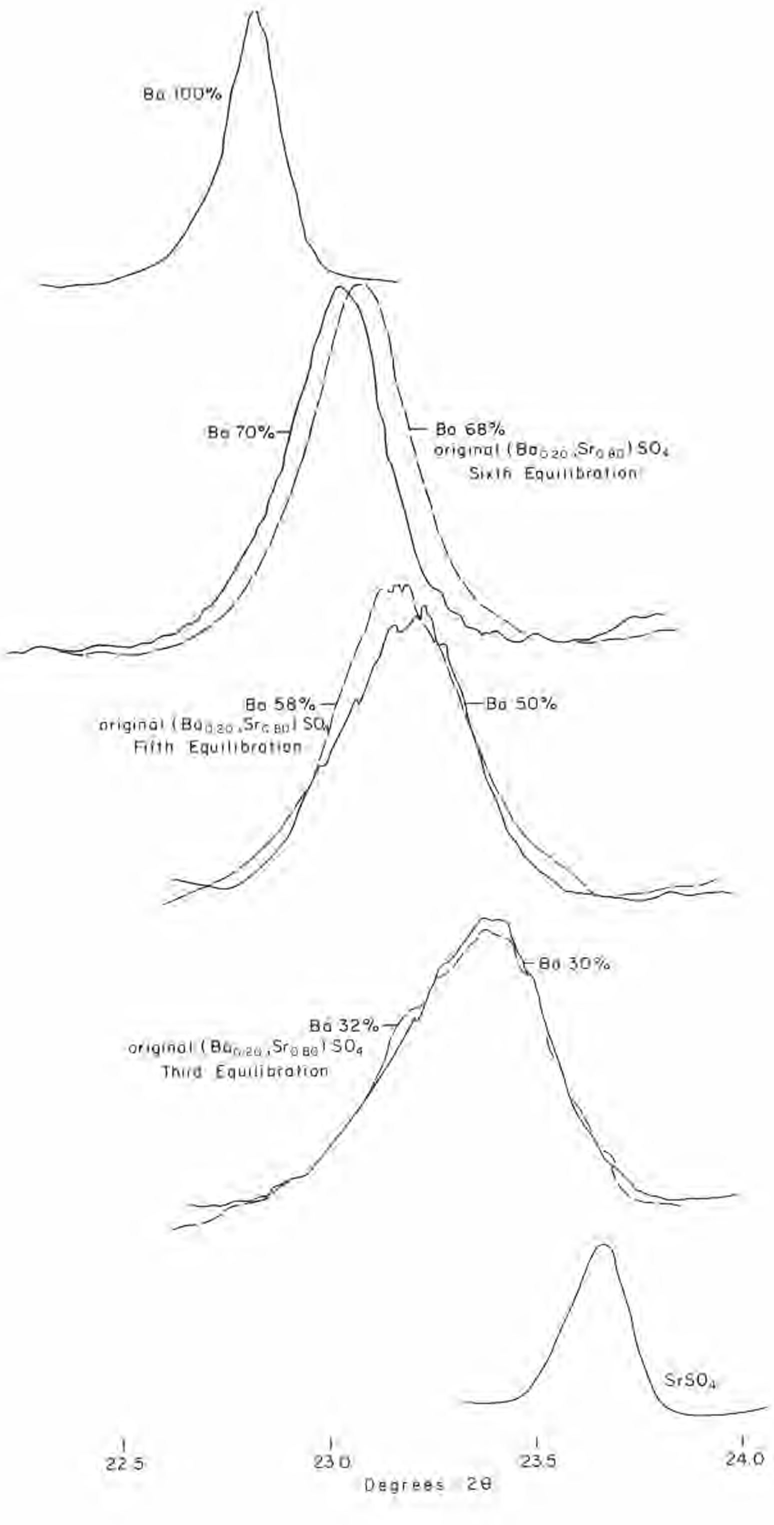

Figure 5B. Variation in shape of 002 diffraction peak with change in mole fraction.
—— freshly precipitated sample; ..... leached sample
$BaSO_4$ and $SrSO_4$, 500 cps = full scale
$(Ba, Sr)SO_4$, 200 cps = full scale.

