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THE GYPSUM—ANHYDRITE EQUILIBRIUM AT ONE ATMOSPHERE PRESSURE[1]

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ABSTRACT

The equilibrium temperature for the reaction $CaSO_4 \cdot 2H_2O = CaSO_4 + 2H_2O_{(liq.\ soln)}$ has been determined as a function of activity of H_2O (a_{H_2O}) of the solution. Synthetic gypsum and anhydrite or 1:1 mixtures were stirred in solutions of known a_{H_2O} (calculated from vapor pressure data for the Na_2SO_4 and H_2SO_4 solutions), at constant temperature for as much as 12 months. The reversible equilibrium was approached from both sides and is defined by: $a_{H_2O} = 0.960$ at 55°, 0.845 at 39°, 0.770 at 23°C. Provided the solids do not change in composition, the equilibrium at constant P and T is a function of a_{H_2O} only and is independent of the constituents in solution. Extrapolation to the bounding system $CaSO_4$-H_2O ($a_{H_2O} = 1.000$) yields 58°±2°C. This is within thermodynamic calculations (46°±22°C) but higher than solubility measurements (38° to 42°C). The new data indicate that in sea-water saturated with halite and gypsum should dehydrate above 18°C. The scarcity of anhydrite in modern evaporite deposits is predicted by the present results. The available data on the temperature-salinity conditions under which anhydrite and gypsum exist in the Recent supratidal flat sediments of the Trucial Coast, Persian Gulf, are compatible with the present experimental data.

INTRODUCTION

The stability relations of gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) are of considerable interest because most natural marine evaporite deposits consist essentially of gypsum and/or anhydrite interbedded with dolomite, limestone and clastic sediments (*e.g.*, Stewart 1963, Table 18). In the binary system $CaSO_4$-H_2O, the reaction $CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 + 2\ H_2O_{(liq.)}$ has been studied experimentally at one atmosphere pressure by van't Hoff *et al* (1903), Partridge and White (1929), Toriumi and Hara (1934), Hill (1934), Posnjak (1938) and D'Ans *et al* (1955). Kelley, Southard and Anderson (1941) measured the thermochemical properties of the solid phases of the system at atmospheric pressure, and from these data calculated an equilibrium temperature for the gypsum-anhydrite transition. Marsal (1952), MacDonald (1953), Zen (1965) and Hardie (1965, pp. 25–30) calculated the effect of pressure on the reaction.

The effect of salt solutions on the gypsum-anhydrite equilibrium at atmospheric pressure has been considered in some detail by several workers, all of whom have verified that the transition temperature is lowered with increasing salinity. The system $CaSO_4$-$NaCl$-H_2O has been investigated experimentally by van't Hoff *et al* (1903), D'Ans *et al* (1955), Madgin and Swales (1956), Bock (1961) and Zen (1965). MacDonald

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[1] This paper is taken from a Ph.D. dissertation submitted by L. A. Hardie to the Department of Geology, The Johns Hopkins University, Baltimore, Maryland.

(1953) calculated the effect of NaCl solutions on the equilibrium temperature. The transition in sea water has been studied by Toriumi *et al* (1938) and Posnjak (1940). Other pertinent laboratory studies are those of Hill and Wills (1938) and Conley and Bundy (1958) in the system $CaSO_4$-Na_2SO_4-H_2O, D'Ans and Höfer (1937) in the system $CaSO_4$-H_3PO_4-H_2O, and Ostroff (1964), who converted gypsum to anhydrite in NaCl-$MgCl_2$ solutions.

For the most part the results of the different workers are in poor agreement. For this reason, and because the methods used were largely indirect (*e.g.* solubility and dilatometer measurements, thermodynamic calculation), a re-examination of the problem, using a different laboratory approach, seemed desirable.

The conversion of gypsum to anhydrite, and anhydrite to gypsum, was studied at atmospheric pressure as a function of temperature and activity of H_2O (a_{H_2O}). For the reaction

$$CaSO_4 \cdot 2H_2O_{(s)} \rightleftharpoons CaSO_{4(s)} + 2H_2O_{(\text{liquid, in solution})}$$

the equilibrium constant may be defined in terms of activities, as follows:

$$(K_a)_{p,T} = \frac{a_{CaSO_4} \cdot a^2_{H_2O}}{a_{CaSO_4 \cdot 2H_2O}}$$

If the standard states of the components of the reaction are considered to be pure H_2O liquid water, pure crystalline $CaSO_4$ and pure crystalline $CaSO_4 \cdot 2H_2O$ at one atmosphere total pressure and at the temperature of reaction, the equilibrium constant simplifies to

$$(K_a)_{T,p=1} = a^2_{H_2O}$$

It follows that the dehydration of gypsum to anhydrite, at atmospheric pressure, is a function of temperature and activity of H_2O only. Therefore, provided the solids do not change in composition, the equilibrium is independent of the components in the co-existing solution.

The activity of H_2O of the solutions co-existing with gypsum or anhydrite was varied by adding Na_2SO_4 or H_2SO_4: these were chosen because the gypsum$\rightleftharpoons$anhydrite conversion rates were found to be relatively rapid in sodium sulfate or sulfuric acid solutions. In the system $CaSO_4$-Na_2SO_4-H_2O neither gypsum nor anhydrite can co-exist with a solution of Na_2SO_4 concentration greater than that fixed by the one atmosphere isothermally invariant assemblage gypsum (or anhydrite)+glauberite ($CaSO_4 \cdot Na_2SO_4$)+solution+vapor. The a_{H_2O} of the invariant solutions varies from about 0.90 at 25°C to about 0.96 at 70°C. This limits the study to very dilute solutions only, a considerable disadvantage because many natural calcium sulfate deposits must have formed in brines with activities of H_2O at least as low as 0.75, as defined by the assemblage gypsum (or anhydrite)+halite+solution+vapor in the "haplo-evaporite" (Zen, 1965, p. 125) system $CaSO_4$-NaCl-H_2O. In the system $CaSO_4$-H_2SO_4-H_2O, however, the stability fields of gypsum and anhydrite are not limited by double-salt formation. Thus, the reaction may be studied in H_2SO_4 solutions which have a range of activity of H_2O comparable to that found in natural waters, that is, from near 1.00 to about 0.70.

EXPERIMENTAL METHODS

Starting Materials. The solid starting materials were artificial $CaSO_4 \cdot 2H_2O$, $CaSO_4$ (anhydrous) and Na_2SO_4 (anhydrous) of reagent grade.

The $CaSO_4 \cdot 2H_2O$ (Baker Analyzed, Lots No. 25692 and 25286) was fine-grained but variable-sized material (0.1 mm to less than 0.01 mm), which showed the characteristic morphology of gypsum euhedra. The X-ray diffraction pattern was indistinguishable from that of natural gypsum, and the material was used as such with no further treatment. The $CaSO_4$ (Baker Analyzed anhydrous [*sic*] Lot No. 90128) yielded an X-ray pattern consistent with bassanite $CaSO_4 \cdot nH_2O$ ($n \leq 0.5$). When this material was heated at 450°C to 550°C for 2 to 5 days, a very fine-grained powder was produced which gave an excellent anhydrite X-ray pattern. In the experimental runs with anhydrite as a starting material, the heat-treated $CaSO_4$ was used. Zen (1965, p. 151) found that artificial anhydrite, prepared by dehydrating gypsum overnight at 300°C, readily reverted to gypsum when brought into contact with water; he therefore considered such anhydrite unsuitable as a starting material. In the present investigation no such rehydration of artificial anhydrite occurred—even in stirred runs of 6 months duration—under conditions where anhydrite was considered to be stable. Critical experiments however, were repeated using natural gypsum and/or anhydrite. The gypsum was large clear selenite plates from Montmartre, Paris, and the anhydrite was massive fine-grained material from Richmond Co., Nova Scotia (Williams Collection, The Johns Hopkins University).

The Na_2SO_4 (Baker Analyzed, anhydrous, Lots No. 25581 and 22088) gave a sharp thenardite X-ray pattern and was used without further refinement.

