

Thermodynamics of the dehydration of Gypsum

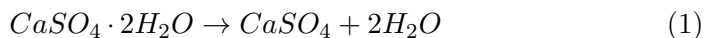
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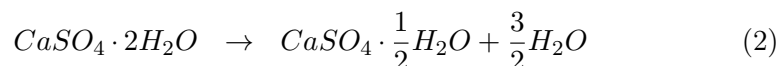
1 Introduction

The dehydration of gypsum is a well known, important reaction, with wide applications. It forms the core of the cement and plaster industry and it is of great import for the conservation and restoration of buildings and of paintings (Charola, Pühringer, and Steiger 2007). It is also a very important reaction for geology, as it is used as a model system to help and understand tectonic systems in which dewatering and porosity genesis plays a central role. A very large body of knowledge has accumulated over the years, addressing the wide variety of aspects of the dehydration (Charola, Pühringer, and Steiger 2007; Freyer and Voigt 2003). Notwithstanding the progress made, important questions remain.

The reaction schemes of the dehydration of gypsum have been written out as



in which gypsum dehydrates directly into anhydrite, or



in which gypsum first dehydrates into the hemi-hydrate bassanite which in turn dehydrates into γ -anhydrite a compound which can rehydrate back to bassanite and gypsum (it takes prolonged heating at higher temperatures to obtain stable, water-resistant anhydrite). Both these reactions have been used to describe what happens during dehydration, and experimental evidence has been reported in the literature to support both. The single-step reaction is supported by Carbone, Ballirano, and Caminiti 2008; Prasad, Chaitanya, Prasad, and Rao 2005, while the two-step reaction is supported by Ballirano and Melis 2009; Chang, Huang, and Hou 1999; Sarma, Prasad, and Ravikumar 1998; Seufert, Hesse, Götz-Neunhöffer, and Neubauer 2009.

2 Crystallography

The crystallographic properties of the different compounds are listed in this Table

Table 1: Crystallography of CaSO_4 minerals							
Substance	Space Group	Z	a (Å)	b (Å)	c (Å)	β (°)	V_m ml
gypsum	C_{2h}^6 -I12/a1	4	5.679(5)	15.202(14)	6.522(6)	118.43	74.545
bassanite	C_2^3 -I121	12	12.0317(4)	6.9269(2)	12.6713(3)	90.27	52.997
γ -anhydrite	D_2^6 -C222	6	12.0777(7)	6.9723(4)	6.3040(2)	90.00	53.281
anhydrite	D_{2h}^{17} -Cmcm	4	6.993(2)	6.995(2)	6.245(1)	90.00	45.991

The data sources are Bezou, Nonat, Mutin, Christensen, and Lehmann 1995; Bideaux, Blath, and Nichols 1990; Hahn 1992; Hawthorne and Ferguson 1975; Pedersen and Semmingsen 1982.

We can glean immediately from this table that the dehydration is accompanied by a volume reduction, regardless of the reaction scheme followed. It is also clear that the dehydration causes an increase in symmetry of the crystals, as we move from the monoclinic gypsum (space group 15), over the monoclinic bassanite (space group 5) to the orthorhombic γ -anhydrite (space group 21) and orthorhombic anhydrite (space group 63).

The organisation of the atoms and molecules in their respective crystal lattices (see Figure) is of direct relevance. The disposition of the water molecules as sheets perpendicular to the c-axis between the calcium and sulfate layers in the gypsum lattice (Figure) helps to explain the excellent cleavage properties of the mineral (Freyer and Voigt 2003). It also shows the relative freedom of the water molecules and the potential for electrostatic interaction amongst themselves (Schofield, Knight, and Stretton 1996). These interactions go quite some way in helping to explain the much larger heat capacity of gypsum, compared to the other compounds.