The temperature dependence of $SrSO_4$ solubility is shown by a plot of log K vs 1000/T where T is absolute temperature in fig. 6 and the slope determined at points corresponding to 25° and 61°C. The enthalpies calculated from equation (15) are + 0.54 and + 3.8 kcal/mole respectively and agree with 20 percent of the calorimetry values.

$$\frac{d(\log K)}{d(1/T)} = \frac{-\Delta H}{2.3\ R}$$

The temperature dependence of $BaSO_4$ solubility was measured and log K plotted versus 1000/T as shown in fig. 7. Enthalpies calculated from the slope at 25° and 61°C are -5.2 and -2.3 kcal/mole respectively and agree within 25 percent of those determined by calorimetry.

Although the solubilities of $BaSO_4$ and $SrSO_4$ are markedly increased by a rise in ionic strength, the ratio of the molar solubilities of the two sulfates does not change significantly. Preliminary experiments show that in the presence of sodium chloride, $SrSO_4$ will be selectively leached from $(Ba,Sr)SO_4$. Roedder et al. (1968) report that fluid inclusions in barite are saline; therefore barite either formed or recrystallized from a saline medium.

Since an increase in temperature up to the boiling point of water decreases K_{SrSO4} and increases K_{BaSO4} the possibility exists that at temperatures consistent with hydrothermal vein deposition the two values could be equal and intermediate $(Ba,Sr)SO_4$ could precipitate from a sulfate-deficient system. In fig. 8 the log K versus 1000/T data have been extrapolated to their temperature of intersection. Barium sulfate and strontium sulfate would have the same solubility in water at not less than 360°C.

Helgeson (1969) has calculated from thermodynamic data values of K_{BaSO4} at high temperature which are listed as follows:

T°C	Log K
25	9.7
50	9.42
60	9.34
100	9.22
150	9.34
200	9.76
250	10.34
300	11.05

The trend of increased solubility with rise in temperature reverses at approximately 125°C. If Helgeson's calculated values are correct, the equilibrium constants for barium sulfate and strontium sulfate probably do not intersect at any temperature.

Data given by Roedder et al. (1968) determined by fluid inclusion thermometry indicate that barite deposition occurs between 130-170°C. Thus, in low temperature hydrothermal environments, the solubilities of barite and celestite are probably not equal, and except in the case of a stoichiometric excess of SO_4
expect celestite to precipitate.