The sulfuric acid solutions were prepared by diluting Baker Analyzed 95 percent H_2SO_4 with double-distilled water to the required concentrations. The exact concentration in weight percent H_2SO_4 was then determined by titration of carefully weighed aliquots of each solution against 1N NaOH solution (CO_2 free) using methyl orange as an indicator (Welcher, 1962, p. 540). The results were checked against the H_2SO_4 concentration determined by specific gravity measurements, using the calibration curve of Hodgman (1953, p. 1894).

Experimental procedure

(a) Static Method. At the start of the study a technique similar to that used in hydrothermal work was employed. Finely ground mixtures of anhydrite, or gypsum, and thenardite were accurately weighed, with the required amount of distilled water, into pyrex glass tubes (7×60 mm) which were then sealed using an oxy-acetylene torch. Loss of distilled water was successfully avoided during the sealing process by wrapping the tubes in wet filter paper. The sealed tubes were then totally immersed in thermostatically controlled water-baths. At the end of the run periods, which varied from several days to many months, the tubes were broken open and the solid products separated from the solution on absorbent paper. Samples were immediately examined, both under the microscope and by X-ray diffraction. Although by this technique many runs can be carried out simultaneously, it has the obvious disadvantage that the solution volumes are too small for analysis. Unfortunately, the method proved to have an even greater disadvantage; in many runs equilibrium was not attained even after periods of many months. When it was apparent that some form of agitation was required to promote the reactions, the static method was abandoned. However, it was possible to salvage enough significant information to warrant discussion and comparison with the results of runs carried out with the dynamic method (continuous stirring of the charge), which was used through the rest of the study.

(b) Dynamic Method. Approximately 200g of starting materials were weighed (±0.1%) into a 250-ml Erlenmeyer flask, fitted with a mercury-in-glass air-tight seal through which the solution was stirred sufficiently to keep all the solid material in constant agitation. The charged reaction vessels were immersed in water baths of capacity 30 liters, thermostatically controlled to ±0.1°C.

A maximum variation of ±0.5°C was observed over a period of six months.

At intervals, one milliliter of the suspension-charged solution was withdrawn with a pipette and rapidly pressure-filtered through a Buchner funnel: this removed almost all the solution. The solid material was immediately washed several times with acetone and air-dried. A portion of the sample was examined under the petrographic microscope; the remainder was hand-ground under acetone and a smear mount prepared for x-ray diffraction.

Determinations of activity of H_2O in solutions. The activity of any constituent of a solution is given by the ratio of the fugacities:

$$a_i = f_i/\overset{0}{f_i}$$

At one atmosphere total pressure, water vapor may be regarded as an ideal gas so that the fugacities may be safely replaced by the partial pressures of H_2O:

$$a_{H_2O} = p_{H_2O}/\overset{0}{p}_{H_2O}$$

The standard state is taken as pure liquid water, at one atmosphere pressure and at the temperature of reaction, for which the activity is unity.

The solubilities of gypsum and anhydrite in sodium sulfate and sulfuric acid solutions are very low (less than 0.25 percent by weight). Therefore, the vapor pressures of these solutions saturated with $CaSO_4$ are given, within experimental measurement, by the vapor pressures of the $CaSO_4$*-free* solutions.

For the sodium sulfate solutions the vapor pressure data given in International Critical Tables (III, p. 371) were used to calculate a_{H_2O}. The a_{H_2O} of each solution was computed at the temperature of each experiment. At the end of a run the total dissolved solids content of the equilibrium solution was determined. This value was compared with the starting Na_2SO_4 content to provide a check on the assigned a_{H_2O} value. The activities of H_2O of the sulfuric acid solutions were taken from Harned and Owen (1958, p. 574). These data, reproduced in Table 1, show that within the range of H_2SO_4 concentration used in the study, a_{H_2O} values determined by EMF measurements are in excellent agreement with those calculated from vapor pressure measurements. The initial gypsum and (or) anhydrite constituted only about 3 percent of the total charge. Consequently the H_2SO_4 concentration of the solution, and hence the activity of H_2O, was not significantly changed by the H_2O released or absorbed by the gypsum-anhydrite conversion. The H_2SO_4 content of the solution was checked by titration at the completion of each run.

The a_{H_2O} of the final solution in each of two runs (one in H_2SO_4 and one in Na_2SO_4) was measured directly using an H_2O-sensing apparatus (Hardie, 1965a, p. 252); the values did not differ measurably from the activities of H_2O determined in the $CaSO_4$-free solutions.

TABLE 1. ACTIVITY OF H_2O IN AQUEOUS SULFURIC ACID SOLUTIONS
(After Harned and Owen, 1958, p. 574)

Moles H_2SO_4/1000 moles H_2O	Wt. % H_2SO_4	25°C		40°C	60°C
		emf	v.p.	emf	emf
1	8.93	0.9620	0.9620	0.9624	0.9630
1.5	12.82	0.9391	0.9389	0.9402	0.9415
2	16.40	0.9136	0.9129	0.9155	0.9180
3	22.73	0.8506	0.8514	0.8548	0.8602
4	28.18	0.7775	0.7795	0.7850	0.7950
5	32.90	0.6980	0.7030	0.7086	0.7229
6	37.05	0.6200	0.6252	0.6288	0.6505
7	40.71	0.5453	0.5497	0.5608	0.5815

DESCRIPTION AND PROPERTIES OF THE SOLID PHASES

The gypsum synthesized by hydration of anhydrite (hereinafter referred to as "synthetic gypsum") commonly consists of thin plates flattened parallel to (010), with the characteristic monoclinic outline (Fig. 1). Between crossed nicols the thin plates show first-order white or grey interference colors and oblique extinction. In runs where gypsum was converted to anhydrite, the first stage of the process was recrystallization of the fine-grained artificial gypsum used as a starting material to coarser bladed crystals. This recrystallized gypsum, seemingly of a more

FIG. 1. Photomicrograph of synthetic gypsum, prepared from anhydrite at 40°C and 1 atmosphere in 22% H_2SO_4 solution, with seeding, in 50 days (Run LS 23). Average length of crystals 0.2 to 0.3 mm.

stable habit than the original smaller crystals, was morphologically and optically indistinguishable from the synthetic gypsum.

The optical properties of the synthetic gypsum were not significantly different from those of the natural material.

Wooster (1936) has determined the crystal structure of gypsum. In the *ac* plane two sheets of SO_4 tetrahedra are bound by Ca atoms within them. Between these sheets lie layers of water molecules. The Ca atoms are linked to 6 oxygens of SO_4 tetrahedra and to 2 water molecules. Water molecules thus occupy important structural positions and even partial dehydration must result in the destruction of the gypsum structure.

Unit cell parameters of the synthetic gypsum were determined by X-ray powder diffraction methods with either silicon or quartz as internal standard, and found to be in excellent agreement with those given by Deer *et al.* (1962) for natural gypsum.

Anhydrite synthesized from gypsum appeared under the microscope as a mass of minute birefringent grains; individual crystal outlines were barely distinguishable under high power, and refractive index measurements were unreliable.

The presence of synthetic anhydrite could be readily detected in the reaction flask by inspection: a fine white mass stayed in suspension long after the stirrer was stopped. In contrast, the well-crystallized synthetic and seed gypsum settled very rapidly, leaving, in the absence of anhydrite, a remarkably clear solution.

In one run (LS 51, Table 2), anhydrite grains as large as 0.3 mm across were synthesized from gypsum in 22 percent sulfuric acid solution at 50°C. They showed a stubby prismatic to equant shape with very high interference colors and parallel extinction.

The cell parameters of synthetic anhydrite were in excellent agreement with those given by Swanson *et al.* (1955).

Bassanite ($CaSO_4 \cdot nH_2O, n \leq 0.5$) was encountered only in static runs in which NaCl had been added to the charges. It was identified by X-ray diffraction techniques only, using the data of Posnjak (1938, p. 253). No distinction was made between calcium sulfate hemidydrate ($CaSO_4 \cdot 1/2H_2O$) and soluble anhydrite ($CaSO_4$) because there is considerable uncertainty as to the relationship between these two phases (Deer, Howie and Zussman, 1962, v. 5, pp. 207–208).

