

ANHYDRITE-GYPSUM EQUILIBRIUM RELATIONS*

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ABSTRACT. Thermodynamic calculations show that gypsum will break down to anhydrite plus water below 14° C. in the presence of a saturated NaCl solution. Gypsum will begin to precipitate out of a concentrated sea water solution at temperatures below 34° C. Anhydrite is the first calcium sulphate to precipitate if the temperature is above 34° C. Pressure acting equally on all phases raises the temperature of dehydration. A mean pressure acting on the solid phases 2.4 times as great as that acting on the liquid phases lowers the dehydration temperature. The depth to which gypsum will be found in nature will depend on the temperature gradient, composition of groundwaters and ratio of lithostatic to hydrostatic pressure acting on the calcium sulphate deposit.

INTRODUCTION

QUANTITATIVE consideration of the anhydrite-gypsum equilibrium relations can lead to a better understanding of the factors controlling the deposition of these minerals and the alteration of one to the other. Solubility measurements (Posnjak, 1938) have shown that above 42° C. in a saturated solution of CaSO_4 , anhydrite is the stable form.

There is, however, little experimental information as to the effect of concentrated salt solutions on the gypsum-anhydrite transition temperatures, and there is no information as to the effect of pressure on the transition. A careful study of the thermodynamic properties of gypsum and its dehydration products has been made by Kelley, Southard and Anderson (1941). Their data make possible the calculation of the effect of pressure and salt solutions on the transition temperature.

The study of this dehydration illustrates the numerical magnitude of factors that may be of considerable importance in the breakdown of hydrous minerals. It is possible to calculate with a considerable degree of accuracy the effect of different pressures on the liquid and solid phases.

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CaSO₄—H₂O SYSTEM

Kelley et al. (1941, p. 69) found six solid phases in the CaSO₄—H₂O system with distinct thermodynamic properties. These are: CaSO₄·2 H₂O (gypsum), two polymorphs of CaSO₄·1/2 H₂O, two polymorphs of soluble CaSO₄, and one insoluble CaSO₄ (anhydrite).¹ A plot of Kelley's free energies of the dehydration reactions shows that anhydrite and gypsum are the two most stable phases in the system (compare curve B-B with other curves in figure 1). The other forms appear in the commercial production of plaster of Paris and in experimental work in the system.

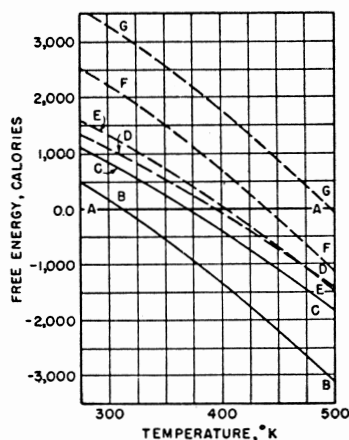


Fig. 1. Free energies of reaction (after Kelley et al., 1941).

Curve A-A $\Delta G = 0$ along this curve.

Curve B-B $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{CaSO}_4 (\text{insol.}) + 2 \text{H}_2\text{O} \quad (1).$

Curve C-C $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O} (\alpha^*) + 3/2 \text{H}_2\text{O} \quad (1).$

Curve D-D $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O} (\alpha) + 3/2 \text{H}_2\text{O} \quad (1).$

Curve E-E $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O} (\beta) + 3/2 \text{H}_2\text{O} \quad (1).$

Curve F-F $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{CaSO}_4 (\text{sol. } \alpha) + 2 \text{H}_2\text{O} \quad (1).$

Curve G-G $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{CaSO}_4 (\text{sol. } \beta) + 2 \text{H}_2\text{O} \quad (1).$

¹ There is some uncertainty as to the nature of the hemihydrates and soluble anhydrites. Thermodynamic measurements by Kelley et al. (1941) show that the solid phases mentioned above have distinct thermodynamic properties. The α and β forms of the hemihydrates give almost identical X-ray patterns. Analysis of the hemihydrates shows a variable amount of water. These facts have led some workers to postulate that the soluble anhydrites and hemihydrates are structurally identical but have varying amounts of zeolitic water. If this is so, it is quite remarkable that the various forms give such consistent physical chemical data. The literature on the subject is summarized by Kelley and by Kruis and Späth (1951).