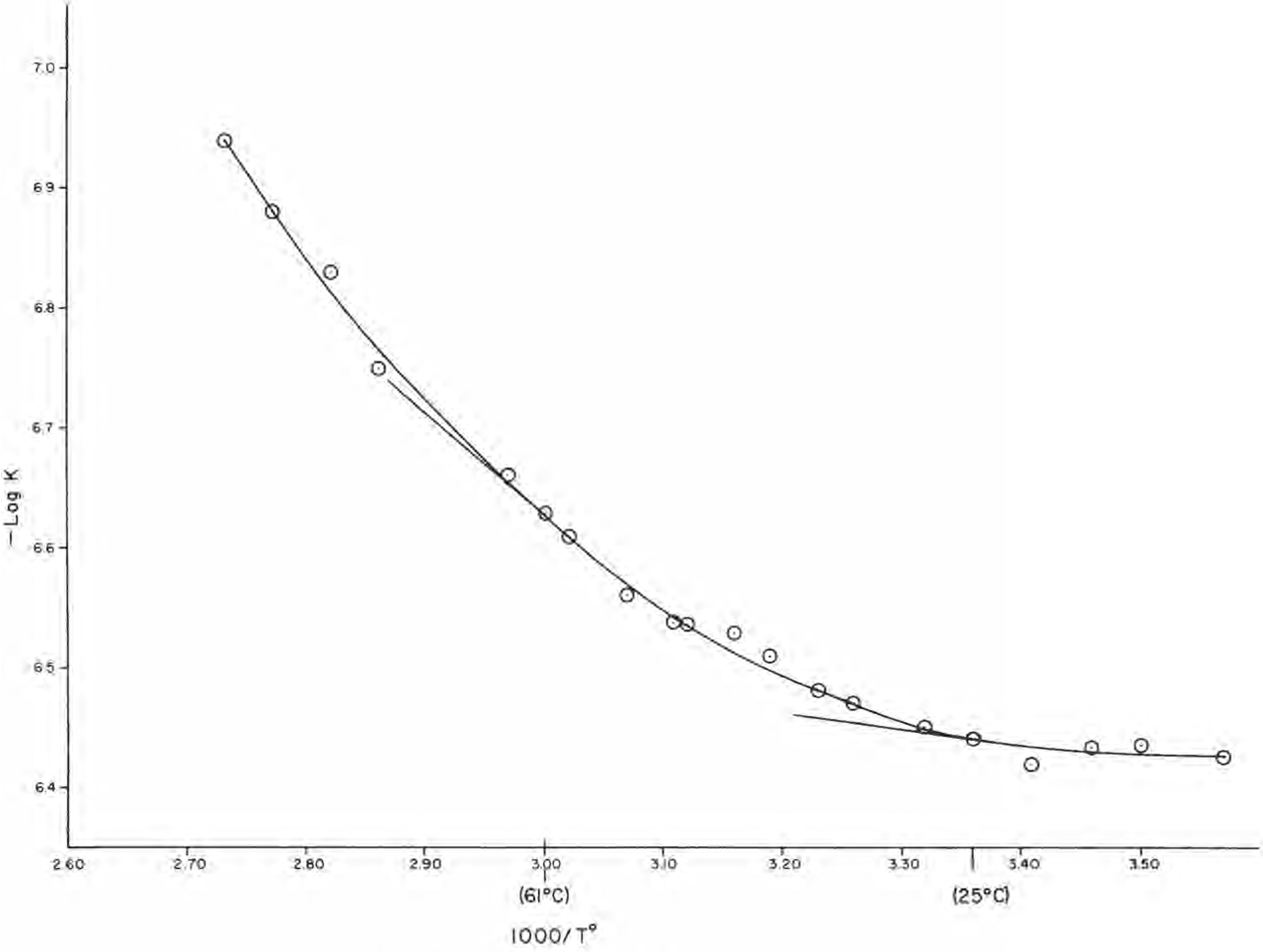

Figure 6 Log K versus $\frac{1000}{T}$ for $SrSO_4$.