EXPERIMENTAL RESULTS

Results of dynamic runs. The data used to define the position of the a_{H_2O}-temperature equilibrium curve for the reaction

$$\text{gypsum}=\text{anhydrite}+2H_2O_{(\text{liquid, in solution})}$$

are given in Table 2 and plotted in Figure 2.

Determination of the curve rested on the ability to convert gypsum to anhydrite, and *vice versa*, and on the ability to reverse the conversion when either one of the parameters was varied.

A run in which no change occurred in the starting phase, even after a reaction time of many months, was not considered evidence of stability of that phase, although in many cases such data provided confirmation of reversed runs. Taken by itself, a run in which no reaction occurs is at best inconclusive since metastable persistence of starting phases is commonly encountered in experimental studies of mineral equilibria. In the present study this was particularly true of the rehydration of anhydrite in sulfuric acid solutions, and induced nucleation by seeding proved necessary. Anhydrite remained unchanged in most unseeded runs for up to eight months; the addition of seeds of gypsum promoted relatively rapid conversion of the anhydrite (compare runs LS 5 and LS 14 at 35°C, Table 2). In the system $CaSO_4$-H_2O, the dehydration of gypsum to anhydrite has been shown to be incredibly slow (*e.g.* run AG 1, 70°C, Table 2) but, according to Posnjak (1938, p. 262) seeds of anhydrite do initiate the reaction.[1] Considerable doubt has been thrown on the determination of stability by experiments in which seeds have been added to the charge because metastable growth of a phase from solution on seeds of its own kind is known to occur (Fyfe *et al.*, 1958, p. 83). However, it has never been demonstrated that seeding would promote the disappearance of a stable phase and growth of a less stable one. In the present study, charges containing equal parts by weight of gypsum and anhydrite were used. The proof of stability in these seeded runs was growth of one phase and disappearance of the other. When the extent of reaction exceeded about 7 to 10 percent, metastable precipitation of either phase on seeds could be ruled out. This follows from a consideration of the solubilities of gypsum and anhydrite in Na_2SO_4 and H_2SO_4 solutions (maximum about 0.3 percent $CaSO_4$ by weight), the mass of solution in the reaction vessel (about 200–250 g) and the mass of excess starting solids (about 10 g). The extent of reaction was gauged by microscope and X-ray examination of a series of samples taken from the reaction vessel at intervals. From the X-ray diffraction patterns, the relative intensities of the 020 peak of anhydrite (3.499 Å) and the 140 peak of gypsum (3.065 Å) were measured. The amount of gypsum in each sample was read from a calibration

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[1] This was not substantiated in the present work, perhaps because the runs were not of sufficient duration. However, it was found that the presence of lime-water ($a_{H_2O}=1.00$, pH$=12.4$), with no seeding, markedly increased the dehydration rate where a seeded run in distilled H_2O showed no reaction (compare AG 1 and AG 5, 70°C, Table 2).

TABLE 2. EXPERIMENTAL DATA FOR GYPSUM AND ANHYDRITE STABILITY AS A FUNCTION OF ACTIVITY OF H_2O AND TEMPERATURE AT ATMOSPHERIC PRESSURE. RESULTS OF DYNAMIC RUNS ONLY.

Run no.	Starting materials			a_{H_2O} sol'n	Temp. °C	Time days	Solid products	Result
	Solid phases	Solution (wt. %)						
		Na_2SO_4	H_2SO_4					
AG1	95g, 5a	100% H_2O		1.000	70°	359	95g, 5a	n.c.
AG5	100g	limewater		1.000	70°	193	93g, 7a	g→a
LX9	100g	12.3		0.965	70°	6	100g	
						19	42g, 58a	
						46	5g, 95a	
						147	100a	g→a
LX22	g, gl	12.3		0.965	70°	26	100a	g→a
LX25	100g	18.9		0.942	70°	9	gl, a	g→a
LS30-2	90g, 10a*		9.43	0.961	60°	43	45g, 55a	g→a
LX49-2	100g	15.0		0.955	60°	46	94g, 6a	g→a
LS20	50g, 50a		4.03	0.985	55°	42	94g, 6a	a→g
LS22	50g, 50a		9.43	0.961	55°	51	100g	a→g
LS30-1	50g, 50a*		9.43	0.961	55°	51	90g, 10a	a→g
LS8	100g		9.56	0.960	55°	35	55g, 45a	g→a
LX49-1	100g	15.0		0.954	55°	50	100g	n.c.
LX46-1	a, gl	19.3		0.941	55°	99	a, gl	n.c.
LS52	100g		22.24	0.866	55°	99	100a	g→a
LS21	50g, 50a		4.03	0.985	52.5°	42	95g, 5a	a→g
LS18	50g, 50a		9.56	0.960	52.5°	35	95g, 5a	a→g
AG3	95g, 5a	100% H_2O		1.000	50°	278	95g, 5a	n.c.
LS1	100g		9.56	0.960	50°	262	100g	n.c.
LS16	50g, 50a		9.56	0.960	50°	25	95g, 5a	a→g
LX17	100g	15.0		0.953	50°	155	100a	n.c.
LX11	100g	15.0		0.953	50°	47	100g	
						94	95g, 5a	
						319	95g, 5a	g→a(?)
LX48	a, gl	20.6		0.930	50°	23	a, gl, (g)	a→g(?)
LS51	100g		22.24	0.863	50°	211	50g, 50a	g→a
LS32-2	80g, 20a*		22.24	0.863	50°	111	60g, 40a	g→a
LS2	100g		9.56	0.959	45°	148	100g	n.c.
LS7	100a		9.56	0.959	45°	127	100a	n.c.
LS15	50g, 50a		9.56	0.959	45°	138	100g	a→g
LX15	100g	15.0		0.952	45°	156	100g	n.c.
LX16	100a	15.0		0.952	45°	156	70g, 30a	a→g
LS50	100g		22.24	0.862	45°	211	93g, 7a	g→a
LS4-2	100g		23.60	0.846	45°	62	65g, 35a	g→a
AG4	95g, 5a	100% H_2O		1.000	40°	277	100g	a→g
LS9	50g, 50a		9.56	0.959	40°	55	100g	a→g
LX12	100a	15.0		0.951	40°	255	93g, 7a	a→g
LX18	100g	21.0		0.926	40°	88	100g	n.c.
LX19	100g	22.2		0.922	40°	88	100g	n.c.
LS23	50g, 50a		22.24	0.860	40°	50	95g, 5a	a→g
LS33-1	50g, 50a*		22.24	0.860	40°	49	75g, 25a	a→g

g—gypsum
a—anhydrite
gl—glauberite
th—thenardite
mr—mirabilite
n.c.—no detectable change.
*—natural gypsum and anhydrite
( )—trace

TABLE 2—(*Continued*)

Run no.	Starting materials			a_{H_2O} sol'n	Temp. °C	Time days	Solid products	Result
	Solid phases	Solution (wt.%)						
		Na_2SO_4	H_2SO_4					
LS3-1	100g		23.60	0.845	40°	23	100g	n.c.
LS3-2	100g		23.60	0.845	40°	40	20g, 80a	g→a
LS19	50g, 50a		23.60	0.844	37.5°	35	95g, 5a	a→g
LS32-1	50g, 50a*		22.24	0.859	35°	51	80g, 20a	a→g
LS4-1	100g		23.60	0.843	35°	21	100g	n.c.
LS5	100a		23.60	0.843	35°	232	100a	n.c.
LS14	50g, 50a		23.60	0.843	35°	83	94g, 6a	a→g
LX40	g, th	24.5		0.907	30°	195	g, gl	n.c.
LS4-3	50g, 50a		23.60	0.842	30°	56	100g	a→g
LS6	100a		23.60	0.842	30°	197	100a	n.c.
LS11	100g		28.61	0.773	30°	67	90g, 10a	g→a
LY5	100a	14.3		0.952	25°	189	80g, 20a	a→g
LY6	100a	15.8		0.948	25°	189	80g, 20a	a→g
LS10	50g, 50a		23.60	0.840	25°	55	100g	a→g
LS12	100g		28.61	0.771	25°	67	40g, 60a	g→a
LS17	50g, 50a		28.61	0.771	25°	69	20g, 80a	g→a
LY1	100a	10.1		0.943	20°	28	g, mr	a→g
LG2-1	100a	10.1		0.943	20°	1	a, g, mr	a→g
LS13	100a		28.61	0.768	20°	67	45g, 55a	a→g

