American Mineralogist, Volume 58, pages 323-331, 1973

Gypsum–Anhydrite Equilibria in Systems $CaSO_4$–H_2O and $CaCO_4$–NaCl–H_2O

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Abstract

The equilibria of gypsum and anhydrite with solution and vapor were studied by the use of solubilities, which were in part gained from downward extrapolation of solubilities measured at high temperatures to avoid kinetic difficulties encountered below 70°C. The 4–phase invariant equilibrium of gypsum, anhydrite, simple H_2O solution, and vapor is set at 56°C ± 3°C and 124 ± 9 torr. The pressure change required to increase the univariant equilibrium temperature of gypsum, anhydrite and H_2O solution 1°C is about 78 bars, which agrees well with values calculated from thermochemistry. The 3–phase univariant equilibrium of gypsum, anhydrite, and vapor ranges from 124 torr at 56°C to 13.6 torr at 20°C. The effect of NaCl concentration on the 4–phase univariant equilibrium of gypsum, anhydrite, NaCl–H_2O solution, and vapor, is to lower the equilibrium temperature from that of the invariant point, 56°C for zero NaCl concentration, to: 48°C, 2 molal NaCl; 36°C, 4 molal NaCl; and 20°C, 6 molal NaCl. The uncertainty in the temperatures in NaCl solutions is ± 4°C.

Introduction

Gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) occur as minerals in diverse environments. Knowledge of the temperature and pressure conditions under which the two minerals coexist stably with aqueous solutions is essential to understanding the genesis of specific mineral associations. This paper presents results of studies on equilibrium relations of gypsum and anhydrite in the presence of saturated aqueous solutions and vapor.

A schematic representation of phase relationships in the system $CaSO_4$-H_2O is presented in Figure 1. The phases stable in the temperature and pressure ranges of this study, 15 to 70°C and 0.01 to 1000 bars, respectively, are designated by capital letters, as follows: G, gypsum; A, anhydrite; L, saturated solution; and V, vapor. Figure 1 shows that four curves representing univariant three-phase equilibria intersect at a point representing the invariant four-phase equilibrium G + A + L + V. The conditions at the invariant point and along the univariant curves of G + A + L and G + A + V have been determined as part of this study.

In addition, the effect of dissolved NaCl on the univariant four–phase equilibrium G + A + L* + V (L* represents NaCl–H_2O solution), was determined as a function of NaCl concentration.

Previous Studies

G + A + L + V Equilibrium in system $CaSO_4$-H_2O. The four-phase equilibrium G + A + L + V has received much attention from previous workers, most of whom used methods based on solubility measurements. Controversy exists as to the exact conditions prevailing at the point. Zen (1965) and Hardie (1967) include summary statements of the topic, useful to readers who wish to pursue the subject. The temperatures reported to hold at the invariant point range from 63.5°C (Hoff *et al.*, (1903) to a value of 38°C (Toriumi and Hara, 1938).

Most workers have accepted Posnjak's (1938) solubility based value of 42°C. More recent solubility studies by D'Ans *et al.* (1955), Bock (1961) Marshall and Slusher (1966) and Power *et al.* (1966) also support a transition temperature of 40 to 42°C. The 40°C value calculated from thermochemical data by Kelley *et al.* (1941) must be regarded as fortuitous. Zen (1965) and Hardie (1967) in reviewing the thermochemical data showed that there was a large uncertainty (±22°C)

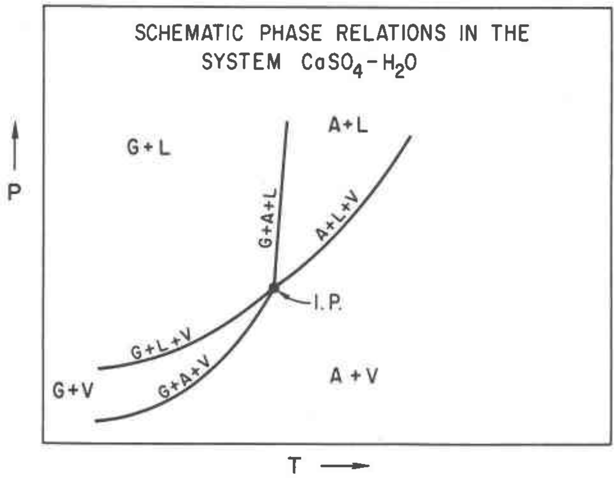

FIG. 1. Schematic phase relations in the system $CaSO_4$-H_2O projected onto the temperature–pressure plane. Four three–phase univariant equilibria are represented by curves that meet at the four–phase invariat point, *I.P.* Phase designations are: Gypsum, G; anhydrite, A; H_2O solution, L; and vapor, V.

inherent in the calculations. Zen (1965) also called attention to the significance of the sluggish reaction of anhydrite with simple aqueous and NaCl-H_2O solutions, which below about 70°C is so slow that no experimenter has successfully reversed solubility determinations. Although some difficulties have been met in reacting gypsum with solutions (Hulett, 1901; Hara *et al.,* 1934), the determinations have been reversed in adequate detail over a wide range of temperature. Determinations of the G + A + L + V invariant point from plots of the apparent solubility of anhydrite and the true solubility of gypsum yield only estimates of minimum temperatures.

