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USE OF HYDROTHERMAL SOLUTION EQUIPMENT TO DETERMINE THE SOLUBILITY OF ANHYDRITE IN WATER FROM 100°C TO 275°C AND FROM 1 BAR TO 1000 BARS PRESSURE*

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ABSTRACT. Specially designed "hydrothermal solution" equipment was used to determine the solubility of anhydrite in H_2O from 100°C to 275°C and from 1 bar to 1000 bars. The solubility of anhydrite decreases with increasing temperature and increases with increasing pressure.

The hydrothermal solution equipment consists of a deformable teflon sample cell held in a stainless steel pressure vessel and sealed in such a way as to prevent interchange of material between the sample cell and the steel bomb. Separate pressure lines leading to the sample cell and to the steel bomb allow liquid to be pumped into or taken out of each container independently. Liquid and solid phases may be allowed to come to equilibrium in the teflon cell at constant temperature and pressure. The experimental mixtures are stirred by means of a teflon-coated bar magnet turned by an externally applied pulsating magnetic field. An internally filtered liquid sample can be withdrawn without significant disturbance of the equilibrium temperature and pressure, by pumping liquid into the steel vessel at the same rate that saturated solution is removed from the teflon cell.

From the solubility data obtained the following geologic conclusions can be drawn. Initially saturated solutions of anhydrite in water, migrating toward the Earth's surface, would become undersaturated. The increase in solubility caused by decreased temperature more than compensates for the decrease in solubility caused by decreased pressure. Anhydrite would precipitate from saturated solutions in sediments as burial takes place and the temperature rises, or from ground waters moving downward to regions of higher temperature. Anhydrite would precipitate from saturated solutions moving from a region of high pressure to a region of low pressure, as would be the case in rocks near openings toward which a fluid pressure gradient exists.

INTRODUCTION

Physical chemical data on systems containing water and metal salts at elevated temperatures and pressures are needed to clarify understanding of the origin of many mineral deposits. Geologists reasoning from studies of hot springs and spatially associated minerals as well as from studies of other epithermal ore deposits are in general agreement that aqueous solutions of one kind or another are involved in the deposition of gangue and ore minerals of most epithermal ore deposits. Little experimental work has been done, however, on pertinent aqueous systems, particularly at elevated temperatures and pressures. Possible physical and chemical processes important in the precipitation or solution of ore and gangue minerals can be deduced from the solubilities of minerals determined as functions of temperature, pressure, and composition. The limited extent to which this field has been investigated is partly the result of experimental problems.

In the use of ordinary pressure vessels to determine solubilities of minerals at elevated temperatures and pressures several difficulties have been encountered, such as contamination of the solutions by reaction with the pressure vessel and variation of temperature and pressure during removal of

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samples from the pressure vessel, causing departures from equilibrium conditions. Moreover, in the absence of internal filtering of the solutions, there has been uncertainty as to whether solid material suspended in the liquid being withdrawn was precipitated during sampling or was present in the liquid inside the pressure vessel.

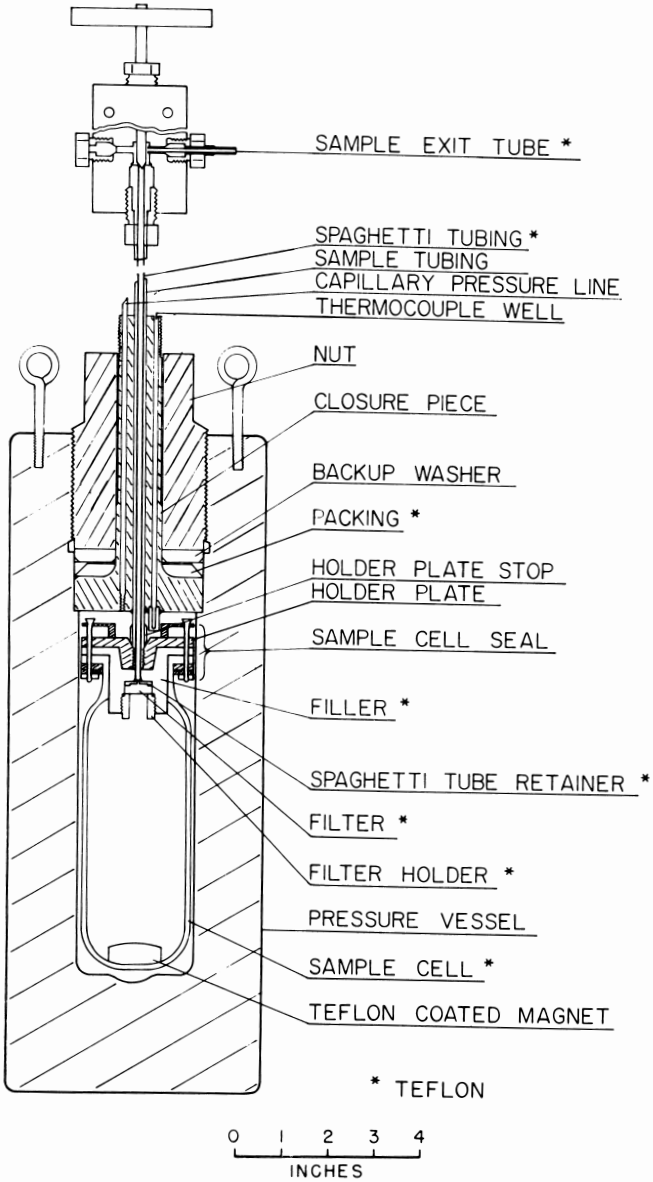

Fig. 1. Hydrothermal solution pressure vessel.