Soluble CaSO_4 and $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ are rare in nature. Professor Frondel pointed out to the author that the mineral bassanite may have the composition $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$. In all major deposits of CaSO_4 , however, we are dealing with the relatively most stable solid phases in the $\text{CaSO}_4\text{—H}_2\text{O}$ system. If equilibrium is maintained, gypsum will break down directly into anhydrite and water. There will be no intermediate hemihydrate formed, since the hemihydrates are unstable with respect to gypsum and anhydrite plus water (see fig. 1).

BREAKDOWN OF GYPSUM TO ANHYDRITE PLUS WATER

Kelley et al. (1941, p. 44) give equation (1) as the free energy for reaction $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{CaSO}_4 \text{ anhydrite} + 2 \text{H}_2\text{O}$ liquid. This equation is based on the calorimetric determination of the heat of hydration of anhydrite, heat capacity measurements, and vapor pressure measurements.

$$(1) \quad \Delta G = 163.89 T + .0215 T^2 - 65.17 T \log_{10} T - 2495$$

where ΔG is free energy of reaction in calories per mole and T is the temperature in degrees Kelvin.

For $\Delta G = 0$ the above equation gives 40°C. as the temperature at which gypsum, anhydrite and pure liquid water can coexist at one atmosphere total pressure (Kelley et al., p. 44, 1941). Below 40°C. gypsum is the stable phase, and above 40° anhydrite in the presence of water is the most stable form. However, 40°C. is the transition temperature only when anhydrite is in the presence of pure liquid water and when the total pressure on the system is one atmosphere.

EFFECT OF PRESSURE ON THE REACTION

An increase of total pressure on the system will favor the assemblage of lesser volume. When the pressure is acting equally on all phases of a system, the pressure dependence of the free energy of reaction is given by the following equation:

$$(2) \quad \frac{\partial \Delta G}{\partial P} = \Delta V$$

ΔV for the gypsum-anhydrite reaction is 6.66 cc per mole of anhydrite. An increase of total pressure will favor the formation of gypsum.

Employing the relations

$$(3) \quad d \Delta G = \left(\frac{\partial \Delta G}{\partial P} \right)_T dP + \left(\frac{\partial \Delta G}{\partial T} \right)_P dT$$

$$(4) \quad d \Delta G = -\Delta S dT + \Delta V dP$$

and equation (1), setting $d \Delta G = 0$, we obtain

$$(5) \quad \frac{dP}{dT} = \frac{-135.59 - .043 T + 65.17 \log_{10} T}{\Delta V}$$

ΔV is assumed to be constant over the temperature interval 0-50° C. and the pressure interval 1 to 500 bars. This equation could easily be integrated, giving an analytic relation between the transition temperature and pressure. For the present purpose it is sufficient to obtain the initial slope $\left. \frac{dP}{dT} \right|_{40^\circ \text{ C.}}$ and

consider the transition curve as a straight line.

We find that

$$(6) \quad \left. \frac{dP}{dT} \right|_{40^\circ \text{ C.}} = 85.4 \text{ bars/deg.}$$

The transition temperature at 500 bars is 46° C.

Neglecting the effect of dissolved solids on the free energy of the water, the case considered above would correspond to the conditions prevailing during deposition of anhydrite or gypsum, since during deposition from a body of water the same total pressure would act on both the solid and liquid phases. However, this is not applicable once the gypsum and anhydrite are buried, if the water has free access to the surface. In this case, the water pressure should be approximated very closely by the hydrostatic pressure of water whose height is equal to the depth of burial. Measurements of water pressure in oil reservoirs show that for depths down to about 4000 feet the water pressure is equal to the calculated hydrostatic pressure (Cannon and Craze, 1938; Dickinson, 1953).