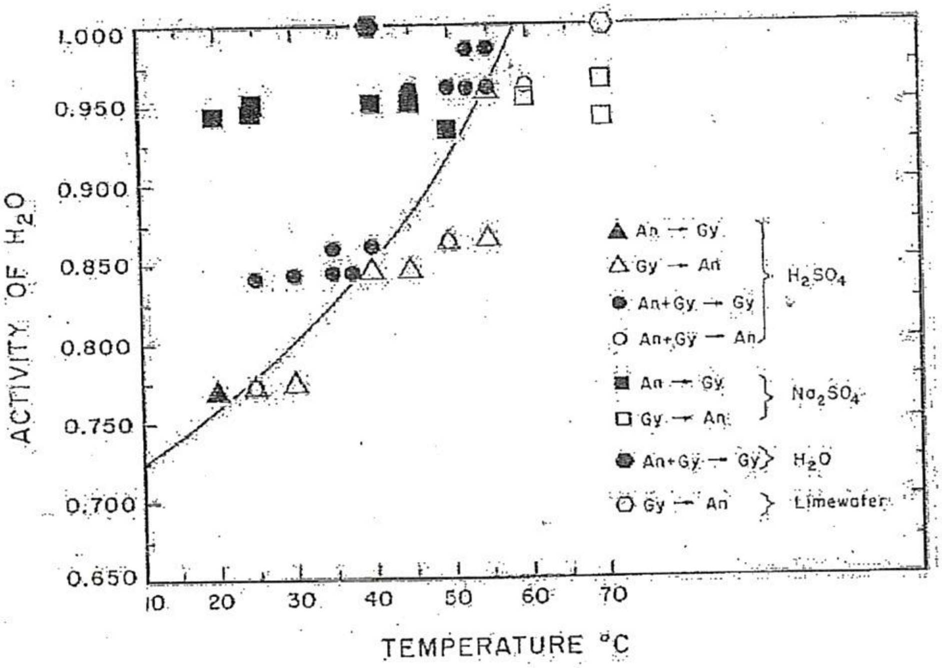

FIG. 2. The stability of gypsum and anhydrite determined experimentally as a function of temperature and activity of H_2O at atmospheric pressure. Only runs in which a conversion was achieved are plotted.

curve of I(anhydrite)/I(gypsum) against weight percent gypsum with a reproducibility of better than 2 percent.

Because of the time limit, most of the runs were stopped before complete conversion of one phase to the other had occurred. Those runs which were allowed to react completely provided material for optical and X-ray studies.

Figure 2 shows that the experimental data, in general, are consistent. However, some exceptions must be noted. At 50°C, in 15 percent sodium sulfate solution ($a_{H_2O}=0.953$), anhydrite started growing at the expense of gypsum after about 90 days reaction time (run LX 11, Table 2). However, the reaction apparently stopped (!) as no further growth of anhydrite occurred in 10 months. Under the same conditions, anhydrite as a starting phase remained unaltered after 5 months (run LX 17). With sulfuric acid of about the same activity of H_2O, anhydrite was converted to gypsum at 50°C in a seeded run within a month (run LS 16), while gypsum was unchanged in an unseeded run of 9 months (run LS 1). The anomaly remains unexplained. An inconsistent result was also obtained at 55°C and $a_{H_2O}=0.96$. In an unseeded run, gypsum was converted to anhydrite in sulfuric acid solution (run LS 8, about 50 percent reaction); in seeded runs both synthetic and natural anhydrite were transformed into gypsum (runs LS 22 and LS 30-1). These results are taken to indicate that the runs are very close to the equilibrium curve.

TABLE 3. ACTIVITY OF H_2O AND TEMPERATURE THAT DEFINE THE EQUILIBRIUM GYPSUM ⇌ ANHYDRITE + 2 $H_2O_{\text{liq. soln.}}$ AT ATMOSPHERIC PRESSURE

Temperature °C(±2°)	$^{a}H_2O$ (±0.005)	Remarks
58°	1.000	extrapolated
55°	0.960	measured
50°	0.915	interpolated
45°	0.880	interpolated
39°	0.845	measured
35°	0.825	interpolated
30°	0.800	interpolated
23°	0.770	measured
18°	0.750	extrapolated
12°	0.725	extrapolated

With the exception of run LX 11, then, the results obtained using sulfuric acid solutions are perfectly consistent with those obtained using sodium sulfate solutions.

The a_{H_2O}-T values which define the equilibrium curve are given in Table 3.

Results of static runs. The results of experiments on the gypsum-anhydrite reaction carried out under static conditions are not included in Figure 2 or Table 2 because the method was soon abandoned in favor of agitated runs. A discussion of the data, however, is warranted. All the static runs were made with sufficient Na_2SO_4 to produce glauberite ($CaSO_4 \cdot Na_2SO_4$) as an additional phase. Synthetic anhydrite was the starting solid, although in a few runs natural anhydrite or synthetic gypsum were used instead. Seeds were not added to any of the charges. Reaction times varied from a few days to over 12 months. The results were most unexpected: anhydrite was found to rehydrate to gypsum at temperatures as high as 75°C. The reverse reaction, the dehydration of gypsum to anhydrite, was never achieved. Several possible explanations come to mind. First, the properties of the synthetic anhydrous $CaSO_4$ may be different from those of natural anhydrite. However, the results of the dynamic runs indicate that the differences, if any, are not significant. Another possibility is solid solution between gypsum and sodium sulfate. Unfortunately, this could not be checked by chemical analysis due to separation difficulties. However, no significant change in cell dimensions of the gypsum was observed, which suggests little or no substitution of Na^+ for Ca^{++} in the gypsum structure. Indeed, a direct substitution is impossible since it would create a charge imbalance. The substitution of Na^+ for Ca^{++} perhaps could be achieved if accompanied by an HSO_4^- for $SO_4^=$ substitution. Chemical analyses of natural gypsum and anhydrite (Stewart, 1963, p. 33; Deer, Howie and Zussman, 1962, p. 206 and p. 221) show no evidence of this: sodium only occurs in trace amounts, if at all.

A third possibility is related to the experimental method. In the preparation of the charges, water was added to a solid mix of anhydrite + thernardite. Local high concentrations of sodium sulfate solution certainly existed, and probably persisted, in the initial stages of the runs. Conley and Bundy (1958) and Hardie (1965, p. 126) have shown that anhydrite reacts very rapidly with concentrated Na_2SO_4 solutions to form Ca-Na double sulfates. These double-salts are unstable in dilute Na_2SO_4 solutions (Hardie, 1965, p. 136; Hill and Wills, 1938, p. 1652) and decompose to gypsum and/or glauberite. In distilled water they immediately decompose to gypsum + Na_2SO_4 solution at all temperatures up to 100°C. It is possible, therefore, that in the static runs early formation of double-salts occurred in the regions of local high Na_2SO_4 concentration. This reaction removed anhydrite from the system. With time, diffusion led to a uniformly concentrated solution too low in Na_2SO_4 content for double-salt stability. Decomposition followed, giving gypsum + glauberite as products. Then, with prolonged time the gypsum should convert to anhydrite. This is a plausible explanation because in all runs (static or stirred) in which the starting anhydrite was added to pre-mixed, uniformly concentrated sodium sulfate solution, no anomalous formation of gypsum was observed.

The work of Conley and Bundy (1958) is pertinent here since they proposed essentially this mechanism for the conversion of anhydrite to gypsum in salt solutions. They suggested that the reaction for the conversion with activator solutions such as sodium or potassium sulfate is:

$$CaSO_4 \xrightarrow[H_2O]{act.} Ca^{++} + SO_4^{=} \xrightarrow{H_2O} CaSO_4 \cdot 2H_2O$$

and is primarily dependent upon temperature and concentration. However, they achieved the conversion only by washing the reaction products with water. This in fact really only demonstrates that anhydrite will react rapidly at low temperatures and high alkali sulfate concentrations (see Conley and Bundy, 1958, Figs. 1 and 2) to form double-salts which decompose in water to give gypsum and salt solution. It certainly does not prove, as they maintained in the abstract of their paper (p. 57), that "contrary to recent hypothesis of gypsum dehydration by concentrated salt solutions, double salts and/or gypsum are stable phases below a temperature of 42°C."