Hardie (1967) put forth a temperature of 58°C, based on a novel method, which revived interest in the matter. D'Ans (1968) objected to Hardie's determination, regarding it as too high, and re-stated his preference for Posnjak's temperature of 42°C. The major points raised by D'Ans revolve about kinetic considerations, such as the possibility that metastable phases had appeared unheeded during Hardie's experiments. D'Ans raised interesting questions, but his death has prevented clarification of his arguments. Cruft and Chao (1970) state their preference for the 40–42°C transition temperature. They failed, however, to present any evidence to support this preference. Hardie (1967) determined the equliibrium relations of gypsum and anhydrite by a method that compensated for the slow reaction of anhydrite with solution. He reacted mixtures of gypsum and anhydrite with solutions of Na_2SO_4 and H_2SO_4 of various concentration at several different temperatures. By noting which phase, gypsum or anhydrite, tended to increase during long reaction times, he was able to delineate the stability fields of G + L and A + L. Extrapolating his data to zero dissolved substance concentration permitted him to estimate the temperature at the four-phase point to be 58° ± 2°C. Hardie's work was done carefully; he examined the solid phases at regular intervals to make sure only gypsum and anhydrite were present, and he successfully reversed the reactions.

$G + A + L^* + V$ equilibria in system $CaSO_4$-NaCl-H_2O. Dissolved salts decrease the temperature at which G + A + L* + V coexist. Figure 3 presents a summary of previous significant studies. Sea water brines at various concentrations were used in the study by Toriumi and Hara (1938). Their solubility-based results compare very well with those obtained by D'Ans (1955) in NaCl solutions on a moles chlorine per kilogram of water basis. Posnjak (1940) reported an equilibrium temperature of 30°C in sea water solutions 4.8 times normal salinity which is equivalent to a 3 moles NaCl/kg H_2O (3 molal NaCl) solution. This is about 4°C higher than the results of Toriumi and Hara or D'Ans. MacDonald (1953) calculated the change in equilibrium temperature with NaCl concentration using thermochemical data. Bock (1961), Power *et al.* (1966) and Marshall and Slusher (1966) evaluated equilibrium temperatures from solubility data in NaCl solutions with results that agreed with Posnjak and MacDonald. Zen's (1965) study cast doubt on the anhydrite solubilities below 70°C, and suggested that the equilibrium temperature must be higher than the solubility studies indicate.

Hardie (1967) evaluated the effect of solutions of different ionic strengths (activities of H_2O) by the method described earlier. Hardie's results are illustrated in Figure 3 in which his H_2O activities are related to NaCl concentration using vapor pressure data from the International Critical Tables (1929). Hardie's temperatures are distinctly higher than other workers over most of the concentration range. While anhydrite-solution reactions may be too sluggish for equilibrium to be obtained in H_2O or NaCl-H_2O solutions, reactions in Na_2SO_4 and H_2O_4 solutions do proceed rapidly enough.

$G + A + L$ equilibrium in system $CaSO_4H_2O$. Manikhin and Kryukov (1968) measured gypsum