Assuming that the mean density of the rocks overlying the deposit of gypsum and anhydrite is 2.4, the mean pressure acting on the solid phases would be 2.4 times the pressure acting on the liquid phase. The slope of the curve in such a case

$$(7) \quad \frac{dP}{dT} = \frac{\Delta S}{\Delta V_s + V_{H_2O} / 2.4}$$

where ΔV_s is the difference in volume of one mole of anhydrite

and gypsum, V_{H_2O} is the volume of 2 moles of pure H_2O , and P is the pressure on the solid phases.

$$\Delta V_s = -29.48 \text{ cc per mole of anhydrite}$$

$$V_{H_2O} / 2.4 = 15.06 \text{ cc per two moles of water}$$

$$(8) \quad \left. \frac{dP}{dT} \right|_{40^\circ \text{ C.}} = -39.45 \text{ bars/deg.}$$

A pressure on the solid phase 2.4 times the pressure on the liquid phase lowers the dehydration temperature of gypsum one degree for 39.45 bars. At a pressure of 500 bars the dehydration temperature is 27° C.

The curves A and B of figure 2 show the relation of dehydration temperature to pressure; curve A represents a case where the same pressure is acting on all phases, curve B represents the case of a lithostatic pressure acting on the solid phases and a hydrostatic pressure acting on the liquid phase.

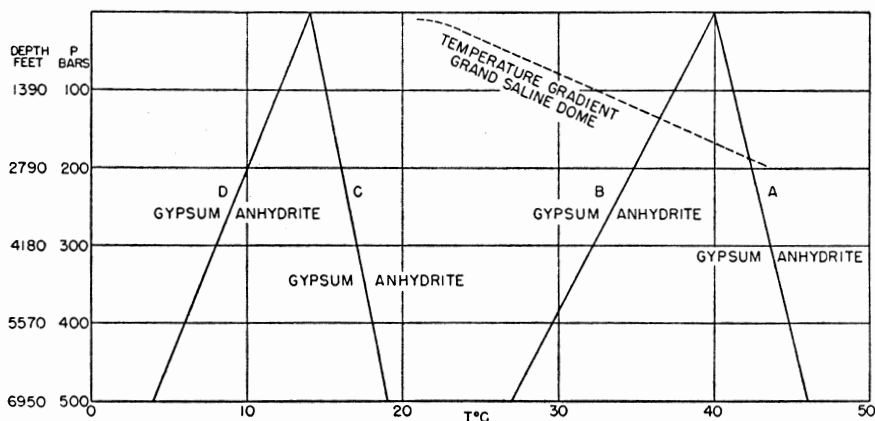


Fig. 2. Pressure-temperature relations for the reaction
gypsum = anhydrite + water.

- Curve A — Same pressure acting on all phases, in presence of pure water
- Curve B — Rock pressure acting on solid phases, hydrostatic pressure acting on pure water
- Curve C — Same pressure acting on all phases in presence of saturated NaCl solution
- Curve D — Rock pressure acting on solid phases, hydrostatic pressure acting on saturated NaCl solution

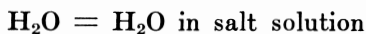
EFFECT OF DISSOLVED SOLIDS ON THE REACTION

In the above calculations it is assumed that the water in equilibrium with gypsum and anhydrite is pure water. Let us consider the effect of dissolved solids on the free energy of water. The assumption is made that the water vapor in equilibrium with water can be treated as an ideal gas (a reasonable assumption for vapor pressures less than 1 bar at temperatures above 0° C.).

Salts dissolved in the water will lower the vapor pressure of the water. This lowering of vapor pressure can be related to the change in free energy of the vapor by

$$(9) \quad \Delta G = RT \ln p/p_0$$

ΔG is the change in free energy of the vapor in going from a vapor pressure p_0 to a vapor pressure p . Since the water in solution will be in equilibrium with the vapor above it, ΔG also represents the change in free energy of the liquid water. Therefore, for the reaction



$\Delta G = RT \ln p/p_0$ where p_0 is vapor pressure of pure water at temperature T and p is the vapor pressure of water vapor over the salt solution at the same temperature. Considering the reaction $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{CaSO}_4 \text{ anhydrite} + 2 \text{H}_2\text{O}$ in salt solution and equations 1 and 9, ΔG is given by

$$(10) \quad \Delta G = 163.89 T + .0215 T^2 - 65.17 T \log_{10} T - 2495 \\ + RT \, 2.303 \log_{10} p/p_0$$