Comments on the mechanism of dehydration of gypsum to anhydrite. Three different mechanisms by which gypsum in contact with an aqueous medium could dehydrate to anhydrite appear possible:

(1) a solution-precipitation process.
(2) direct dehydration to anhydrite (loss of structural water).
(3) step-wise dehydration through the intermediate hydrate, bassanite.

The present experimental results throw some light, albeit very diffuse, on the problem.

In a few of the runs in which anhydrite was produced from gypsum, a rind, presumed from X rays to be anhydrite, was observed on the surface of, and along cleavage cracks in, gypsum crystals (Fig. 3). It is conceivable that the rind material is bassanite, formed as an intermediate dehydration product, but no trace of this phase was identified in the charges by X rays even though perhaps as many as 10 to 15 percent of the gypsum grains showed some alteration. If the rind is anhydrite, the process would appear one of direct dehydration to anhydrite beginning at the crystal surfaces where H_2O may be transferred to the solution phase. The effect of seeding on the dehydration rate could not be gauged with any certainty because too few duplicate runs were made. However, in

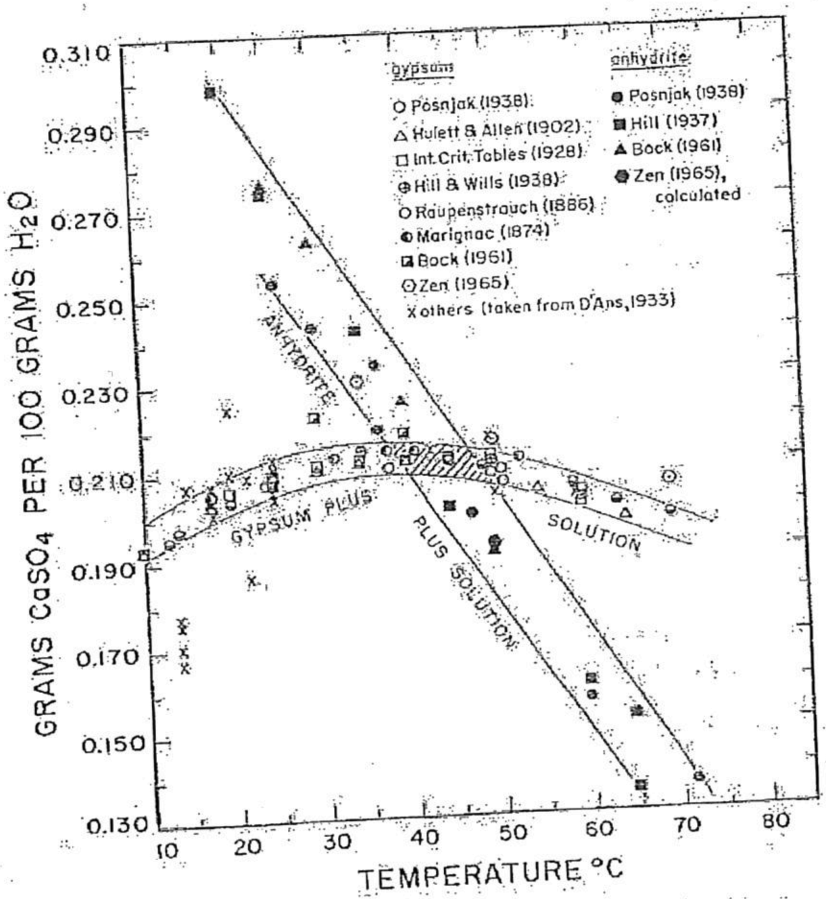

FIG. 4. The solubility relations of gypsum and anhydrite in the system $CaSO_4$-H_2O as a function of temperature at atmospheric pressure: a compilation of previous work.

solubility data therefore must be regarded as yielding minimum values only. The argument is crucial, for if the points plotted in Figure 4 for anhydrite are indeed minimum values then the transition point must lie at some temperature above at least 44°C, Zen's (1965) data being taken as the upper limit of gypsum solubility. Hill (1934, 1937) did recognize the necessity for approaching a solubility curve from both sides, and, indeed, reported his anhydrite values as obtained from both undersaturated and supersaturated solutions. The data, however, were extrapolated from solubilities measured in potassium sulfate solutions because he was unable to achieve supersaturation with respect to anhydrite using pure water at temperatures below 65°C. At this and higher temperatures he apparently was successful, but, unfortunately, he neither described the procedure nor reported direct precipitation of anhydrite from solution.

A similar criticism applies to the available gypsum and anhydrite solubility measurements made in salt or acid solutions, and probably explains why the results of different workers are in such poor agreement. Comparison of the results of these workers is most easily made by computing the activity of H_2O of the solutions reported to be in equilibrium with gypsum+anhydrite. Because the $CaSO_4$ content of these solutions is very low, activity of H_2O may be obtained with considerable accuracy from the water vapor pressures of the $CaSO_4$-free salt or acid solutions. The vapor pressure data for the NaCl and Na_2SO_4 equilibrium solutions were taken from the International Critical Tables (1928, III, pp. 370–371) and those of sea water from Arons and Kientzler (1954). For the phosphoric acid solutions the vapor pressure values of Kablukov and Zagwosdkin (1935) were used. The results are summarized in Table 4 and shown graphically in Figure 5.

TABLE 4. THE EFFECT OF SALT SOLUTIONS ON THE GYPSUM—ANHYDRITE TRANSITION: A COMPARISON OF PREVIOUS WORK

Investigator	Trans. temp. °C	Co-existing solution	a_{H_2O}
van't Hoff *et al.* (1903)	50°	sat'd. $NaBrO_3$	0.900
Hill & Wills (1938)	45°[1]	20.0 % Na_2CO_4	.932
Bock (1961)	40°	5.88% NaCl	.965
Taperova & Shulgina (1945)	40°[1,2]	31.0 % H_3PO_4	.885
Bock (1961)	35°	11.85% NaCl	.920
Zen (1965)	35°	15.25% NaCl	.891
D'Ans *et al.* (1955)	34°	6.09% NaCl	.963
Bock (1961)	30°	16.09% NaCl	.883
Posnjak (1940)	30°	13.06% NaCl 1.82% $MgCl_2$ 0.82% $MgSO_4$ 0.43% K_2SO_4	.89
van't Hoff *et al.* (1903)	30°	sat'd. NaCl	.754
D'Ans *et al.* (1955)	28.5°	11.49% NaCl	.922
Bock (1961)	25°	20.08% NaCl	.840
Madgin & Swales (1956)	25°	18.02% NaCl	.864
D'Ans & Hofer (1937)	25°	45.36% H_3PO_4	.790
Taperova (1940)	25°[1,2]	40.0 % H_3PO_4	.845
D'Ans *et al.* (1955)	24°	16.33% NaCl	.881
D'Ans *et al.* (1955)	20.5°	20.6 % NaCl	.835
D'Ans *et al.* (1955)	18°	26.31% NaCl	.751

[1] Extrapolated by the present author.

[2] The results of these two studies were taken from Seidell (1958, pp. 665–667).