The hydrothermal solution equipment (fig. 1) was designed to avoid such difficulties. In essence, the equipment consists of a bottle-shaped sample cell of tetrafluorethylene resin (teflon), held in a stainless steel pressure vessel. Teflon was chosen because of its chemical inertness and its easy deformability. The sample cell is isolated from the interior of the steel pressure vessel and is provided with an exit tube through which liquid may be withdrawn or injected. A teflon filter is located at the lower end of the exit tube at the top of the cell. The basic principle of the equipment is simple: the sample cell changes shape in response to a pressure change in fluid surrounding it, thus allowing the internal pressure to become equal to the external pressure. The equipment provides an inert environment of teflon for the experimental mixtures; it allows essentially constant temperature and pressure to be maintained during sampling by the pumping of fluid into the steel pressure vessel at the same rate that liquid is withdrawn from the sample cell; it provides for internal filtering; it allows pressures up to 1500 bars to be maintained for long periods of time at temperatures up to 275°C; it provides for stirring by means of a bar magnet spun by an externally applied magnetic field; and finally it permits recharging the sample cell with a fresh supply of aqueous solution without the necessity of breaking open the pressure vessel and without gross disturbance of the temperature and pressure.

By the use of this equipment the solubility of anhydrite ($CaSO_4$) in water was determined as a function of temperature and pressure. The choice of the solubility of anhydrite in aqueous solutions of $CaSO_4$ for the first experimental investigation with the new equipment was made for the following reasons: (1) data by previous workers on the solubility of anhydrite in water under appropriate conditions were available for comparison purposes; (2) relations in the system $CaSO_4$–H_2O are of much geologic interest; (3) the solubility of anhydrite is known to increase with decreasing temperature. eliminating the possibility that solid phase would precipitate in cooler portions of the sample exit tube; and (4) the relatively noncorrosive nature of saturated solutions of anhydrite in water minimized the hazard to the equipment in case of leakage.

PREVIOUS WORK

Previous studies of the solubility of anhydrite in water have been carried out by Melcher (1910), Hall, Robb, and Coleman (1926), Partridge and White (1929), Hill (1937), Posnjak (1938), Booth and Bidwell (1950), Morey and Hesselgesser (1951), and Styrikovich and Khokhlov (1957). With the exception of the last two studies, all of the previous work was done at atmospheric pressure at temperatures below 100°C or at the vapor pressure of the system at temperatures above 100°C. The solubility data obtained with use of the hydrothermal solution equipment at pressures slightly above the vapor pressure of the system are in good agreement with previous data (fig. 2).

EXPERIMENTAL EQUIPMENT

A schematic diagram of the hydrothermal solution equipment is presented in figure 1. The equipment consists of a variable volume sample cell suspended in a stainless steel pressure vessel. The interior of the sample cell is isolated

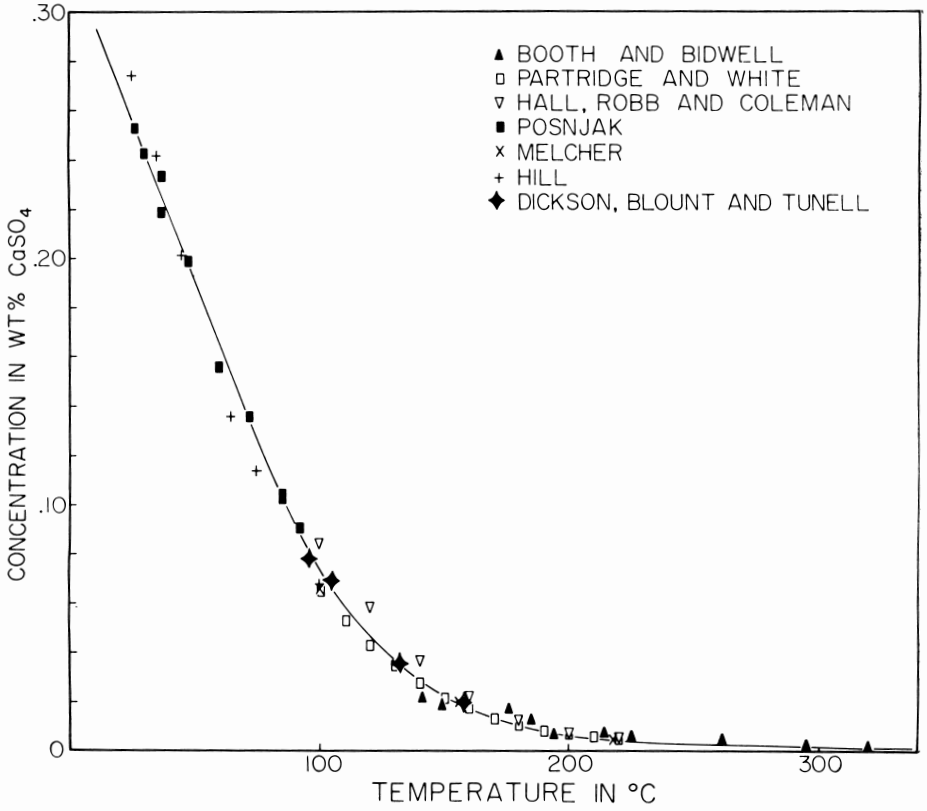

Fig. 2. Comparison of the work of Dickson, Blount, and Tunell with work of previous investigators on the solubility of anhydrite at 1 atmosphere below 100°C and at the vapor pressure of the system above 100°C.

from the interior of the pressure vessel by means of a spring-loaded sealing device. No passage of material normally can take place in either direction between the sample cell and the interior of the pressure vessel.