The disposition of the water molecules in bassanite (Figure) is very different from that found in gypsum. Instead of sheet-like layers, we find two types of water molecules. There are relatively tight clusters of 4 molecules, regularly disposed in about 4 Å diameter channel-like conduits along the c-axis, left open between CaO_8 polyhedra and two, much more isolated molecules (Freyer and Voigt 2003). This led Voigtländer, Winkler, Depmeier, Knorr, and Ehm 2003 and Comodi, Nazzareni, Dubrovinsky, and Merlini 2009 to describe bassanite as a nanoporous host-guest system in which the sulfate molecules play host and water molecules the guest.

The lower amount, as well as the different organization of the water molecules in bassanite help to explain its significantly lower heat capacity, compared to the fully hydrated gypsum.

3 Thermodynamics

3.1 Gibbs Free Energy of a reaction reaching equilibrium

Reactants \rightarrow Products

Such a reaction will achieve equilibrium when

$$\Delta G_r(T_e, P_e) = 0 \quad (4)$$

$$= \Delta G_{f,Products}(T_e, P_e) - \Delta G_{f,Reactants}(T_e, P_e) \quad (5)$$

The question then is, what are

$$\Delta G_{f,Products}(T_e, P_e), \Delta G_{f,Reactants}(T_e, P_e) = ? \quad (6)$$

We can calculate the Gibbs Free Energy at equilibrium T and P from

$$\Delta G_f(T_e, P_e) = \Delta G_f^0(T_0, P_0) - \int_{T_0}^{T_e} S_f(T) dT + \int_{P_0}^{P_e} V_f(P) dP \quad (7)$$

and, as a result, we can write that

$$\Delta G_r(T_e, P_e) = \Delta G_{r,f}^0(T_0, P_0) - \int_{T_0}^{T_e} \Delta S_r(T) dT + \int_{P_0}^{P_e} \Delta V_r(P) dP \quad (8)$$

In actual practice, we need to get access to the Entropy in order to be able to calculate the Gibbs Free Energy. This follows directly from

$$S(T_e) = \int_0^{T_e} \frac{C_p}{T} dT \quad (9)$$

Since the heat capacity is usually available in various tables as polynomials in T, this integration can be carried out very easily.

We also need a Volume function, something that is not immediately obvious. We can define the properties

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T} \quad (10)$$

$$\beta = -\frac{1}{V} \frac{\partial V}{\partial P} \quad (11)$$

the isobaric thermal expansion and isothermal compressibility, respectively. Measurements on a wide variety of minerals and rocks show that

$$\alpha = 1 - 4 \cdot 10^{-5}/K \quad (12)$$

$$\beta = 0.5 - 3 \cdot 10^{-11}/Pa \quad (13)$$

and so, the volume function of solids can be considered constant over substantial temperature and pressure ranges (Carmichael 1977).

The end result is that we can write the Gibbs Free Energy of the reaction at T and P as

$$\Delta G_r(T_e, P_e) = \Delta G_{r,f}^0(T_0, P_0) - \int_{T_0}^{T_e} \Delta S_r(T) dT + (P_e - P_0) \Delta V_r \quad (14)$$

in which the $\Delta G_{r,f}^0(T_0, P_0)$ is the algebraic (and stoichiometrically correct) sum of the Gibbs Free Energy of formation at standard temperature and pressure of all the compounds present in the reaction scheme (which can be found in standard tables for a great many minerals). The entropy function again can be calculated from the algebraic and stoichiometrically correct sum of the participating compounds (best through simple polynomials in T), again available from standard tables.

3.2 Volatiles

The discussion up til now addressed the thermodynamics of reactions of solids. Once volatiles or fluids appear, the matter becomes more complex. The increased complexity is due of course to the Volume function, which for volatiles or fluids is usually not a simple function of T and P.

The question we have to address for volatiles is

$$\int_{P_0}^{P_e} V_f(P) dP = ? \quad (15)$$

There are fortunately two ways in which we can try and solve this question. One way is through the Gibbs Energy, and the other is through the fugacity

$$\int_{P_0}^{P_e} V_{vol}(P) dP = G_{vol}(T_e, P_e) - G_{vol}(T_e, P_0) \quad (16)$$

$$= RT_e \log_e \frac{f(T_e, P_e)}{f(T_0, P_0)} \quad (17)$$

Both for H_2O and CO_2 , tables exist listing properties over a wide range of temperature and pressure conditions.