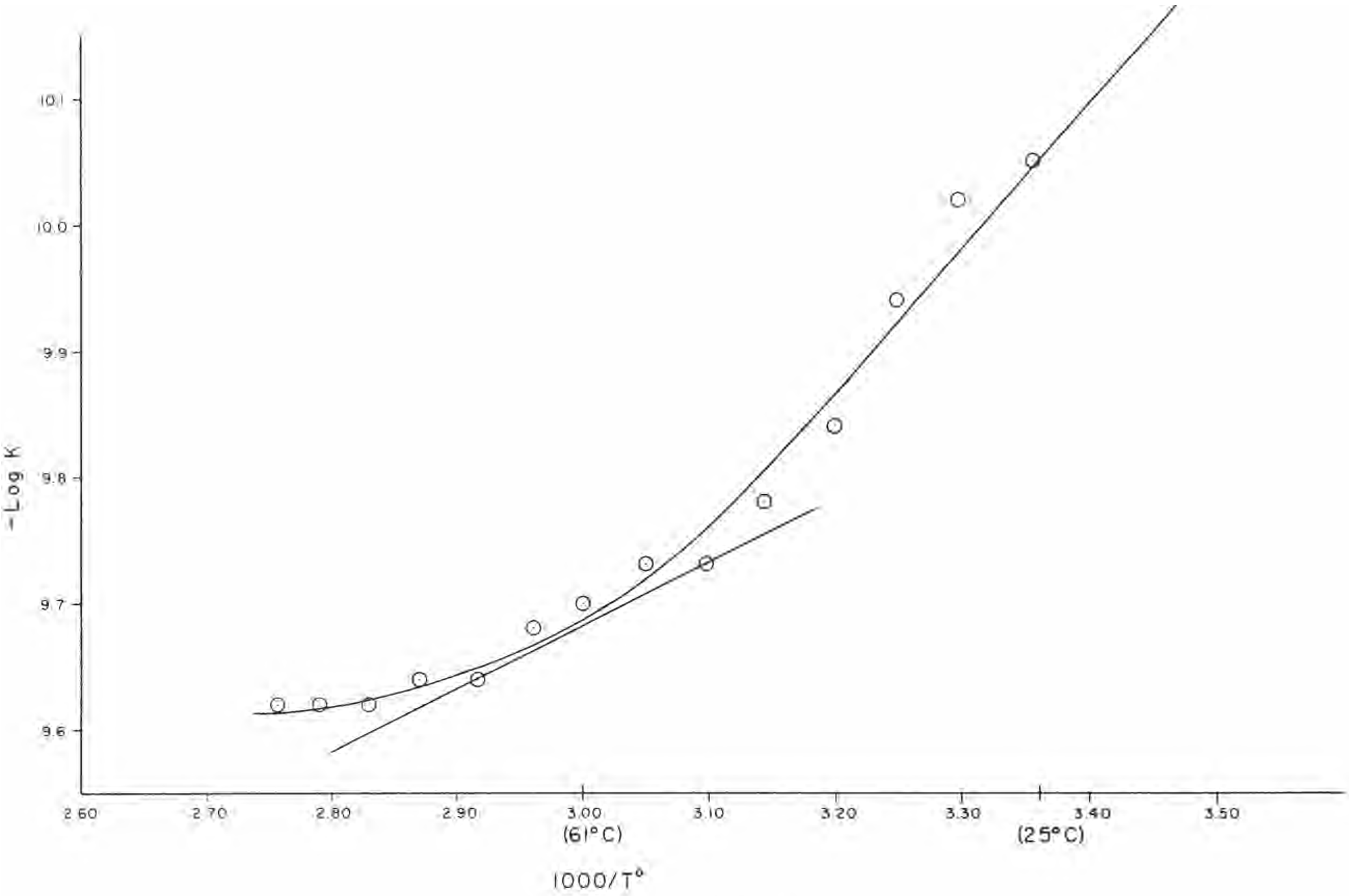

Figure 7. −Log K versus $\frac{1000}{T}$ for $BaSO_4$.