Sample cells were constructed from dense tetrafluoroethylene resin (teflon 7x) bars fabricated specifically for this purpose. The first cell made was a bellows (thickness of walls, 0.05 inch; maximum capacity, 150 ml) from which 100 ml could be withdrawn. Thicker walled bottles (thickness of walls, 0.125 inch; maximum capacity, 300 ml), from which 170 ml could be withdrawn, were used in the later stages of this study. The bottles possessed the advantages over the bellows of being simpler to construct and of providing a larger volume.

Both the bellows and the bottle expanded or contracted in response to a change in pressure of the fluid surrounding the cell, thus causing the pressure inside the cell to adjust to very nearly the value of the external pressure. Immediately after a pressure change, a small initial difference in pressure existed between the inside and outside of the cell. The teflon walls possessed sufficient

strength to resist complete adjustment immediately. Within a few hours the walls adjusted by slow creep and the pressure differential diminished to zero. The volume of liquid in the inner cell was kept between predetermined limits to prevent damage to the cell by excessive expansion or contraction.

The sample cell and sealing device were attached to the lower portion of the centrally located sample tube. The sampling tube, a 14-inch-long piece of stainless steel high pressure tubing, was welded to the face of the closure piece. The lower end of the sampling tube was threaded. A tight contact between the stainless steel holder and the stop provided a seal to prevent leakage of fluid into or out of the sample cell along the threads. The sampling tube was lined with teflon spaghetti tubing. The lower end of the spaghetti tubing was flared and held in place by a cone on the spaghetti tube retainer. The teflon filler at the top of the sample cell fitted snugly against the holder piece and served to isolate the teflon bottle from the metal parts of the sample cell seal. The upper flanged portion of the sample cell fitted snugly on the filler and was held in position by the sealing device. The sealing assembly was compressed by six sealing bolts. Two split metal backup rings were used to protect the flange of the sample cell and uniformly distribute the pressure of the sealing spring. When adjusted properly the sealing spring provided a tension of about 100 lbs.

A sintered teflon filter disk in a receptacle above the spaghetti tube retainer was held in place by a threaded teflon retainer ring. The filter disk removed suspended solid particles greater than three microns in diameter.

Stirring of the experimental mixtures was accomplished by a teflon-covered stirring magnet in the bottom of the sample cell, which turned in response to an oscillating magnetic field. The magnetic field was generated by a pair of opposed electromagnets embedded in the furnace shell (fig. 3). Reversing the current flowing through the magnet windings every four seconds reversed the polarity of the electromagnets.

Access to the large pressure vessel was through a high pressure capillary stainless steel tube. Pressures were built up by a variable speed high pressure pump connected to the capillary through a suitable valving system (fig. 3). Pressures were measured to an accuracy of plus or minus four bars by the use of Bourdon tube gauges previously calibrated against dead weight piston gauges.

The stainless steel pressure vessel had an outside diameter of 5.5 inches, an inside diameter of 2.5 inches, and a volume of 600 ml. Type 321 stainless steel was used because of its inertness, high resistance to intergranular carbide precipitation, and low magnetic permeability. Pressure vessels of this design have been used continuously at 1500 bars pressure and 270°C for periods up to four months with no detectable creep of the material. The vessel was sealed by means of a modified Bridgman unsupported area packing, using teflon as the packing material.

Temperatures were established by electric muffle furnaces controlled by standard commercial proportioning off-on controllers, using chromel-alumel thermocouple sensing elements. Sample cell temperatures were determined by e.m.f. measurements of a thermocouple located in the closure piece about two inches from the sample cell. Before beginning the experiments, the thermo-

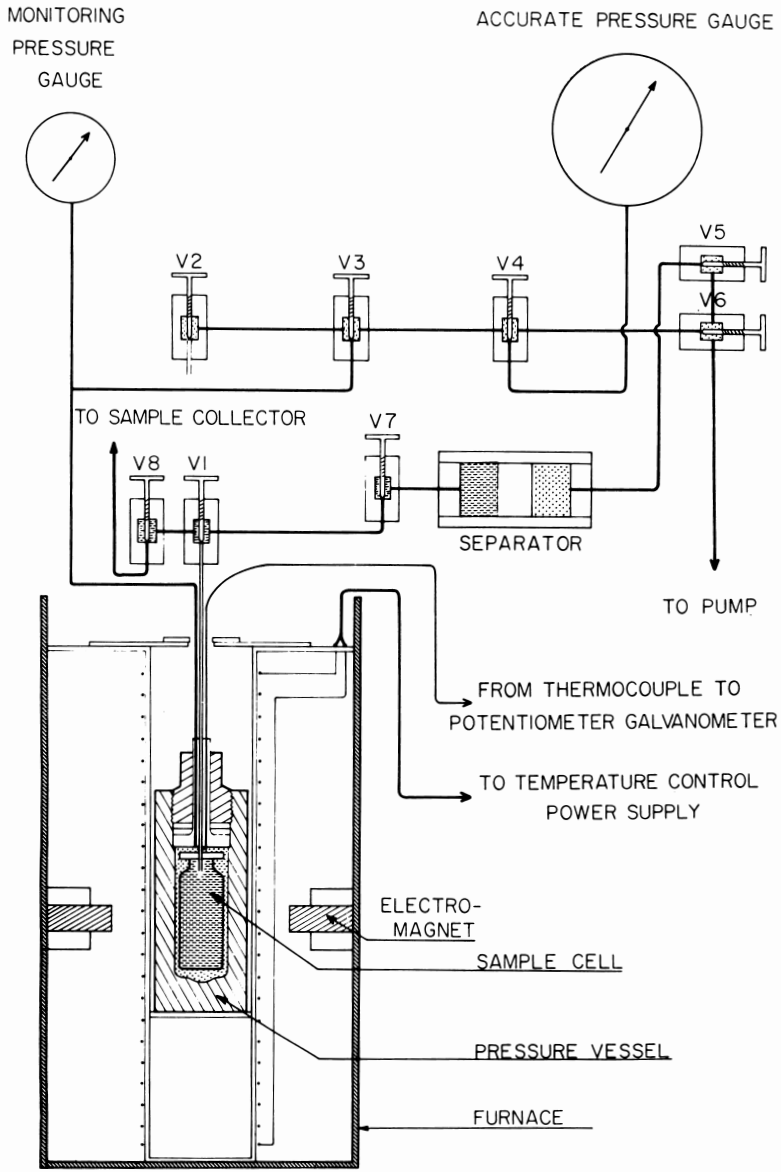

Fig. 3. Schematic diagram of hydrothermal solution equipment including pressure vessel, furnace, control valves, and pressure gauges.