3.3 Thermodynamic properties from calorimetry

The basic thermodynamic properties of the three sulfates have been measured calorimetrically (Kelley, Southard, and Anderson 1941), but these measurements necessarily shy away from temperatures at which hydration or dehydration take place (see Figure). The measurements of heat capacity allowed the calculation of the other, fundamental thermodynamic properties, summarized in this table (from Wagman, Evans, Parker, Schumm, Halow, Barley, Churney, and Nuttall 1982)

Table 2: Thermodynamic Properties					
Substance	ΔH_f^0 (kJ/mol)	ΔG_f^0 (kJ/mol)	S^0 (J/K mol)	C_P (J/K mol)	V (ml)
gypsum	-2022.5	-1796.9	194.10	186.31	74.545
bassanite	-1576.2	-1436.2	130.63	119.74	52.997
γ -anhydrite	-1425.2	-1313.4	108.40	100.21	53.281
anhydrite	-1433.6	-1321.2	106.76	99.65	45.991
water(l)	-286.0	-237.4	69.99	75.35	18.015
water(g)	-242.0	-228.8	188.85	33.60	

The data can and have then been used to calculate the Haas-Fisher polynomials for the heat capacity. As these polynomials do not extrapolate at all well, the validity range of the polynomials remains restricted to the temperature interval of the actual measurements.

3.4 Reaction thermodynamics

Applying Hess's law, we can use these standard thermodynamic properties to calculate energy, entropy and estimate the equilibrium temperature of the reactions and obtain the results shown in this table.

Table 3: Reaction thermodynamics					
Reaction Products	ΔH_r^0 (kJ/mol)	ΔG_r^0 (kJ/mol)	ΔS_r (J/K mol)	T_{eq} (K)	ΔV_r (ml)
bassanite + water(g)	83.32	17.58	219.81	379.0	-21.55
bassanite + water(l)	17.26	4.68	41.51	415.7	5.45
γ -anhydrite + water(g)	113.28	25.98	292.00	387.9	-21.26
γ -anhydrite + water(l)	25.20	8.78	54.27	464.3	14.74
anhydrite + water(g)	104.92	18.20	290.36	361.3	-28.55
anhydrite + water(l)	16.84	1.00	52.63	320.0	7.45

These theoretical calculations fit the values measured by Kelley, Southard, and Anderson 1941 very well.

The negative values for the reaction volumes in Table indicate that the volume of the reaction products upon completion is larger than that of the start product. It means that there is only sufficient space to accomodate part of the water liberated through dehydration. In a closed system, this would entail a pressure build-up which follows immediately from the ideal gas law, i.e.,

$$p = \frac{n R T}{V} \quad (18)$$

$$= \frac{1.5 R 388}{21.33 \cdot 10^{-6}} \quad (19)$$

$$= 225 \text{ MPa} \quad (20)$$

in which V is the volume available after the conversion of gypsum to bassanite. We can conclude from this that the dehydration reaction in a closed system will come to a halt well before completion.

3.5 Thermodynamic properties from vibrational data

The application of statistical mechanics allows us to estimate heat capacity, entropy and free energy from vibrational spectra (Kieffer 1979; Hofmeister, Hoering, and Virgo 1987). Using the results obtained by Iishi 1979 and Ross 1974 for the vibrational spectra (see Figure), calculations fail to fit the measured heat capacity (see Figure) for the hydrated components. Clearly, the nature of the water molecules within the crystal lattice and its interactions (both with the oxygen atoms of the sulfate groups as with other water molecules) is more complex than the models proposed by Kieffer 1979 and Hofmeister, Hoering, and Virgo 1987 cater for.

4 Data and Analysis

For now, here is the collection of octave code used to carry out the various calculations, but these have to be re-organised and brought into the correct order.

Procedure to calculate the stability fields in the dehydration reaction of gypsum over bassanite to gamma anhydrite using thermodynamical principles based on minimising the Gibbs Free Energy of the reaction.