Complete data on the lowering of vapor pressures by various salts as a function of temperature and concentration are given in the *International Critical Tables* (1933). Sodium chloride is the most abundant salt in sea water and probably the major constituent of solutions that might come into contact with buried gypsum-anhydrite deposits. The lowering of the vapor pressure of the water by natural salts is approximated by the lowering of vapor pressure by sodium chloride. Representative values of p/p_0 and of ΔG for solutions of sodium chloride of various concentrations and temperatures are given in table 1.²

² Table 1 computed from data given in *International Critical Tables*.

TABLE 1

Temperature °C.	Molality of Solution	Chlorinity in Parts/Thousand	p/p ₀	Δ G in Calories
20	6.136*	160	.7521	— 166
30	6.168*	161	.7500	— 174
40	6.207*	162	.7250	— 177
20	4.967	136	.8120	— 121
30	4.967	136	.8113	— 126
40	4.967	136	.8116	— 130
20	1.901	61	.9359	— 39
30	1.901	61	.9363	— 40
40	1.901	61	.9350	— 42

* Saturated solution

Data given in part in table 1, together with equation (10), determine the transition temperature as a function of concentration of sodium chloride. This dependence is shown in figure 3, and various values of the transition temperature are listed in table 2. Although the curve was drawn using data for sodium chloride, it can be used as an approximation for concentrated solutions of sea water of given chlorinity.³

In the presence of a solution containing 5 moles of sodium chloride, gypsum is in equilibrium with anhydrite at 21° C. At temperatures below 21° C. gypsum is the stable form. Similarly in a concentrated solution of sea water containing 115 parts per thousand of chlorine, gypsum and anhydrite are in equilibrium at 26° C.

In considering the effect of pressure on the transition in the presence of a concentrated salt solution, the proper molar volume of water in the salt solution must be used. For the same total pressure acting on all the phases;

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

Since $-\Delta S = \frac{\partial \Delta G}{\partial T}$, differentiating equation (10) results in

$$(11) \quad \Delta S = -135.59 - .043 T + 65.17 \log_{10} T \\ - 2.303 R \log_{10} p/p_0$$

³ Chlorinity, as used in this paper, is the mass of chlorine equivalent to the mass of halogens contained in one kilogram of sea water (Harvey, 1945). Sea water has a chlorinity of about 19 parts per thousand parts of solution.

Adams (1931) gives the partial molar volume of water in a sodium chloride solution at 25° C. for various concentrations of sodium chloride. These partial molar volumes are given in table 2. Using these data, assuming ΔV is constant over the temperature-pressure interval considered and using equation (11), dP/dT is determined for various concentrations of salt solutions. The values of dP/dT obtained are listed in table 2.

TABLE 2

Moles NaCl in Solution	Partial Molar Volume of Water (at 25° C.)	Dehydration Temperature at one bar	dP/dT in bars/deg.
.90	18.05	37	85.8
1.90	18.02	34	86.5
3.02	17.97	30	87.7
4.28	17.92	25	88.9
5.70	17.86	17	90.3
6.15*	17.84**	14	90.8

* Saturated

** Extrapolation

In a concentrated sodium chloride solution the transition curves have a greater initial slope than for pure water.

The effect of differential pressure on the dehydration reaction in the presence of salt solution can now be calculated. A rock density of 2.4 is assumed. The density of the liquid is assumed to be that of a sodium chloride solution of the given concentration. The slopes of the dehydration curves for differential pressures are given in table 3.

TABLE 3

Moles NaCl in Solution	Density of Solution	dP/dT in bars/deg.
.90	1.03	-40.6
1.90	1.07	-42.4
3.02	1.11	-44.1
4.28	1.15	-45.9
5.70	1.19	-47.7
6.12*	1.20	-48.3

* Saturated solution

The relation of temperature of dehydration to pressure in the presence of a saturated sodium chloride solution is shown in figure 2. Curve C represents the case of a differential pressure.