The values of van't Hoff *et al* (1903) alone are higher than those of the present study. The approach of van't Hoff and his co-workers to the problem was brilliantly conceived. They first partially converted gypsum to anhydrite in saturated sodium chloride solution in a dilatometer at 70°C. The rate of conversion of gypsum to anhydrite and *vice versa* at different temperatures was then measured by the rate of change of volume of the contents of the dilatometer. At the equilibrium temperature there should be no volume change. They observed a volume decrease at 25°C and an increase at 35°C, so the transition temperature was taken as 30°C. The partial pressure of H_2O of the solution co-existing with gypsum, anhydrite and halite at 30°C was then measured, giving a value of 24 mm. The method was repeated using saturated sodium bromate solution and a transition temperature of 50°C was obtained; the water vapor pressure of the equilibrium solution was measured as 83.3 mm. Using these two points in the relationship

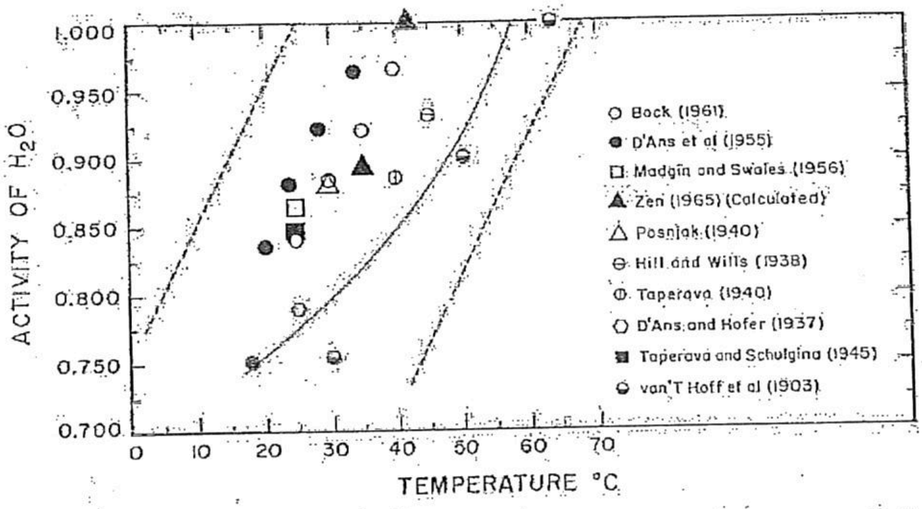

FIG. 5. Temperature-activity of H_2O relations of gypsum and anhydrite at atmospheric pressure: a comparison of previous work. Solid curve: this study; dashed curves: maximum and minimum limits predicted by thermodynamic calculations.

$$\log p = \log p^\circ + A - B/T$$

they were able to extrapolate to solutions in the system $CaSO_4$-H_2O. Implicit in this approach is the principle that the gypsum-anhydrite transition is independent of the constituents in solution and that the equilibrium temperature is a function of the ratio p/p°. This is, of course, the principle on which the present study is based!

Figure 5 also shows that although the results of different workers are in very poor agreement, they all fall within the limits predicted by the thermodynamic calculations (Appendix)!

GEOLOGICAL IMPLICATIONS

It has been suggested by some workers that most, if not all, calcium sulfate of natural evaporites was originally deposited as gypsum (Posnjak, 1940; Bundy, 1956; Conley and Bundy, 1958; Murray, 1964; Zen, 1965). The agrument is based on (1) petrographic observations that much anhydrite is pseudomorphous after twinned gypsum, (2) the scarcity of anhydrite in modern evaporites deposits, and (3) experimental evidence that anhydrite cannot be synthesized under pressure-temperature conditions consistent with natural evaporite environments.

It is clear that the present relationship between gypsum and anhydrite in the pre-Recent marine evaporites of the world, to a great extent, is secondary, due to the effects of post-depositional burial. Gypsum at surface may be traced downward into anhydrite so that at depths below about 2000–3000 feet gypsum is practically absent (MacDonald, 1953; Stewart, 1963). Evidence of replacement is abundant. Anhydrite psuedomorphous after twinned gypsum has been reported by Schaller and Henderson (1932) in the Salado formation of Texas and New Mexico, by Stewart (1953) in the Permian evaporites of Yorkshire, England, and by Borchert and Baier (1953) in the German Zechstein. At shallower depths gypsum has been shown to have replaced anhydrite (Stewart, 1953; Goldman, 1952; Ogniben, 1955; Sund, 1959); such replacement has been recorded recently at a depth as great as 3500 feet (Murray, 1964). Therefore, both gypsum and anhydrite in sedimentary deposits may be metamorphic but this evidence does not prove that the replaced gypsum, or anhydrite, was primary in origin, a point emphasized by Zen (1965, p. 147).

More significant evidence is provided by the distribution of gypsum and anhydrite in Recent marine and nonmarine evaporites where effects due to burial are not involved. In these deposits gypsum is ubiquitous and, in all certainty, primary (Bramkamp and Powers, 1955; Morris and Dickey, 1957; Masson, 1955; Phleger and Ewing, 1962; Wells, 1962; and others) whereas anhydrite has been reported from only one locality, in supratidal flat sediments on the Trucial Coast, Persian Gulf (Curtis *et al*, 1963; Kinsman, 1964).[1] This single occurrence of Recent sedimentary

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[1] Other occurrences of Recent anhydrite have been reported recently by Hunt *et al.* (1966, p. 59) as a surface layer in Death Valley, California, and by Moiola and Glover (1965) from a sediment dump on Clayton Playa, Nevada. In both cases the anhydrite has formed from gypsum, via bassanite, in the absence of a liquid phase. This dehydration process

$$CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 \cdot \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O\ (g)$$
$$CaSO_4 \cdot \tfrac{1}{2}H_2O \rightleftharpoons CaSO_4 + \tfrac{1}{2}H_2O\ (g)$$

involves a set of thermochemical conditions very different from those encountered in "wet" evaporite deposits.

anhydrite is of great import because, if not evidence of primary precipitation of anhydrite, it is, at least, proof that metamorphism of gypsum on burial is not *essential* to anhydrite formation. Even accepting that anhydrite can be primary, an inconsistency between the field evidence from modern evaporites and available experimental evidence exists. Temperature-salinity conditions necessary for anhydrite stability, as predicted from solubility experiments and thermodynamic calculations, are commonly found in modern evaporite environments, yet gypsum is the common phase of such deposits. This observation, coupled with the inability of experimenters to synthesize anhydrite at low temperatures, has led workers such as Murray (1964) to conclude that gypsum is always the primary precipitate. Further, under conditions theoretically favoring anhydrite, this gypsum will persist metastably (except where temperatures at surface are very high) until burial causes dehydration to anhydrite.

The present experimental results have a two-fold bearing on the problem. First, it is demonstrated that anhydrite can be synthesized at one atmosphere pressure under geologically reasonable conditions of temperature and activity of H_2O in a geologically reasonable time, reckoned in months. Primary precipitation of anhydrite, however, could not be achieved, indeed, has not been achieved by previous workers. This would suggest, but, of course, not prove, that gypsum is always the first formed $CaSO_4$ phase on evaporation of natural waters.[1] Be that as it may, the experiments do show that gypsum, maintained in the stability field of anhydrite, would be dehydrated to anhydrite soon after deposition. Second, it is demonstrated that higher temperatures than previously were entertained are required for anhydrite formation. This, qualitatively, is more in keeping with the observation that gypsum is the common phase in Recent evaporites.

Quantitative application of the experimental results to natural deposits is valid and possible but is hindered by the paucity of precise information on the temperature and a_{H_2O} of natural solutions co-existing with gypsum and anhydrite. Fortunately, the Persian Gulf deposit is an important exception. Quantitative data have been collected by D. J. J. Kinsman (personal communication, 1964). Brine temperatures range from 24° to 39°C and anhydrite is found in carbonate muds of the *sabkha*, or supratidal salt flat, where ground water chlorinities exceed about 130°/₀₀ (about 24 percent salinity). Part of the anhydrite deposit

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[1] It is possible, of course, that natural waters differ from experimentally tested solutions in that they contain additional components which would induce direct precipitation of anhydrite, as, for example, trace elements ("impurities") have been found to influence the nucleation of aragonite and calcite (Wray and Daniels, 1957).

TABLE 5. DATA ON SOLUTIONS CO-EXISTING WITH GYPSUM OR ANHYDRITE IN NATURAL EVAPORITE DEPOSITS

Locality	Mineral Assemblage	Solution			Investigator
		T°C	Chlorinity ‰	a_{H_2O}	
Trucial Coast, Persian Gulf	gypsum	27–34°	50–110	0.95–0.85	Bramkamp & Powers (1955)
	gypsum, carbonate	24°[1] to	64 91 96	0.93 .88 .87	D. J. J. Kinsman (written communication, 1964)
	anhydrite, carbonate	39°	134[1] 152[1] 159 166	.80 .77 .75 .73	
Boccana de Virrila, Peru.	gypsum	27°	108[2]	.85	Morris & Dickey (1957)
Saline Valley, Calif.	gypsum	9–39°	16–50	0.99–0.95	Hardie (1965)
Salina fm., Mich. (Silurian)	anhydrite, halite[3]	32–48°	satd. NaCl	≤0.75	Dellwig (1955)

[1] Anhydrite in the zone of capillary draw. Chlorinities as given are for the underlying groundwaters. Actual solutions in which anhydrite formed presumably were more concentrated.