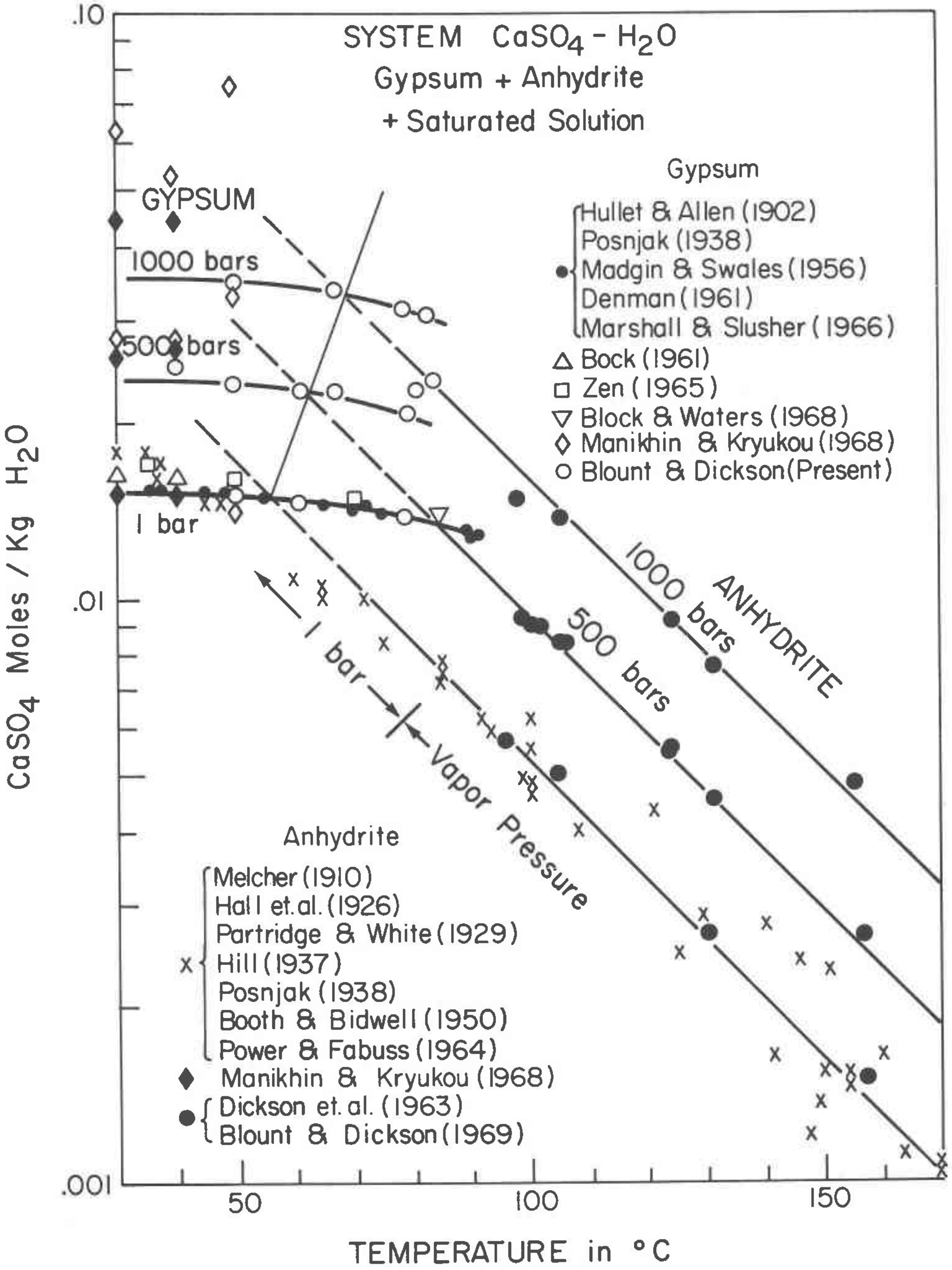

FIG. 2. The logarithm of gypsum and anhydrite solubility in molality in system $CaSO_4$–H_2O plotted versus temperature at 1 bar or the vapor pressure of the solution, 500 bars, and 1000 bars. Solid lines represent solubilities calculated from equations of Table 2; dashed lines represent extrapolated portions of the calculated anhydrite solubility curves. The line connecting the intersections of the isobaric curves is the projection onto the composition–temperature plane of curve separating G + L from A + L in Figure 1.

and anhydrite solubilities at high pressures from 0 to 50°C. Their results are shown in Figure 2. The pressure effect on the equilibrium has been calculated to be 83 bars/°C (Marsal, 1952) and 85.4 bars/°C (MacDonald, 1953). Zen (1965) obtained a value of 71 ± 1.9 bars/°C using the thermochemical data of Kelley *et al.* (1941), 46°C as the equilibration temperature, and more recent data on the molar volumes of gypsum and anhydrite.

G + A + V equilibrium in system $CaSO_4$-H_2O.

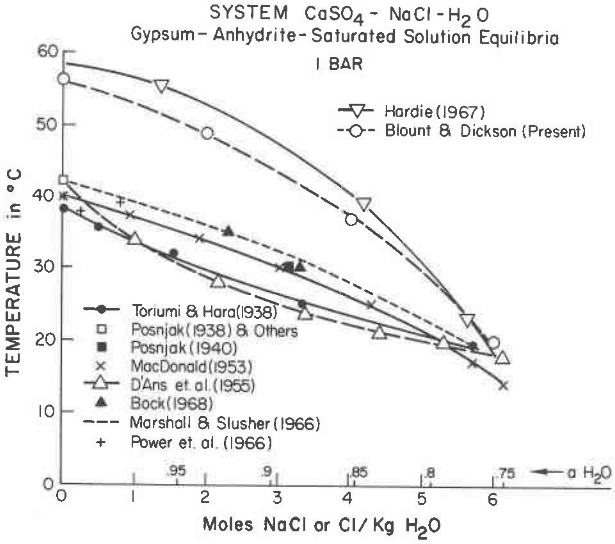

FIG. 3. The effect of NaCl or Cl concentration and activity of H_2O on the equilibrium temperature of the gypsum, anhydrite, solution, and vapor assemblage, at 1 bar total pressure in the system $CaSO_4$-NaCl-H_2O. H_2O vapor pressure ranges from 124 torr at 56°C and zero NaCl concentration, to 13.6 torr at 20°C and 6 molal NaCl.