The transition temperature of gypsum to anhydrite at one bar pressure as a function of salt concentration is given in figure 3. The effect of pressure on the transition in the presence of salt solutions is given by values of dP/dT listed in tables 2 and 3.

By using these data it is possible to calculate a set of curves similar to A, B, C, and D of figure 2. The curve defining the transition in the presence of a 1.9 molar solution of NaCl has an initial point at 34° C. (fig. 3). The slope of the curve for the case of different pressures acting on the liquid and solid phases is -42.4 bars/degree (see table 3). Similarly, transition curves for other salt concentrations can be calculated.

COMPARISON OF CALCULATION WITH EXPERIMENT

On the basis of solubility measurements Posnjak (1938) determined the temperature of dehydration of gypsum to anhydrite to be 42° C. at one atmosphere pressure. This value is 2° higher than the value calculated using thermodynamic

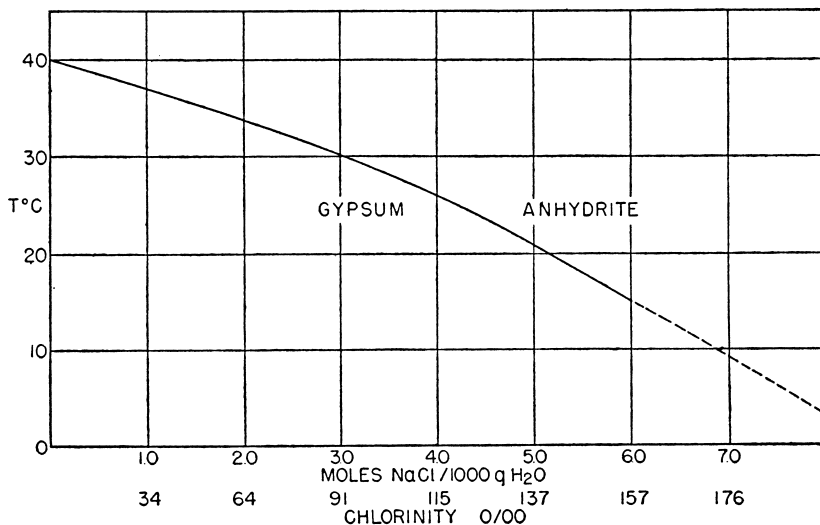


Fig. 3. Dependence of the dehydration temperature of gypsum on concentration of NaCl in solution at one bar pressure.

data. Posnjak (1940) determined the solubilities at 30° C. of anhydrite and gypsum in a salt solution of essentially the composition of concentrated sea water. The transition of anhydrite to gypsum took place at 30° C. in a solution containing 93 parts per thousand of chlorine. The calculated temperature for a solution of this chlorinity is 30° C. (fig. 3). There is no experimental information as to the effect of pressure on the dehydration temperature.

GEOLOGIC CONSIDERATIONS

Deposition.—About 1.26 grams of calcium sulphate are present in 1000 grams of natural sea water; this amount is less than the solubility of calcium sulphate in water. The total salinity of sea water has to be increased by a factor of 3.35 to obtain saturation with respect to calcium sulphate (Posnjak, 1940). This salinity corresponds to a chlorinity of about 65‰. Assuming that the above solubility relations, obtained at 30° C., hold over the temperature interval considered, figure 3 shows that in a solution of this chlorinity the transition temperature is 6° less than in pure water. Therefore gypsum will precipitate out of sea water at all temperatures below 34° C.⁴ if the deposition is an equilibrium process. The value often quoted in the literature is 42° (Phillips, 1947) based on Posnjak's work. This value refers to a solution saturated with CaSO_4 but containing no other salts. The presence of other salts in the proportion found in natural sea water will lower the transition temperature by about 6°. Therefore, anhydrite will be the phase precipitated out of sea water if the temperature is above about 34°. Pressure has little effect on this temperature; a pressure of 100 bars will raise the temperature to 35° C.