couple had been compared with a second thermocouple in the sample cell subjected to the extremes of experimental conditions.

The properties of teflon set the upper limit of temperature at which the equipment can be used. Teflon undergoes a phase transition somewhat above 300°C, which involves undesirable and irreversible change in physical proper-

ties. No difficulty was encountered in the use of teflon at temperatures as high as 275°C over periods of a month and longer. Teflon tends to be permeable to substances such as CO_2 and H_2S, and the permeability becomes greater with increasing temperature. During experiments carried out over several months $CaSO_4$ in aqueous solution did not migrate through the teflon walls of the sample cell in sufficient quantity to be detected in the water surrounding the sample cell.

EXPERIMENTAL PROCEDURE

The sample cell was loaded and the equipment assembled in the following way: A known volume, usually about 300 ml, of boiled distilled water, about five grams of anhydrite, and the teflon-coated stirring magnet were placed in the teflon sample cell. The sample cell was then attached to the holder piece and sealed by tightening the sealing bolts. The sealing spring was adjusted to provide a total force of about 100 lbs. During the sealing process excess water was forced through the sample tube, flushing air out of the system. The closure piece with the attached sample cell was placed in the large steel pressure vessel, previously loaded with sufficient water to fill the steel vessel after the sample cell was in place. The steel pressure vessel was sealed, placed in the furnace, and allowed to come to the desired temperature. The pressure was adjusted by pumping into or leaking out of the steel pressure vessel. To avoid rupture of the teflon cell by excessive expansion of the contained solution, account had to be taken of the extent to which the specific volume of water changed during the process of bringing the equipment to the elevated temperature and pressure.

Sampling was done by gently opening the valve at the top of the sample tube, allowing liquid in the sample cell to be forced through the filter into the exit tube and out through the valve into a cooled glass container. As the sample

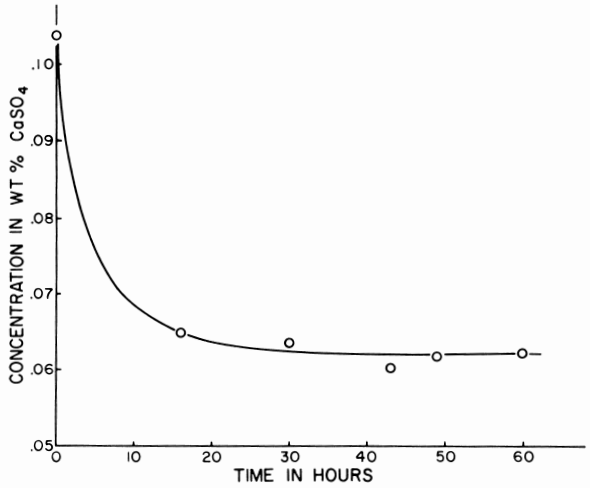

Fig. 4. Approach to equilibrium concentration of $CaSO_4$ with lapse of time at 131°C and 500 bars. The system originally had been at equilibrium at 131°C, 1000 bars, and 0.104 percent $CaSO_4$.

was drawn off, fluid was pumped simultaneously into the steel pressure vessel at the same rate that liquid was removed from the sample cell, thus keeping the pressure constant to ± 5 bars. The first two-milliliter portion was discarded inasmuch as it included solution that occupied the exit tube at lower temperatures than that of the sample cell. Taking a sample as large as 25 ml caused only a negligible change (of the order of 2°C) in the sample cell temperature.

Repeated samples were taken until successive analyses showed no change in composition of the solution. Figure 4 shows the change in concentration with time for 131°C and 500 bars. At most temperatures equilibrium was attained between anhydrite and solution in less than 48 hours. After equilibrium was obtained, a new experimental run was begun by changing the pressure or the temperature. When about 150 ml of the original 300 ml of solution had been taken from the sample cell, the cell was recharged with water by reversing the sampling procedure; that is, by pumping water into the sample cell while bleeding water from the steel pressure vessel. The amount of anhydrite in the cell was in large excess; hence it was possible to re-establish equilibrium between the anhydrite and newly injected solution. In this manner it was possible to carry on the experiments for months without opening the system.