The equilibrium of gypsum and anhydrite with vapor cannot be measured directly because of the excessive times required to equilibrate the solids with the vapor phase. The position of the curve as evaluated from Hardie's temperature versus ionic strength data, combined with data on the vapor pressure of NaCl-H_2O solutions as a function of temperature and ionic strength, is presented in Figure 7.

Summary of previous work. Controversy exists as to the temperature at the 4-phase invariant point, as well as to the quantitative effect on lowering the temperature created by dissolved salts. Hardie's work contrasts with the studies of most previous workers, who have reported lower temperatures. The effect of pressure on the univariant equilibrium of gypsum, anhydrite and saturated simple H_2O solutions has not been established experimentally, but it has been calculated from thermochemical data. The temperatures and H_2O pressures of the anhydrite, gypsum, and vapor equilibrium have been estimated from Hardie's (1967) data. Some additional work is clearly needed to clarify gypsum-anhydrite relations.

Present Work

We have used the solubility method of determining equilibrium conditions of phase assemblages. The method is simple in principle; it consists of experimentally determining the temperatures and pressures at whch gypsum and anhydrite show the same solubilities in a particular solution type. We used solubility data from the literature and unpublished solubilities of our own, measured for this purpose. The solubilities were cast into empirical equations, which related gypsum and anhydrite solubilities to temperature, pressure, and NaCl concentration. Anhydrite solubilities in the kinetically hindered region below 70°C were estimated by downward extrapolating higher temperature data.

Anhydrite and gypsum solubilities. The solubilities of anhydrite and gypsum were measured by the use of the hydrothermal solution equipment, previously used to measure the solubility of anhydrite in H_2O solutions from 100° to 275°C and 1 to 1000 bars (Dickson *et al.,* 1963) and in NaCl-H_2O solutions from 100 to 450°C and 1 to 1000 bars (Blount and Dickson, 1969). One new determination of anhydrite solubility was made at 80°C–1000 bars; efforts to measure the solubility at lower temperatures failed. Gypsum solubilities were determined from 40 to 83°C at 1, 500, and 1000 bars in simple H_2O solutions (Table 1).

The procedures followed in the anhydrite and gypsum solubility determinations were those of Dickson *et al.* (1963). Well-crystallized artificial anhydrite and gypsum, and carefully purified H_2O, free of CO_2, were used. Gypsum equilibrated with solution within one day, in contrast to anhydrite, which required three days to attain equilibrium at 80°C. Selected solubilities were reversibly determined. The maximum estimated uncertainty in the values of Table 1 is ±2.5 percent of the solubility value, ±2°C and ±4 bars.

Gypsum and anhydrite solubilities are illustrated in Figure 2. There is good agreement between the 1 bar gypsum solubilities obtained during this study and those obtained by Hullet and Allen (1902), Melcher (1910), Posnjak (1938), Denman (1961), Marshall and Slusher (1966). The 1 bar gypsum solubilities obtained by Bock (1961), Zen (1965), Block and Waters (1968) are significantly higher. The reasons for this disagreement are unknown. However, Hullet (1901), Hullet and Allen (1902), Tanaka *et al.* (1931) and Hara *et al.* (1934) discuss high apparent solubilities for gypsum when it is either poorly crystalline or very fine grained. Hullet (1901) pointed out that gypsum was very soft and easily ground to a fine powder when stirred. Because of the possibility that the high gypsum

TABLE 1. The Solubility of Gypsum in H_2O Solution as a Function of Temperature and Pressure

Pressure in Bars (± 4 bars)	Temperature in °C (± 2° C)	Gypsum Solubility in Mols $CaSO_4$/Kg of H_2O (± 2.5%)
24	50	.0155 u
476	50	.0228 u
457	50	.0226 u
995	50	.0337 u
986	50	.0339 u
986	50	.0348 u
468	60	.0218 s
498	60.5	.0223 s
24	61	.0147 s
140	79	.0152 -
5	79.5	.0139 s
3	79	.0138 s
470	79.5	.0203 u
474	79	.0200 u
990	77.5	.030 u
1010	77.5	.0301 u
565	41	.0264 u
548	40	.0260 u
902	67	.030 u
902	68	.031 u
904	67	.030 u
892	67	.0307 u
515	67	.0228 s
500	67	.0224 s
502	67	.0228 s
992	66.5	.033 -
1002	66.5	.034 u
999	67	.0335 u
998	83	.0309 s
1001	83.5	.0314 s
1002	83	.0313 s
1004	83	.0307 s

u = solubility approached from undersaturation.
s = solubility approached from supersaturation.