The history of crystallization of calcium sulphates from a body of sea water can be traced if a sea water temperature is assumed. At 25° C. salts will be concentrated by evaporation until a chlorinity of 65‰ is reached. At this point gypsum will begin to precipitate. Gypsum will continue to precipitate until the chlorinity reaches a value of 119‰; then anhydrite will precipitate. Gypsum in contact with sea water at chlorin-

⁴ Here, and in the discussion which follows, temperatures derived from thermodynamic data will be used. As mentioned previously, these temperatures are within 2° of experimentally determined dehydration temperatures.

ity above $113^{\circ}/\text{oo}$ will be unstable and will break down to anhydrite.

In saturated NaCl solutions gypsum will precipitate only at temperatures below 14° C. as is shown in table 2. In concentrated sea water gypsum and halite will precipitate together at a chlorinity of $184^{\circ}/\text{oo}$ and at temperatures below 7° C. The presence of salts other than NaCl in concentrated sea water lowers the maximum temperature at which gypsum and halite can coexist from 14° C. to 7° C.⁵

Relation of gypsum to depth.—A knowledge of the temperature gradient in a region of calcium sulphate deposits and the data calculated above determines a maximum depth at which gypsum will be stable. There probably is a transition region over which both gypsum and anhydrite will appear. Below this region no gypsum will be found.

Deposits of calcium sulphate are commonly found with salt domes. Since temperature gradients over salt domes are available, a comparison of the predicted depth to which gypsum should be found and observed depths is possible for calcium sulphate deposits associated with salt domes.

Hawtoff's (1930) gradient over the Grand Saline Dome in Van Zandt County, Texas, is plotted in figure 2. A mean rock density of 2.4 has been assumed. This temperature-depth curve intersects the dehydration curve for a differential pressure acting on the solid and liquid phases at a depth of 1820 feet. For this temperature gradient, gypsum would not be in equilibrium with pore water below about 1820 feet.

The depth to which gypsum will be found is dependent on the amount of dissolved solids in the ground water. The dehydration curve for gypsum in the presence of a solution of chlorinity $61^{\circ}/\text{oo}$ ⁶ will intersect the temperature-depth curve at about 1300 feet. Goldman (1952, p. 61) notes that the maximum depth to which gypsum is found in cap rock is about 2000 feet. In the Sulfur Salt Dome, which Goldman studied in detail, gypsum was rarely found below 1180 feet. Considering

⁵ This calculation assumes that salts other than NaCl have no effect on the solubility relations of NaCl. Therefore, 7° C. may be somewhat low for the simultaneous precipitation of halite and gypsum from concentrated sea water.

⁶ Timm and Maricelli (1953) have studied the salinities of formation waters in southwest Louisiana. Salinities up to $4\frac{1}{2}$ times that of natural sea water have been found.

the uncertainty in temperature gradients and groundwater composition, the agreement between calculated and observed depths of disappearance of gypsum is satisfactory.

Curves C and D of figure 3 represent the conditions necessary for the breakdown of gypsum to anhydrite in the presence of a saturated salt solution. Pore water in a halite bed would be saturated with NaCl. Gypsum would not be in equilibrium within this pore water except at temperatures below 14° C. Gypsum is not in equilibrium with buried halite except at temperatures lower than 14° C. Published cross sections of cap rock (Taylor, 1938) show a layer of anhydrite separating the gypsum from the rock salt. This sequence is interpreted in the following way: The pore water near the main body of salt probably has a high concentration of NaCl. Therefore, with any normal temperature gradient, anhydrite would be the phase in equilibrium with the pore water. At a higher level the groundwater will no longer be saturated with NaCl, the temperature will be lower, and gypsum will be the stable calcium sulphate.

Salt deposits.—Major deposits of calcium sulphate are found associated with undisturbed salt beds. A recent detailed study of the Permian salt deposits in Yorkshire by Stewart (1949, 1951a, 1951b) permits a comparison of the sequence of deposition derived from the present paper and that observed in a natural deposit.