Equilibrium was approached at a given temperature and pressure from two directions, that is, from undersaturation and from supersaturation. Figure 5 presents a schematic diagram showing a typical path followed by the composition of the solutions during a series of isothermal experiments. With sufficient elapsed time the same values were attained at a particular temperature

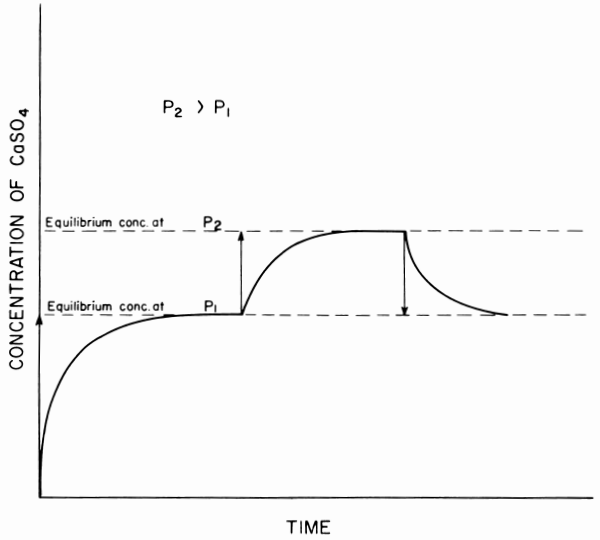

Fig. 5. Schematic diagram showing approach to equilibrium concentration of $CaSO_4$ with time after throwing the system into disequilibrium by changing experimental conditions. This case involves changes in pressure; similar paths result from changes in temperature. Note that the same value for a particular temperature and pressure results regardless of whether equilibrium is approached from undersaturation or supersaturation.

and pressure regardless of the direction from which the equilibrium was approached.

IDENTIFICATION OF THE SOLID PHASE AND ANALYSIS OF SAMPLE SOLUTIONS

The anhydrite used for the experimental work was Baker "Analyzed Reagent" anhydrous calcium sulfate. Under the microscope, the fresh reagent was seen to consist of crystal aggregates containing small cavities. The maximum diameter of the grains ranged from 0.001 to 0.002 mm with the average about 0.015 mm. The solid phase removed from the sample cell after several months at elevated temperatures and pressures had increased slightly in grain size.

Examination of the solid phase by the X-ray diffractometer resulted in a diffraction pattern identical with that of natural anhydrite. Reagent heated to 900°C for one hour yielded the same spacings as the unheated fresh reagent. Material precipitated by evaporating saturated solutions taken from the sample cell, ignited at 600°C for three hours, also gave identical spacings.

The solutions were analyzed for calcium by gravimetric, flame-photometric, and titrometric techniques. Excellent agreement was obtained among analyses carried out by the different methods. The accuracy of the analyses is estimated to be better than plus or minus one percent for most of the values reported.

EXPERIMENTAL RESULTS

The solubility of anhydrite in water as a function of temperature and pressure is given in table 1 and is presented in figures 6, 7, and 8. Our determinations of the solubility of anhydrite as a function of temperature near the vapor pressure of the system are in good agreement with those of previous investigators (fig. 2).

It was not practical to make each run at unvarying temperature and pressure. Temperature and pressure varied slightly, principally because of small fluctuations in the temperature control equipment. A temperature change of 1° caused changes in pressure ranging from 5 to 20 bars. The smoothed solubility values of table 2 were used to construct constant pressure sections (1000, 500, 100 bars) through the pressure-temperature-composition surface (the P-T-X surface) representing the solubility of anhydrite in water. Figure 6 presents the constant pressure sections, along with the curve representing solubilities measured at pressures slightly greater than the vapor pressure of the system. The strong negative effect of increasing temperature on anhydrite solubility is displayed by the curves of figure 6. Constant temperature sections through the P-T-X surface presented in figure 7 illustrate the positive effect of increasing pressure on the solubility of anhydrite. Constant composition sections through the saturation surface shown in figure 8 reveal that temperature is very nearly a linear function of pressure.

The possibility that during the course of the experiments anhydrite had undergone a change of phase, either isochemical or by reaction with water to produce one of the hydrated phases of $CaSO_4$, had to be considered. Solid phase removed from the sample cell at the conclusion of the experiments invariably proved to be anhydrite according to X-ray and microscopic examina-

TABLE 1

Experimental data on the solubility of anhydrite in water in weight percent. Each letter refers to an experimental run at a particular temperature and pressure. The subscript numbers indicate repeated samplings at approximately the same temperature and pressure

Sample	Temperature °C	Pressure bars	Time hours	$CaSO_4$ wt%
a_1	105[5]	1000	24	0.185
a_2	105[5]	1000	29	0.188
a_3	105[5]	1000	43	0.185
b_1	105[5]	480	44	0.113
b_2	104[5]	500	48	0.115
c_1	105[5]	97	40	0.0795
c_2	106[5]	97	136	0.0735
c_3	107[5]	98	160	0.0735
d_1	105[5]	6	72	0.0681
d_2	105[5]	6	106	0.0687
e_1	124	1000	46	0.1255
e_2	124	1000	64	0.1255
e_3	124	1000	75	0.1255
f_1	123[5]	500	38	0.074
f_2	124	500	142	0.075
g_1	131	995	72	0.103
g_2	131	995	90	0.104
g_3	131	1000	120	0.104
h_1	131	500	17	0.0647
h_2	**131**	**500**	**30**	0.0635
h_3	131	500	43	0.0601
h_4	131	500	49	0.0618
h_5	132	506	60	0.0612
i_1	130	100	72	0.0418
i_2	130	100	96	0.0424
j_1	130	5	69	0.0359
j_2	131	5	93	0.0358
k_1	156	1010	72	0.0653
k_2	156	1000	96	0.0651
l_1	157	510	69	0.0359
m_1	157	100	32	0.0231
m_2	157	90	56	0.0217
m_3	157	92	340	0.0220
n_1	157[5]	15	65	0.0201
o_1	183[5]	1000	100	0.0333
o_2	183[5]	1000	125	0.0326
p_1	183[5]	480	216	0.0188
q_1	**183[5]**	100	65	0.0118
q_2	184[5]	100	89	0.0117
r_1	221	980	104	0.0148
r_2	221	984	128	0.0152

TABLE 1 (Continued)

Sample	Temperature °C	Pressure bars	Time hours	$CaSO_4$ wt%
r_3	221	985	152	0.0150
s_1	221	518	96	0.0087
s_2	221	493	240	0.0089
t_1	217[5]	74	168	0.0054
u_1	263	1004	96	0.0068
u_2	263	1000	120	0.0068
v_1	259	455	404	0.0040
v_2	258	493	500	0.0039
w_1	101	482	216	0.1218
x_1	101	102	120	0.0828
y_1	96	2	96	0.0781
z_1*	100	527	168	0.125
z_2**	100	527	168	0.125

* Sample z_1 analyzed using Edta solution to titrate calcium.