TABLE 2. Solubilities of Gypsum and Anhydrite in NaCl–H_2O Solutions at Constant NaCl Concentration in Molality

Phase	NaCl conc. in molality	Empirical Equations*
Gypsum	0.0	$\text{Ln } m = -4.355 + 0.840 \times 10^{-3} p + 0.0105t - 1.700 \times 10^{-4}t^2 + 0.584 \times 10^{-6}t^3.$
Anhydrite	0.0	$\text{Ln } m = -2.87 + 1.220 \times 10^{-3}p - 0.0237t - 0.0028 \times 10^{-3}pt + 0.010 \times 10^{-4}t^2 + 0.140 \times 10^{-7}pt^2.$
	2.0	$= -1.979 - 0.0215t + 0.5955 \times 10^{-4}t^2 - 0.0895 \times 10^{-6}t^3.$
	4.0	$= -2.447 - 0.01435t + 0.3635 \times 10^{-4}t^2 - 0.03667 \times 10^{-6}t^3.$
	6.0	$= -2.926 - 0.01043t + 0.3435 \times 10^{-4}t^2 - 0.0367 \times 10^{-6}t^3.$

* m = solubility in mols $CaSO_4$/kg of H_2O.
p = pressure in bars.
t = temperature in °C.

solubilities are anomalous, they were not used in our calculation of an empirical equation for gypsum solubility as a function of temperature and pressure, Table 2. The closeness of the fit of solubilities calculated from this equation is evident in Figure 2. The values calculated from the empirical equation are within ±2 percent of most of the experimental data used to derive the equation.

There is considerable scatter in anhydrite solubilities obtained by different workers especially at higher temperatures. The data of Dickson *et al.* (1963) and Blount and Dickson (1969) were carried out reversibly and were repeatable. This data was processed to obtain the empirical equation given in Table 2 from which solubilities were calculated to give the graph lines in Figure 2. Logarithms of anhydrite solubility show almost a linear change with temperature from 80°C to 260°C. In general most experimental points are within ±5 percent of the value predicted by this equation. Above 70°C solubilities predicted by this equation are quite close to many of the experimental determinations by a number of other workers (Melcher, 1910; Partridge and White, 1929; Hill, 1937; Posnjak, 1938; Marshall *et al.* 1964).

High results such as those by Hall *et al.* (1926) may represent solubilities of poorly crystalline anhydrite, or some hemihydrate may have been present. Results such as those by Booth and Bidwell (1950) may represent failure to obtain saturation or other experimental problems. Table 3 displays gypsum and anhydrite solubilities calculated for regular intervals of temperature and pressure.

Results on the G + A + L + V equilibrium in system $CaSO_4$-H_2O. The curves representing gypsum and anhydrite solubilities as a function of temperature at 1 bar total pressure (Fig. 2) intersect at 56°C. Considering that the calculated solubilities for anhydrite and gypsum are within ±5 percent and ±2 percent of the equilibrium value respectively, the uncertainty in the transition temperature is ±3°C. This value is within the experimental error of Hardie's value, 58° ± 2°C, and it is in closer agreement with van't Hoff *et al.*'s value of 63.5°C than with any other number reported earlier. The vapor pressure at the invariant point, neglecting the negli-

TABLE 3. Solubilities of Gypsum and Anhydrite in H_2O Solution at Regular Intervals of Temperature and Pressure*

Pressure in bars	Phase	Solubility in Molality Temperature in °C				
		40	50	60	70	80
1	Gypsum	.0154	.0153	.0148	.0143	.0137
1	Anhydrite		.0175	.0138	.0108	.0086
500	Gypsum	.0240	.0233	.0226	.0218	.0205
500	Anhydrite			.0238	.0187	.0147
1000	Gypsum	.0358	.0352	.0344	.0330	.0310
1000	Anhydrite			.0415	.0324	.0253

* calculated from empirical equations of Table 2.

gibly small effect that the dissolved $CaSO_4$ exerts on the vapor pressure of the solution, is 124 ± 9 torr (torr = mm of Hg).

Hardie and we used different methods to get around the difficulty presented by the slow reaction rate of anhydrite at low temperatures. The concordance in the equilibrium temperatures obtained by two different approaches adds strong support for the general correctness of a temperature in the 50 to 60°C range, rather than in the 38 to 46°C range of early workers.