Let us begin with defining various constants and coefficients

```

R    = 8.314510;      # Gas Constant, J/K mol
T_0 = 298;           # Standard Temperature, K
P_0 = 101325;        # Standard Pressure, Pa

```

as well as the various Thermodynamic Data and derived data (Wagman et al, 1982). These are in order Enthalpy (J/mol), Gibbs Energy (J/mol), Entropy (J/ K mol), Heat Capacity (J/K mol), Molar Volume (m³)

```

gypsum      = [-2022500 -1796900 194.10 186.31 74.545e-6];
bassanite   = [-1576200 -1436200 130.63 119.74 52.997e-6];
anhydrite   = [-1425200 -1313400 108.40 100.21 53.281e-6];

```

Straight 3rd degree polynomials of the Entropy, calculated directly from the Kieffer-Hofmeister heat capacity vibrational spectrum fit to the calorimetric data as well. The entropy here is the result of $S = \int_0^T C_p/T \, dT$ between 0 K and T, and fitted with a simple polynomial

```

entropy_anhydrite = [9.5209e-8 -3.1818e-4 4.9417e-1 -13.473];
entropy_bassanite = [1.1212e-7 -3.9129e-4 6.0593e-1 -18.103];
entropy_gypsum    = [1.2741e-7 -5.0015e-4 8.6446e-1 -24.442];

entropy_water     = [      0          0          0    233    ];

```

The integration of the reaction entropy is straightforward as we are using straight (3rd degree) polynomials, valid from 0 K onwards, i.e., $S = aT^3 + bT^2 + cT + d$ and hence $\int(S) = aT^4/4 + bT^3/3 + cT^2/2 + dT + 0$ which we can evaluate directly with octave's polyval

```

function y = entropy_integral(entropy_polynomial,T_0,T_e)
P = [entropy_polynomial 0] .*[1/4 1/3 1/2 1 1];
y = polyval(P,T_e)-polyval(P,T_0);
endfunction

```

Calculate the gibbs free energy of the reaction at (T_e, P₀) of the solid phases only. The part played by H₂O is dealt with separately

```

function y = gibbs_e(gibbs_0,reaction_entropy_polynomial,T_0,T_e)
y = gibbs_0 - entropy_integral(reaction_entropy_polynomial,T_0,T_e);
endfunction

```

Calculate the reaction parameters for the solids only First get reaction changes in Enthalpy, Gibbs Free energy, entropy, heat capacity (which is rather meaningless, so ignore it) and volume through the Hess Law

```

reaction_bassanite = bassanite .- gypsum;
reaction_anhydrite = anhydrite .- bassanite;

```

```

#reaction_full = anhydrite .- gypsum;

```

Calculate the reaction change for the entropy polynomials of the solids using the same logic as for the previous step

```

reaction_entropy_bassanite = entropy_bassanite .+ ...
    1.5 .* entropy_water .- entropy_gypsum;
reaction_entropy_anhydrite = entropy_anhydrite .+ ...
    0.5 .* entropy_water .- entropy_bassanite;

#reaction_entropy_full = entropy_anhydrite .+ ...
#    2.0 .* entropy_water .- entropy_gypsum;

```

Loop over Temperature to calculate the Gibbs energy

```

for i = 1:201
    T_e = 272 + i;
    bassanite_gibbs_e(i) = gibbs_e(reaction_bassanite(2),
    reaction_entropy_bassanite,T_0,T_e);
    anhydrite_gibbs_e(i) = gibbs_e(reaction_anhydrite(2),
    reaction_entropy_anhydrite,T_0,T_e);

#    full_gibbs_e(i) = gibbs_e(reaction_full(2),
#    reaction_entropy_full,T_0,T_e);

endfor

```

Note that in order to print graphs correctly, gnuplot needs to be specified as graphics toolkit, and, it is also necessary to use the cairo-based output formats (e.g., -dpdfcairo, -depscairo); otherwise you end up with a black rectangle.

```

load ../cache/gibbs_star.d

```

```

for i = 1:201
    gibbs_result_bassanite(:,i) = gibbs_star(:,i).* 1.5 .+ ...
    bassanite_gibbs_e';
    gibbs_result_anhydrite(:,i) = gibbs_star(:,i).* 0.5 .+ ...