** Sample z_2 analyzed gravimetrically by evaporating solution and igniting the residue.

tion. No discontinuities existed in the solubility curves to suggest that a phase change had taken place. The equilibrium temperature of the reaction anhydrite + water = gypsum is 42°C at one bar pressure (Hill, 1937, p. 2244). The effect of pressure increase is to raise the equilibrium temperature but the effect on the temperature is small; calculations by Marshal (1952, p. 291) and MacDonald (1953, p. 887) indicate that a pressure increase of 1000 bars raises the equilibrium temperature to about 54°C, a temperature well below the minimum temperature of 100°C used in this study.

At constant pressure, the solubility of anhydrite as a function of temperature can be expressed by an empirical equation of the form:

$$\log X = A+BT+CT^2+ \ldots\ldots,$$

in which X is the saturation concentration of anhydrite; A.B.C. . . . . are constants; and T is absolute temperature.

Such equations were obtained for several pressures by processing the experimental data of table 2 by an IBM 1620 computer. Log X proved to be a linear function of temperature, and the equations reduce to the form $\log X = A+BT$. Constants A and B for the different pressures are listed in table 2. The average deviation of solubilities calculated from the empirical equations from the experimentally determined solubilities under the same conditions is about 2 percent.

The thermocouple used to determine the experimental temperatures was located above the sample cell (fig. 1) where the temperature was generally a little lower than that of the liquid in the sample cell. The temperature values given by the thermocouple were compared with values given by a thermocouple held in the sample cell subjected to the extremes of experimental condition, and a calibration curve was constructed. The maximum uncertainty in the temperature existed in the higher temperature experiments, and it amounted to about 2°C.

TABLE 2

The solubility of anhydrite in water in weight percent, smoothed to constant pressures; the calculated solubility of anhydrite at various temperatures and pressures; and constants A and B of empirical equations of the form $\log X = A+BT$ expressing the solubility of anhydrite as a function of absolute temperature at constant pressures

Temperature °C	Experimental Solubility wt% $CaSO_4$	Calculated Solubility wt% $CaSO_4$
P = 1000 bars		
105[5]	0.185	0.181
124	0.126	0.124
131	0.104	0.107
156	0.065	0.063
183[5]	0.0333	0.0347
221	0.0151	0.0158
265	0.0068	0.0062
A = 2.75161	B = −0.0092163/°K	
P = 500 bars		
100	0.122	0.125
101	0.123	0.122
104[5]	0.115	0.112
124	0.075	0.074
132	0.061	0.062
157	0.0357	0.0359
183[5]	0.0192	0.0199
221	0.0090	0.0089
258	0.0040	0.0039
A = 2.64087	B = −0.0095014/°K	
P = 100 bars		
101	0.0826	0.0839
107[5]	0.0736	0.0712
130	0.0424	0.0426
157	0.0223	0.0226
184[5]	0.0117	0.0117
217[5]	0.0056	0.0054
310	—	0.00063
A = 2.72446	B = −0.0101624/°K	
Pressure slightly greater than the vapor pressure of the system		
	Pressure bars	
96	2	0.0781	0.0808
105[5]	6	0.0682	0.0644
131	5	0.0357	0.0365
157[5]	15	0.0198	0.0198
310	100	—	0.00063
A = 2.54315		B = −0.0098533/°K	

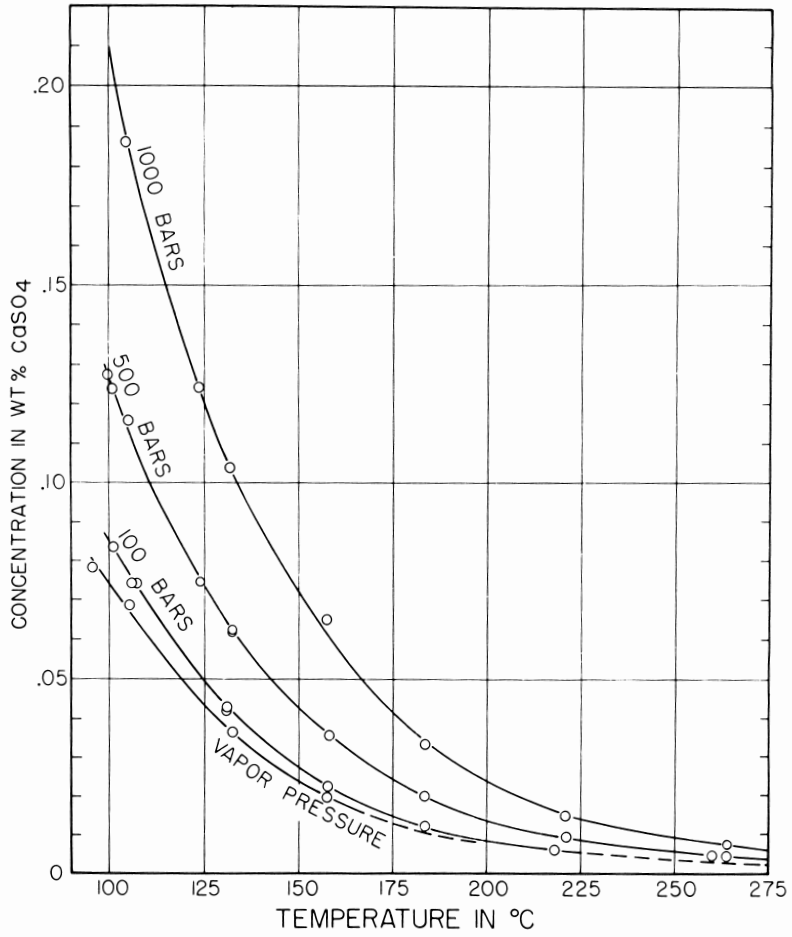

Fig. 6. Constant pressure sections through the P-T-X saturation surface representing the solubility of anhydrite in water, and the variable pressure curve representing solubility of anhydrite at pressures slightly greater than the vapor pressure of the system.