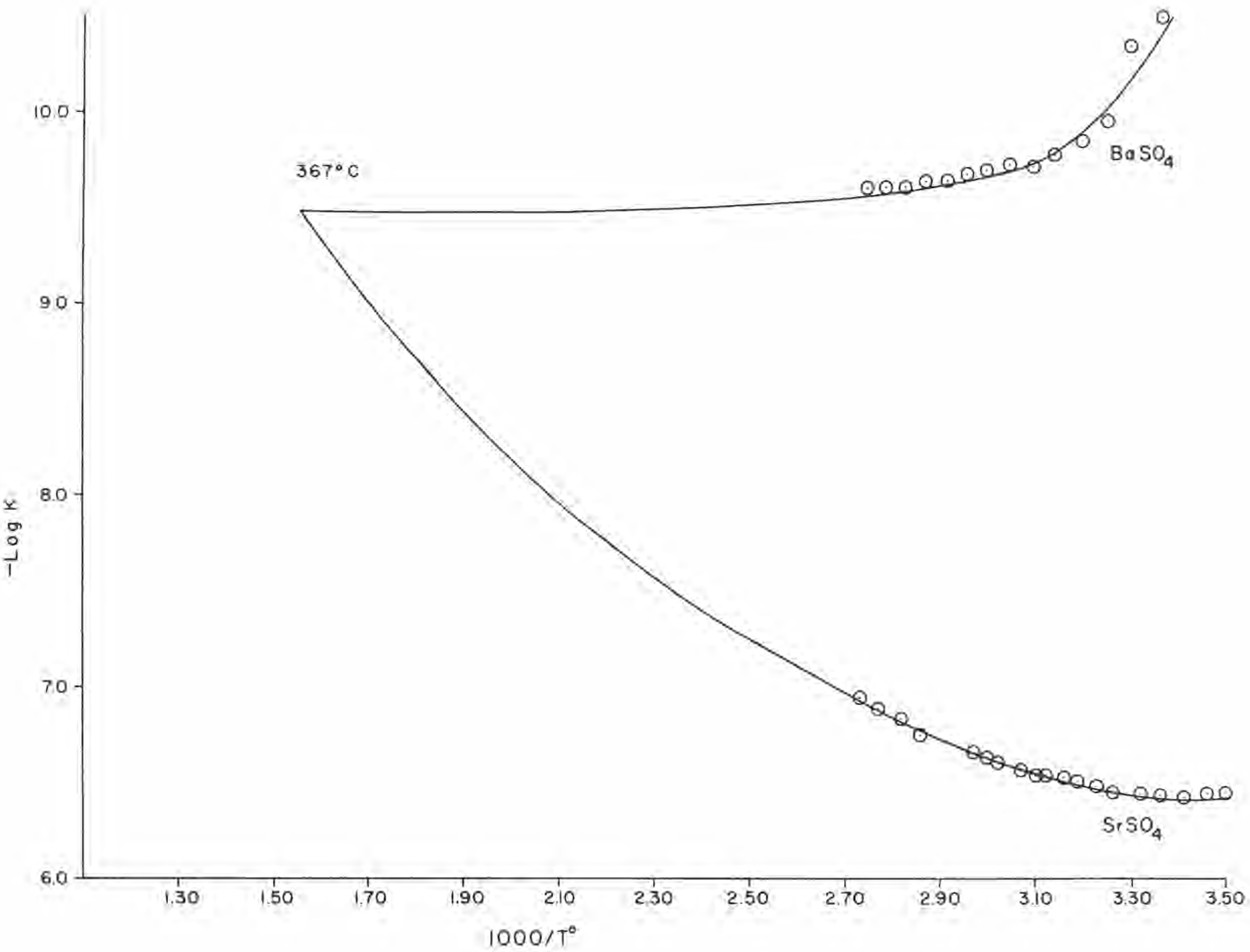

Figure 8. Extrapolation of $-\log K$ versus $\frac{1000}{T}$ to 367°C for $BaSO_4$ and $SrSO_4$.

SUMMARY AND CONCLUSIONS

The enthalpy of mixing $BaSO_4$ and $SrSO_4$ is nearly zero at 25° and 61°C. The entropy of mixing should closely approximate the ideal value,$-R(N_B \ln N_B + N_S \ln N_S)$, and the mixing process should be spontaneous over the entire range of compositions. This implies that in nature the solid solution $(Ba,Sr)SO_4$ should precipitate from an aqueous solution of Sr^{++} and Ba^{++} in any proportion, provided that a stoichiometric amount of sulfate ion is available. However, the rarity of intermediate composition in nature suggests that $SO^{=}$ is often deficient during the deposition of barite or that $SrSO_4$ is removed following deposition.

Strontium sulfate leaches selectively from the solid solution at 25°C, and Sr^{++} and Ba^{++} concentrations in aqueous solution approach the ideal value calculated from the assumption that the chemical activity of each component is proportional to its mole fraction in the solid. In natural systems a sulfate-deficient solution should leach $SrSO_4$ from the solid solution and cause it to be enriched in $BaSO_4$. Our experiments were based on fine-grained material so that the aqueous solution was rapidly saturated with $SrSO_4$; however, if natural crystals are coarse-grained, the process might go very slowly.

Optimum conditions for leaching $SrSO_4$ from $(Ba,Sr)SO_4$ are low temperature and high ionic strength. Carbonate ion, if it were present and equal in concentration to sulfate ion, would have profound effect by forming the more insoluble $SrCO_3$ as shown in equation (3).

The separation of barium and strontium in nature could result from leaching $(Ba,Sr)SO_4$ possibly in conjunction with metathesis by carbonate ion. Strontianite is frequently associated with barite, celestite and calcite either in limestone or in sulfide veins (Palache et al., 1951). Schraut (1951) reports the occurrence of strontianite with barite, witherite and celestite in the Rosiclare Fluorite district, and Graw and Nackowski (1944) report the occurrence of strontianite with fluorite, chalcopyrite, sphalerite, calcite, barite, and witherite in the Southern Illinois Fluorspar district.

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