```



```

anhydrite_gibbs_e';
# gibbs_result_full(:,i) = gibbs_star(:,i).* 2.0 .+ ...
#                               full_gibbs_e';
endfor

temperature = [273:473]';
pressure = [1:201]'.*500;

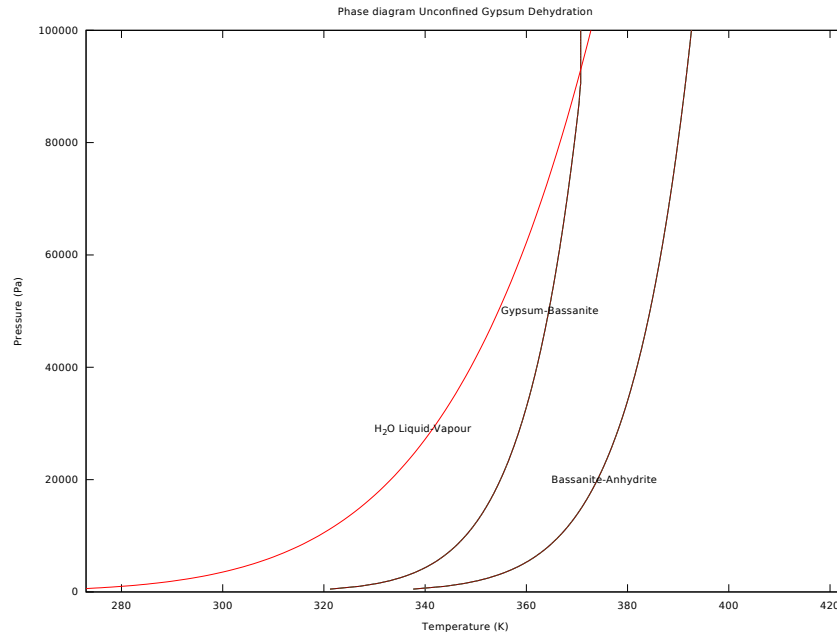
load ../cache/my_pressure.d

graphics_toolkit gnuplot
figure()

hold on;
contour(temperature,pressure,gibbs_result_bassanite',
[-0.001,0,0.001]);
contour(temperature,pressure,gibbs_result_anhydrite',
[-0.001,0,0.001]);
#contour(temperature,pressure,gibbs_result_full',
#        [-0.001,0,0.001]);

plot(my_pressure(:,1),my_pressure(:,2),'-r');
xlabel('Temperature (K)');
ylabel('Pressure (Pa)');
title('Phase diagram Unconfined Gypsum Dehydration');
axis([273,423,0,100000]);
text(330,29000,'H_2O Liquid-Vapour');
text(355,50000,'Gypsum-Bassanite');
text(365,20000,'Bassanite-Anhydrite');
hold off;
print -dpdfcairo ../output/unconfined.pdf;
ans = '../output/unconfined.pdf'

```



4.1 Miscellaneous

```
function S = calc_entropy(poly,T)
    S = poly(1) .+ poly(2).*log(T) .+ poly(3).*T .+ ...
        poly(4)./(T.^2) .+ poly(5).*(T.^2) .+ poly(6)./sqrt(T);
endfunction
```

A similar function can be defined to calculate the isobaric heat capacity C_p , from the Haas-Fischer polynomial $a_1 + a_2 * T + a_3 * T^{-2} + a_4 * T^2 + a_5 * T^{-1/2}$

```
function C = Cp(Mineral,T)
    C = T.*Mineral(2) .+ Mineral(3)./(T.^2) .+ Mineral(4).*(T.^2) .+ ...
        Mineral(5)./(sqrt(T)) .+ Mineral(1);
endfunction
```

4.2 Data Analysis

5 Results

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