The temperature coefficient of solubility can be evaluated at a given temperature and pressure by differentiating the appropriate empirical equation from those listed in table 2. For example, at 1000 bars, $\log X = 2.75161 - 0.0092163T$.

Differentiation yields: $\frac{dX}{dT} = \frac{-0.0092163X}{\log_{10} e}$ in weight percent per °K = $-0.0212X$ in weight percent per °K. At 156°C, 1000 bars and X = 0.065 weight percent $CaSO_4$. $\frac{dX}{dT} = 0.00138$ in weight percent per °K. An uncertainty of 2°C in the temperature introduces an uncertainty of about 0.003 in the solubility value. The experimentally determined value at 156°C and 1000

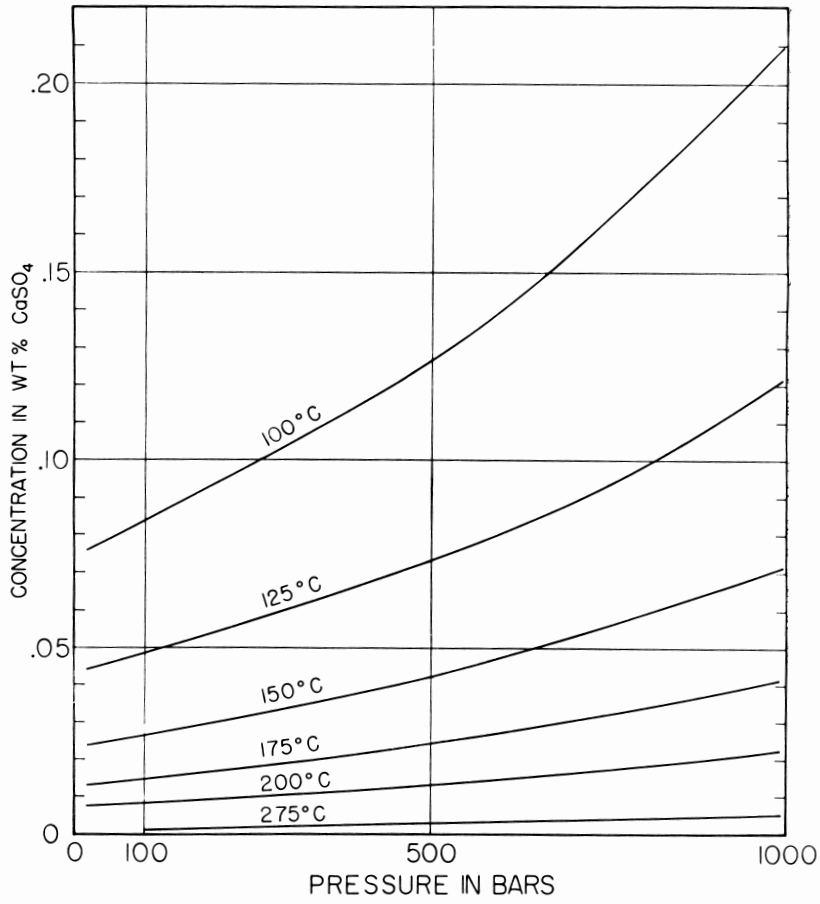

Fig. 7. Constant temperature sections through the P-T-X saturation surface representing the solubility of anhydrite in water.

bars is 0.065 weight percent, and an uncertainty of 0.003 is 3 parts in 65, or almost 5 percent of the reported value.

The analytical procedure was accurate to ± 1 percent of the value reported at concentrations down to 0.02 percent. At concentrations below 0.02 percent the analytical uncertainty progressively increased with decreasing concentration; for the most dilute solutions, which were of the order of 0.0040 percent $CaSO_4$, the analytical uncertainty may have been as much as ± 5 percent.

The determination of pressure was accurate to 4 parts in 1000. The pressure coefficient of solubility is small; for example, at 156°C it is about 6 x 10^{-5} weight percent $CaSO_4$ per bar. Uncertainties in solubility measurements resulting from inaccuracies in pressure measurement were insignificant compared to possible errors caused by other factors.