Results on G + A + L + V equilibria in system $CaSO_4$-$NaCl$-H_2O.* The equilibrium temperatures were determined as a function of NaCl concentration at 1 bar pressure by essentially the same procedure used in the system $CaSO_4$-H_2O. The anhydrite solubility data in $NaCl$-H_2O solutions of Blount and Dickson (1969) and the 70°C data of D'Ans *et al.* (1955) were processed to derive empirical equations that relate anhydrite solubility to temperature at several NaCl concentrations, at 1 bar (Table 2).

Since many anhydrite solubility determinations were at conditions somewhat different from those used for deriving these equations, it was necessary to apply small corrections to the experimental data by graphical interpolation and extrapolation. Since the solubility of anhydrite has been well measured over a range of NaCl, temperature and pressure conditions, this procedure did not introduce significant uncertainties into the solubility values. The empirical equations were derived from graphical plots of the function $\Delta m/m'\Delta T$ in which Δm is the change in molal concentration for the temperature interval ΔT and m' is the mean molal concentration in the interval. The curves obtained were closely approximated by a quadratic equation which was integrated using several data points to obtain the final equation. The equations reproduced the solubility values used in their derivation within ±2 percent over a temperature range from 70° to 250°C. Solubilities based on these equations are illustrated by curves in Figures 4, 5, and 6.

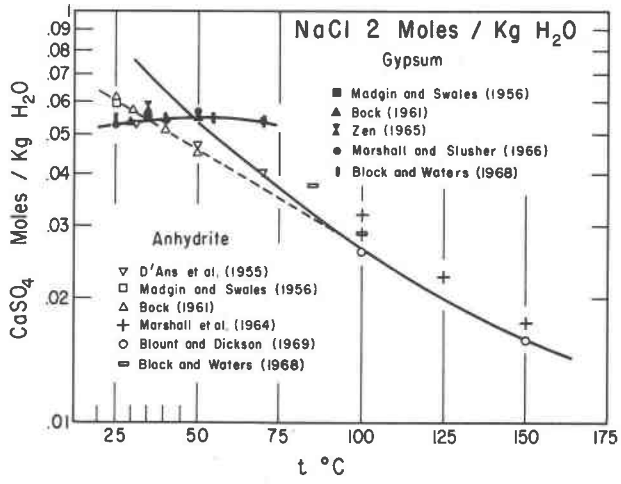

FIG. 4. The effect of temperature on the solubilities of gypsum and anhydrite in 2 molal NaCl solution at 1 bar total pressure.

Solubilities reported for anhydrite in the kinetically hindered region (temperatures below 70°C) are significantly lower than values calculated from the empirical equation. The inclusion of this data would have produced a sharp inflection in the curves of the function $\Delta m/m'\ \Delta T$. Anhydrite solubilities above 100°C reported by Zdanovsky (1949), Marshall *et al.* (1964), Block and Waters (1968) and Glew and Hames (1970) are noticeably higher than those used to derive the equations. If anhydrite solubility were higher than the curves suggest, the gypsum-anhydrite transition temperature would also be higher. The higher solubilities may indicate the presence of hemihydrate or a fine grained poorly crystalline anhydrite in those experiments.

Gypsum solubilities in $NaCl$-H_2O solutions show considerable variation. Since also many determinations are at conditions somewhat different than those desired for comparison purposes, it was necessary to graphically plot this data to obtain interpolated values. In this analysis, considerable attention

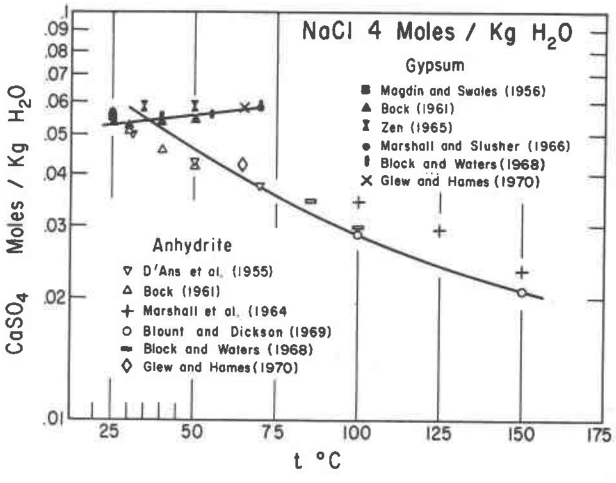

FIG. 5. The effect of temperature on the solubilities of gypsum and anhydrite in 4 molal NaCl solution at 1 bar total pressure.