Stewart describes three evaporite beds, each showing the general sequence (from bottom to top): Anhydrite-carbonate rocks, anhydrite-halite-polyhalite rocks, and rocks consisting dominantly of chlorides. Gypsum was not found in any of the core samples. The absence of gypsum can be explained by the fact that the beds are now at a depth of 3600 feet to 5000 feet. The temperature at 4200 feet is 42° C.; at 3000 feet it is 37° C. (Lees and Tait, 1946, p. 269). Therefore the maximum depth at which gypsum would be stable in the presence of pure water would be about 2500 feet, assuming different pressures acting on the liquid and solid phase (fig. 2). In his earlier paper Stewart (1949, p. 659) stated that the basal anhydrite rock was deposited as primary anhydrite. However, in a recent paper (1953) he reports on evidence that the lower anhydrite-carbonate rocks contain anhydrite pseudomorphs after gypsum. The intermediate zone of the evaporite beds contains

abundant anhydrite pseudomorphs after gypsum; these pseudomorphs are associated with halite. Complexly interbedded with the rocks containing pseudomorphs are rocks made up of primary anhydrite and halite. Stewart (1949, p. 659) interprets the sequence as the result of alternate deposition of gypsum-halite and anhydrite-halite. With this information it is possible to correlate Stewart's observation with material presented in this paper.

On evaporation gypsum is the first calcium sulphate deposited. Continuing evaporation concentrates other salts and eventually anhydrite is deposited instead of gypsum. The concentrated brines are no longer in equilibrium with gypsum and would alter previously deposited gypsum to anhydrite. There then follows a period of alternate deposition of anhydrite-halite and gypsum-halite. Anhydrite-halite rocks were deposited when the temperature of the bottom waters was above about 7° C., and gypsum-halite rocks were deposited when the temperature was below 7° C.

The low bottom water temperatures indicated by the original gypsum-halite assemblage give rise to several possibilities as to the climate of the region. The evaporating basin could have been in a cold but dry area, the temperature of the basin varying only a few degrees about 7° C. Alternatively, the basin could have been in an area of large fluctuations in temperature, the gypsum-halite beds representing warmer periods.

Perhaps the major objection to this picture is the low temperature required for deposition. The treatment presented assumes the proportions of salts in the Permian seas was essentially that of the present time. Decreasing the concentrations of salts other than NaCl and CaSO_4 increases the temperature at which gypsum and halite could form simultaneously, but in no case could gypsum and halite be in equilibrium with water above 14° C.

Another possibility is that gypsum and halite were not deposited at the same time. A history of crystallization compatible with thermodynamic data is as follows: Gypsum is deposited, evaporation leads to deposition of anhydrite, the brines in equilibrium with anhydrite replace the previously formed gypsum. Deposition of halite and anhydrite follows. An influx of fresh water into the basin reduces the concentration of salts, halite is dissolved, and anhydrite is converted

to gypsum. Continuing evaporation results in brines capable of first replacing gypsum with anhydrite and then with anhydrite and halite.

Such a cycle could be repeated several times, leading to a complex interlayering of anhydrite-halite rock and rocks containing pseudomorphs after gypsum. The above sequence could form in water having a temperature lower than 34° C.

SUMMARY

An attempt has been made to correlate available thermodynamic, experimental, and geologic information on the system $\text{CaSO}_4\text{—H}_2\text{O}$.

Using the thermodynamic data, the temperature of breakdown of gypsum to anhydrite plus water as a function of the amount of salt dissolved in the water, has been calculated. High salt contents lower the dehydration temperature.

The effect of pressure on the transition temperature has been calculated. An increase of pressure acting equally on all the phases raises the dehydration temperature of gypsum. On burial of a calcium sulphate deposit the pressure acting on the solid phases is probably unequal to that on the liquid phases. Under these conditions the temperature of transition is lowered.

The maximum depth to which gypsum will be found is a function of the temperature gradient over a region, the composition of pore water, and the ratio of hydrostatic to lithostatic pressure. Using the gradient found over the Grand Saline Dome in Texas, assuming the ground water to contain 10 percent dissolved salts, the maximum depth at which gypsum is stable would be 1360 feet in this locality. Lower temperature gradients would increase the depth to which gypsum is found, as would lower concentrations of salts in the ground water.

Stewart describes rocks that represent alternate deposition of anhydrite-halite and gypsum halite. In light of material presented in this paper this means that the bottom waters in the basin were around 7° C. during the deposition of the halite-gypsum rocks.

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