[2] Precise location in Boccana where gypsum is precipitating is difficult to read from Morris and Dickey's descriptions. Value given here is taken from their data for location C, which may be incorrectly interpreted by the present author as the gypsum site.

[3] Delicately preserved "hopper" crystals which have clearly not suffered alteration since their formation. The same argument must apply to the intimately associated anhydrite. Temperatures of formation of the hopper halite was determined by fluid inclusion studies.

occurs in the zone of capillary draw above the present water table but, more important, anhydrite is found in direct contact with brine (Table 5). Where ground waters are less concentrated (up to about 96‰ chlorinity) gypsum is precipitated within the carbonate muds. These data, together with the limited information from a few other deposits, are summarized in Table 5. To compare these data, chlorinity values have been recalculated to activities of H_2O using the vapor pressure data for seawater of different chlorinities given by Arons and Kientzler (1954). The natural brine data and the equilibrium curve determined in the present study are plotted in Figure 6. Included in this figure is a gypsum-anhydrite transition curve computed from the solubility measurements of Bock (1961) in the haplo-evaporite system $CaSO_4$-NaCl-H_2O. His results are considered representative of the stability range for gypsum and anhydrite predicted by most existing solubility studies (see Fig. 5). If the natural deposits are to be interpreted in terms of this transition curve, then it is clear from Figure 6 that metastable persistence of gypsum in natural brines is the rule. On the other hand, the equilibrium curve of the present study is remarkably compatible quantatively with the data from the natural deposits, particularly that of the Persian Gulf (Fig. 6). This would strongly suggest that chemical equilibrium prevails in each of these deposits. Taken one step further, this could mean that the scarcity of anhydrite in modern evaporite deposits is simply a reflection that the conditions for its formation are seldom reached, or, at least, maintained for any length of time. Metastable persistence of gypsum would not be a necessity.

While this is most plausible it is surely an oversimplification because gypsum is found under nonequilibrium conditions in some modern evaporitic environments. For example, in Laguna Ojo de Liebre, Baja California, gypsum co-exists with halite at temperatures up to 27°C (Phleger and Ewing, 1962) whereas the present experimental data predict that in a seawater brine saturated with halite ($a_{H_2O} \leq 0.75$) gypsum should dehydrate to anhydrite at temperatures above about 18°C (see Fig. 2).

The questions this discussion raises are intriguing. Does the Persian Gulf, where anhydrite is forming, combine a freakish set of chemical and/or physical circumstances not found in other modern evaporite environments? Or, are the conditions under which gypsum is found in Baja California (and perhaps other areas) not maintained for long enough periods of time each year to produce anhydrite? It is clear that the problem is one of kinetics which must, therefore, become a most important consideration in interpreting gypsum-anhydrite deposits, modern or ancient.

SUMMARY

1. The present results show that anhydrite can be synthesized experimentally from gypsum under p, t and a_{H_2O} conditions reasonable for natural evaporite environments.

2. The gypsum-anhydrite equilibrium temperatures determined in the

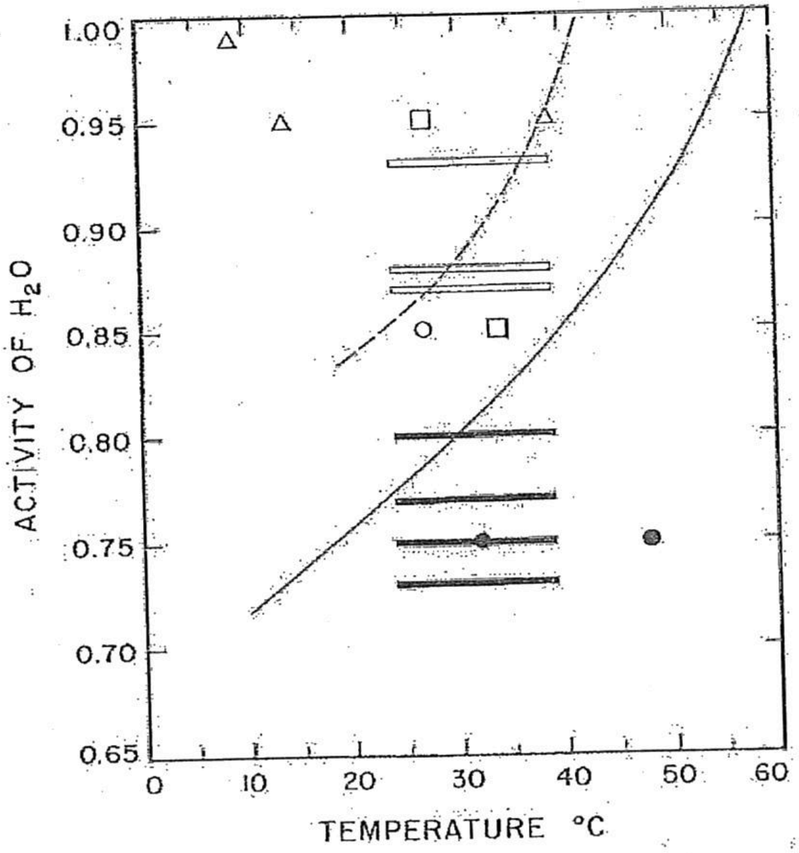

FIG. 6. Temperature-activity of H_2O relations of brines co-existing with gypsum and anhydrite in natural evaporite deposits. Experimentally determined equilibrium relations are shown as curves: *solid curve:* this study; *dashed curve:* solubility data of Bock (1961). The open symbols represent solutions in contact with gypsum and the solid symbols are those in contact with anhydrite.

Open circle:	Morris & Dickey (1957)
Squares:	Bramkamp & Powers (1955)
Triangles:	Hardie (1965)
Solid circles:	Dellwig (1955)
Bars:	Kinsman (pers. comm., 1964)

present study are considerably higher than those based on solubility measurements and on thermodynamic calculations. The new data are considered more reliable than the existing data because (a) the present results are based on reversible reactions whereas in available solubility studies the saturation curves for gypsum and anhydrite were approached only from the side of undersaturation and, therefore, do not necessarily represent equilibrium curves; (b) significant uncertainties exist in the available thermochemical values for gypsum and anhydrite.

3. The new equilibrium values of this study are more compatible with the field observations that gypsum is the common phase, and anhydrite rare, in unmetamorphosed evaporite deposits. Further, these values are quantitatively consistent with the a_{H_2O}-T conditions under which gypsum and anhydrite are found in the Recent evaporite deposit of the Trucial Coast, Persian Gulf.

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APPENDIX. THERMODYNAMIC CONSIDERATIONS

Calculation of the gypsum-anhydrite transition temperature in the system $CaSO_4$-H_2O at one atmosphere pressure. Kelley, Southard and Anderson (1941) measured the thermochemical properties of the solid phases of the system $CaSO_4$-H_2O (Table 6).

For the reaction

$$CaSO_4 \cdot 2H_2O = CaSO_4 + 2H_2O_{(l)}$$

Kelley *et al.* (1941, p. 44) obtained

$$\Delta G^\circ_T = -2495 - 65.17\,T \log T + 0.0215\,T^2 + 163.89\,T \tag{1}$$

This equation gives 313°K (40°C) as the temperature at which gypsum, anhydrite and liquid water are in equilibrium at one atmosphere total pressure, in surprisingly good agreement with the value of 42°C derived from solubility data (Hill, 1937; Posnjak, 1938).