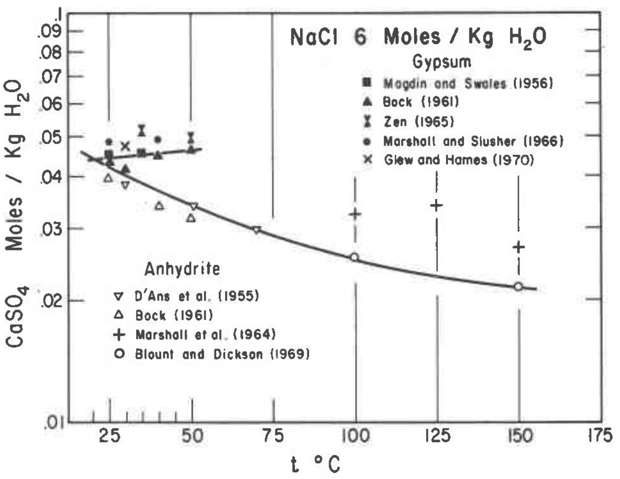

FIG. 6. The effect of temperature on the solubilities of gypsum and anhydrite in 6 molal NaCl solution at 1 bar total pressure.

was paid to what information was available regarding experimental procedures, especially considering the tendency of gypsum to undergo grinding under many experimental situations as discussed previously. Some values in the literature may be anomalously high due to the presence of poorly crystalline or very finely pulverized material. In this effort we attempted to obtain an internally consistent set of data and reject values which appeared either low or high. The gypsum solubility curves illustrated in Figures 4, 5, and 6 are in fair agreement with the results by Madgin and Swales (1956), Bock (1961) Block and Waters (1968), and some of the results of Marshall and Slusher (1966). The results by Zen (1965) and by Marshall and Slusher (1966) (in 6 molal NaCl) are significantly higher. The uncertainty regarding gypsum solubilities are probably around ±3 percent.

The temperatures evaluated by the above procedure were: 48° ± 4°C, 2 molal NaCl; 36° ± 4°C, 4 molal NaCl; and 20° ± 4°C, 6 molal NaCl. The uncertainty in each temperature was estimated following the procedure used for that in H_2O only. Figure 3 shows all data plotted as temperature versus NaCl concentration. Our curve agrees well with Hardie's, but it falls above curves of the other workers, except at high NaCl concentration, where all curves converge. The agreement of our and Hardie's work supports the validity of a higher temperature position for the correct curve.

Results on G + A + L equilibrium in system $CaSO_4$-H_2O. The 3-phase univariant equilibrium of gypsum, anhydrite and saturated H_2O solution was evaluated from solubilities measured as functions of temperature and pressure. Figure 2 shows solubility versus temperature plots for 1, 500, and 1000 bars for gypsum and anhydrite. Solubilities reported by Manikhin and Kryukov (1968) for gypsum agree with previous results at 1 bar but are higher than present results at 500 and 1000 bars. Their anhydrite solubilities are scattered above and below the calculated solubility curves shown in Figure 2. It is doubtful that they achieved equilibrium during their anhydrite solubility measurements. Their gypsum solubilities also seem to be anomalous. The equilibrium temperature obtained from the curves in Figure 2 are 56 ± 3°C, 62 ± 3°C and 69 ± 3°C for 1, 500, and 1000 bars respectively. The uncertainty in the slope, *dp/dt*, is probably not in excess of ±1°C for 1000 bars. Our value of 78 ± 7 bars/°C is not far from values calculated by Marsal (1952) and MacDonald (1953), which were 83 bars/°C and 85.4 bars/°C respectively. Zen (1965) recalculated the pressure coefficient using more recent molar volume data and obtained 70.9 ± 1.9 bars/°C which agrees with our recalculations using Hardie's more recent revised thermochemical equations (Hardie, 1967) and Clark's (1966) molar volume data. In view of the tendency for quantities calculated from thermochemical considerations to show relatively large uncertainties, the agreement of the thermochemically calculated pressure coefficients with the experimental value is excellent.

Results on G + A + V equilibrium in system $CaSO_4$-H_2O. The temperatures and H_2O pressures at which gypsum and anhydrite coexist in the presence of vapor cannot be determined directly because of kinetic hindrances to attainment of equilibrium. They can be estimated from the temperature versus NaCl concentration data presented in Figure 3, together with data on vapor pressures of NaCl-H_2O solutions of different NaCl concentrations and temperatures (*International Critical Tables,* 1933). Two effects have been neglected: the tiny lowering of the vapor pressure of the solutions resulting from dissolved $CaSO_4$; and the small positive effect of the confining pressure of 1 bar on the vapor pressure of the solutions.

The approach is based on the well-known principle of physical chemistry that a multi-phase system in equilibrium at a given temperature and pressure remains at equilibrium if one of the phases is removed, other circumstances being held constant.