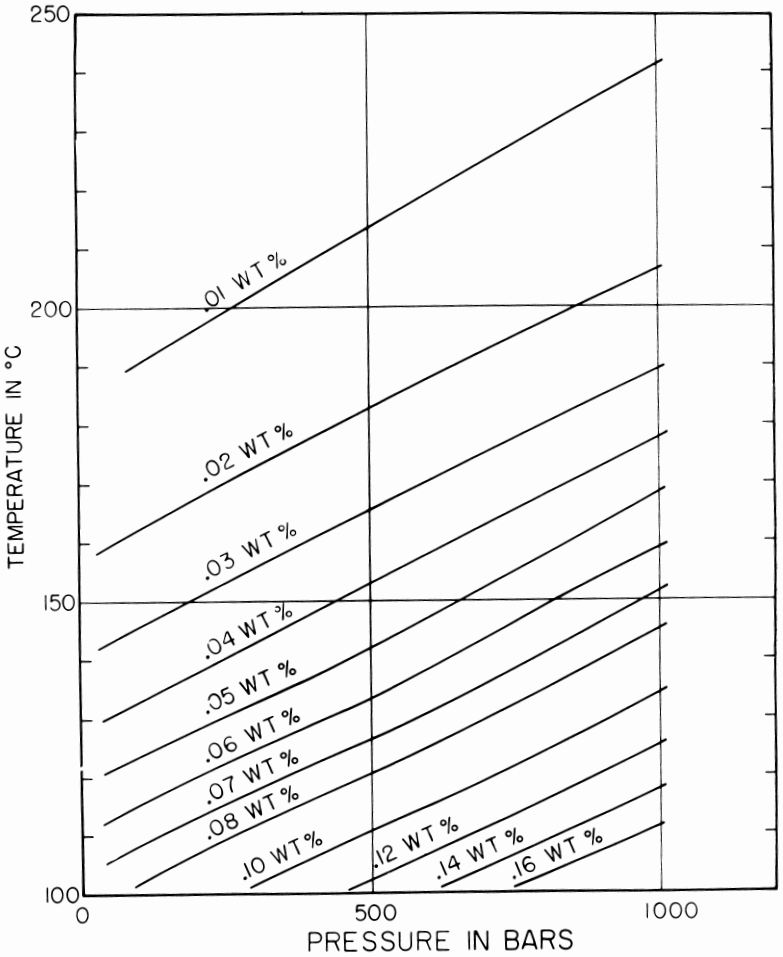

Fig. 8. Constant $CaSO_4$ composition sections through the P-T-X saturation surface representing the solubility of anhydrite in water.

The calculated solubilities of anhydrite at temperatures of 50°, 100°, 150°, 200°, 250°, and 300°C and at several pressures are listed in table 3. These are regarded as the most probable values for the solubility of anhydrite under the conditions given. From these values the pressure coefficient of solubility may be estimated.

Extrapolations to higher or lower temperatures or to higher pressures must be done with caution. Styrikovich and Khokhlov (1957, fig. 6, p. 5) determined the solubility of calcium sulfate in water at temperatures from 400°C to 600°C and at pressures from 220 to 300 atmospheres. Their value at 400°C and 300 atmospheres is of the same order of magnitude as that estimated from the empirical equation at 500 bars after applying a correction for the pressure difference. The solubility at 500°C and 1000 bars determined by

TABLE 3

Calculated solubilities of anhydrite in water in weight percent

Temperature °C	Pressure bars	$CaSO_4$ wt%
50	1	0.229
	100	0.277
	500	0.373
	1000	0.595
100	1	0.0738
	100	0.0859
	500	0.125
	1000	0.206
150	5	0.0237
	100	0.0267
	500	0.0419
	1000	0.0713
200	15	0.0076
	100	0 0083
	500	0 0140
	1000	0.0247
250	38	0.0024
	100	0.0026
	500	0.0047
	1000	0.0085
300	86	0.0008
	100	0.0008
	500	0.0016
	1000	0.0030

Morey and Hesselgesser (1951, p. 832), 0.002 weight percent, is much higher than that predicted from the empirical equation, namely 0.00005 weight percent, under the same conditions. Calculations of the value of the solubility of anhydrite at elevated pressures at temperatures below 100°C do not agree with the values of solubility of anhydrite calculated by Marshal (1952, p. 292). The solubility calculated by the authors at 50°C and 500 bars is 0.37 weight percent, compared to Marshal's calculation of approximately 0.26 weight percent.

Thermodynamic quantities involving $CaSO_4$ in solution, such as partial entropies and volumes, can be calculated from the solubility data from chemical thermodynamics and the dilute solution theory. Treatment of the solubility data is in process in collaboration with Professor Hartland Schmidt of the Chemistry Department, University of California, Riverside, California, and the results will appear in a subsequent paper.

GEOLOGIC CONCLUSIONS

Anhydrite occurs most commonly with saline minerals in marine deposits formed under conditions of lower temperature and pressure than our experimental conditions. However, anhydrite also occurs in some hydrothermal mineral deposits that have formed at temperatures and pressures approximated by our experimental conditions. On the basis of the solubility measurements, conclusions can be made regarding possible factors involved in the deposition of anhydrite from saturated solutions. Any geologic process that increases temperature or decreases pressure would cause the precipitation of anhydrite from solutions saturated with $CaSO_4$.

The solubility of anhydrite generally decreases with depth below the Earth's surface. The increase in solubility resulting from increased pressure is offset by the decrease in solubility caused by higher temperature. Only for the unusual situation in which a temperature gradient as great as 10°C/km is combined with a normal lithostatic pressure gradient would anhydrite precipitate from saturated solutions migrating toward the surface of the Earth.

Interpretation of our solubility data suggests that anhydrite may deposit under at least three different conditions. Saturated solutions at one temperature migrating from interstices in rocks in which lithostatic pressure prevails to a fissure in which the total pressure is hydrostatic would deposit calcium sulfate as anhydrite along the pressure gradient in the country rock and in the fissure. Ground waters saturated with calcium sulfate descending to hotter regions at depth would deposit anhydrite. Anhydrite would precipitate in the pores of sedimentary rock as the result of the increase in temperature accompanying burial of the accumulating sediments, from interstitial waters containing calcium sulfate originally entrapped during sedimentation. Conversely, anhydrite crystals in buried sedimentary rocks would tend to dissolve in interstitial solutions as a consequence of temperature and pressure drop taking place with uplift and erosion of the sediments.

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