Zen (1962; 1965) has pointed out that equation (1) was obtained from inconsistent data. The present calculations confirm Zen's criticism. Differentiation of equation (1) with respect to temperature, $-d\Delta G^\circ/dT = \Delta S^\circ$, yields

$$\Delta S^\circ_T = -135.59 + 65.17 \log T - 0.043\,T \tag{2}$$

and a value of 12.85 cal/deg for 298°K. This is inconsistent with the sum of the individual entropies at 298°K as given by Kelley *et al.* (see Table 6), that is,

$$\Delta S^\circ_{298} = 25.5 + (2 \times 16.8) - 46.4 = 12.7 \text{ cal/deg}$$

The discrepancy arises from the use of an integration constant of -33.18 which is the mean of their own consistent value of -33.03 and the value of -33.34 obtained from the indirect vapor pressures of Toriumi and Hara (1934). The resulting small error in entropy has a con-

TABLE 6. THERMOCHEMICAL PROPERTIES OF THE PHASES OF THE SYSTEM $CaSO_4$-H_2O

Phase	C_p, cal/deg mole (298°–450°K)	$S°$ (298°K) cal/deg mole	Reference[1]
$CaSO_4 \cdot 2H_2O$ gypsum	$21.84+0.076T$	46.4 ± 0.4	I (p. 36 & p. 19)
$CaSO_4$ anhydrite	$14.10+0.033T$ $16.78+0.0236T$	25.5 ± 0.4	I (p. 36 & p. 19) III (p. 46)
H_2O (liquid) water	18.02 18.04	16.8 16.75 ± 0.03	I (p. 36) II (p. 105) III (p. 80)
H_2O (gas) water	$7.45+0.002T$ $7.30+0.00246T$	45.13 45.13 ± 0.03	I (p. 36) II (p. 105) III (p. 80)

[1] I = Kelley *et al.* (1941)
II = Kelley (1950)
III = Kelley (1960)

siderable effect on the free energy values since it is incorporated into the aT term of equation (1).

Recalculation of the entropy for the reaction using the accepted value of $S°_{298} = 16.75$ cal/deg-mole for liquid water (Giauque and Stout, 1936; Kelley, 1960) yields $\Delta S°_{298} = 25.5 + (2 \times 16.75) - 46.4 = 12.6$ cal/deg.

Hence, equation (2) becomes

$$\Delta S^\circ_T = -135.84 + 65.17 \log T - 0.043\, T \tag{3}$$

Using (Kelley *et al*, 1941, p. 44),

$$\Delta H^\circ_T = -2495 + 28.30\, T - 0.0215\, T^2 \tag{4}$$

the free energy expression becomes

$$\Delta G^\circ_T = -2495 + 164.14\, T - 65.17\, T \log T + 0.0215\, T^2 \tag{5}$$

This equation gives 319°K (46°C) as the gypsum-anhydrite equilibrium temperature, an increase of 6°C over the value obtained from the expression of Kelley *et al* (1941) (Equation (1)).

The free energy expression can be further modified by employing the revised heat capacity of anhydrite given by Kelley (1960, p. 46). The following relationships for the reaction are then obtained:

$$C_p = 31.02 - 0.0524\, T$$

and

$$\Delta H^\circ_T = \Delta H^\circ_0 + 31.02\, T - 0.0262\, T^2 \tag{6}$$

Substituting the mean value, $\Delta H^{\circ}_{298}=4030$ cal[1] (Kelley *et al* 1941), of the heat of solution measurements in equation (7):

$$\Delta H^{\circ}_{0} = -2890 \text{ cals}$$

so that

$$\Delta H^{\circ}_{T} = -2890 + 31.02\,T - 0.0262\,T^{2} \tag{7}$$

Using

$$\Delta S^{\circ}_{298} = 25.5 + (2 \times 16.75) - 46.4 = 12.6 \text{ cal/deg. in}$$

$$\Delta S^{\circ}_{T} = \Delta S^{\circ}_{0} + 31.02 \ln T - 0.0524\,T$$

we obtain

$$\Delta S^{\circ}_{T} = -148.55 + 31.02 \ln T - 0.0524\,T \tag{8}$$

From equations (7) and (8) it follows that

$$\Delta G^{\circ}_{T} = -2890 + 179.57\,T + 0.0262\,T^{2} - 71.44\,T \log T \tag{9}$$

This equation gives T(equil.)$=46°$C, demonstrating that the equilibrium temperature is insensitive to small variations in the heat capacity of anhydrite.

If the uncertainties of measurement assigned to each one of the thermodynamic values (Table 6) used in the derivation of equation (9) are assembled, then the confidence to be placed in this equation can be assessed. From the maximum and minimum possible values of each property, except the heat capacity, we obtain two limiting free energy equations:

$$\Delta G^{\circ}_{T} = -2870 + 180.43\,T + 0.0262\,T^{2} - 71.44\,T \log T \tag{10}$$

and

$$\Delta G^{\circ}_{T} = -2910 + 178.71\,T + 0.0262\,T^{2} - 71.44\,T \log T \tag{11}$$

Equation (10), designed to give a maximum temperature, was derived using $\Delta H^{\circ}_{298}=4030+20=4050$ cal and $\Delta S^{\circ}_{298}=25.1+(2\times16.72)-46.8=11.74$ cal/deg. The equivalent values for equation (11), which gives a minimum temperature, are $\Delta H^{\circ}_{298}=4030-20=4010$ cal and $\Delta S^{\circ}_{298}=25.9+(2\times16.78)-46.0=13.46$ cal/deg.

The equilibrium temperatures given by equations (10) and (11) are 68°C and 25°C respectively. It is clear that the available thermochemical data can fix the gypsum-anhydrite transition point at no better than 46±22°C!

Calculation of the effect of dissolved salts on the gypsum-anhydrite transition temperature at atmospheric pressure. For the conversion of gypsum to anhydrite in the presence of any aqueous solution containing dissolved salts, the reaction may be written

$$CaSO_4 \cdot 2H_2O = CaSO_4 + 2H_2O_{(\text{liq}; \text{ soln.})}$$

A simplified equilibrium constant for this reaction can be applied if the compositions of the solid phases remain unchanged (pure liquid H_2O and the pure solids at 1 atmosphere being taken as the standard states):

$$(K_a)_{P=1,T} = a^{2}_{H_2O}$$

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[1] Kelley *et al* (1941, p. 15) give ±20 cals. as the uncertainty in this value.

Now, for any chemical reaction

$$\Delta G_T = \Delta G_T^o + RT \ln K_a$$

Therefore, for the dehydration of gypsum to anhydrite

$$\Delta G_T = \Delta G_T^o + 2RT \ln a_{H_2O} \qquad (12)$$

It follows from this equation that a lowering of the activity of H_2O of the solution (e.g., by increasing the salinity) would decrease the free energy of reaction. The effect would be to lower the dehydration temperature. To evaluate this quantitatively it is necessary to know $\Delta G^o{}_T$ (reaction) and the a_{H_2O} of the solutions in which the reaction occurs.

An expression for $\Delta G^o{}_T$ (reaction) as a function of temperature has been derived (equation 9 above):

$$\Delta G_T^o = -2890 + 179.57\,T + 0.0262\,T^2 - 71.44\,T \log T \qquad (9)$$

Therefore, the change in equilibrium temperature with change in a_{H_2O} of the co-existing solution can be determined from

$$\Delta G_T = -2890 + 179.57\,T + 0.0262\,T^2 - 71.44\,T \log T + 2RT \ln a_{H_2O} \qquad (13)$$

An expression similar to (13) but based on the free energy equation of Kelley *et al* (1941) (equation 1), was derived by MacDonald (1953, p. 889) using a slightly different thermodynamic treatment:

$$\Delta G_T = -2495 + 163.89\,T + 0.0215\,T^2 - 65.17\,T \log T + 2\,RT\,2.303 \log p/p^\circ \qquad (14)$$

From this, MacDonald determined the transition temperature as a function of concentration of sodium chloride.

Kelley *et al* (1941, Fig. 8, p. 41) also had considered the effect of activity of H_2O on the gypsum-anhydrite transition temperature. They presented the results in diagrammatic form only and did not give the equation used in the calculation. This, however, is most certain to be the equation given by MacDonald, who used their data and produced exactly equivalent results.

Equation (13) gives 20°C and equation (14) 15°C for the transition temperature in the presence of halite in the system $CaSO_4-NaCl-H_2O$ ($a_{H_2O}=0.75$). The uncertainties in these temperatures will remain in the order of ±22°C, the uncertainty range for the solution of equation (9).

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