Gypsum and anhydrite equilibrated with NaCl-H_2O solution and vapor remain in equilibrium with the vapor phase even if the NaCl-H_2O solution is removed. The vapor pressure of the series of NaCl-H_2O solutions that are in equilibrium with gypsum and anhydrite at different temperatures can be closely approximated from known data. Figure 7 presents a plot of H_2O pressure versus temperature data for the reaction.

Hardie (1967) did not present his data in this form; however, his H_2O activity versus temperature data on the equilibrium of gypsum, anhydrite, solution and vapor, can be converted conveniently to vapor pressure versus temperature data. His data, when plotted on a diagram such as Figure 7, yield a curve indistinguishable from ours, in view of the uncertainties.

The univariant curve representing the G + A + V equilibrium falls below the vapor pressure curve for H_2O liquid and vapor at all temperatures below 56°C. At 56°C, the G + A + V curve terminates at the invariant point for G + A + L + V. At temperatures above 56°C, the G + A + V equilibrium can only occur metastably.

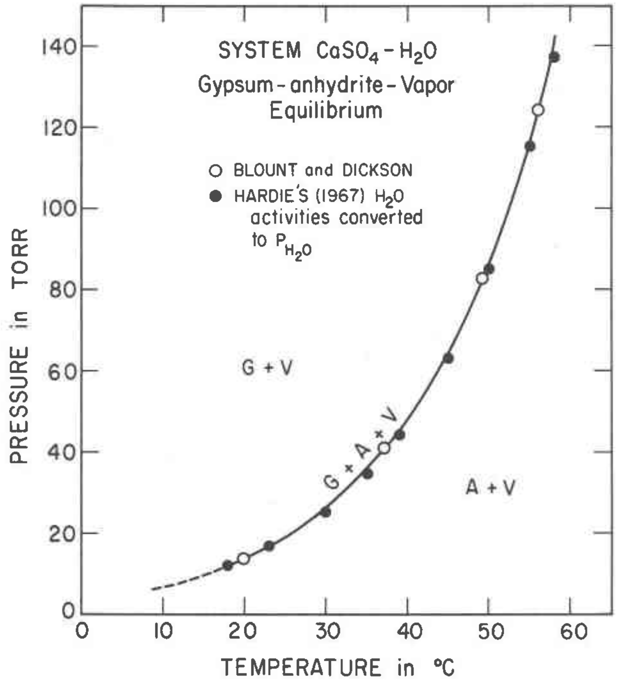

FIG. 7. The equilibrium of gypsum, anhydrite, and vapor, at 1 bar total pressure, represented by a plot of vapor pressure versus temperature. The upper terminus of the curve is at the four-phase invariant point G + A + L + V, located at the uppermost open circle according to Blount and Dickson and at the uppermost solid circle according to Hardie (1967). (torr = mm Hg).

Conclusions

The temperatures of the equilibria of gypsum and anhydrite with solution and vapor, evaluated by most previous workers from solubilities, appear to be too low. The major cause of difficulty is the slowness with which anhydrite reacts with simple H_2O or NaCl-H_2O solutions below 70°C. Hardie (1967) took advantage of the more rapid reaction of anhydrite with H_2SO_4 solutions to evaluate indirectly higher equilibrium temperatures. By application of a still different approach based on downward extrapolation of high temperature solubilities to lower temperatures, we have evaluated equilibrium temperatures which are in general agreement with Hardie's. We feel, therefore, that our results add strong support to the correctness of the higher temperatures reported by Hardie.

Our direct measurements of the solubilities of gypsum and anhydrite in H_2O solutions enabled us to evaluate the pressure effect on the G + A + L equilibrium, which agreed well with the pressure effect calculated from thermochemical data.

The experiences of workers studying the gypsum-anhydrite equilibria by use of the solubility approach illustrates the strengths and weaknesses of the method. The solubility approach avoids many of the kinetic difficulties other methods encounter, such as the appearance of metastable phases. However, for the solubility method to work, equilibrium solubility values must be available. Reversible reactions of the solid and liquid phases are essential to demonstrating that equilibrium has been attained. The history of the studies on gypsum and anhydrite stability relations well illustrates the hazards of accepting steady state or slowly changing concentration values as equilibrium solubilities.

Acknowledgments

The authors are indebted to Professor Konrad Krauskopf, Geology Department, Stanford University, who kindly reviewed the manuscript. Mr. Warren Ervine and Mr. Francisco Querol–Suñe, Geology Department, Stanford University, made valuable comments. The work was supported by the National Science Foundation Grants G7405 and P862.

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Manuscript received, October 4, 1971; accepted for publication October 6, 1972.