

Thermodynamic study of the $\text{CaSO}_4\text{-H}_2\text{O}$ solid-gas transformations: How much water does calcined gypsum contain?

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1 Industrial motivations

Industrial motivations

- Calcination process: Dehydration of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to obtain plaster ($\beta\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) [1]
- Annual production of gypsum > 230 millions tons (2017) [2]

Calcination Furnace

Plaster production
 $\beta\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$

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2 Scientific motivations and objectives

Objective: Understand the solid gas transformations of the $\text{CaSO}_4\text{-H}_2\text{O}$ system

- Thermodynamic study: **water content of calcined gypsum compounds**

Low $P_{\text{H}_2\text{O}}$

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Calcium sulfate dihydrate) \rightarrow $\beta\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (Calcium sulfate hemihydrate) \rightarrow AIII- CaSO_4 (Anhydrite III) \rightarrow AII- CaSO_4 (Anhydrite II)

Divariant behavior: $\text{CaSO}_4 \cdot \varepsilon(T, P_{\text{H}_2\text{O}})\text{H}_2\text{O}$

$\text{CaSO}_4 \cdot \varepsilon(T, P_{\text{H}_2\text{O}})\text{H}_2\text{O}$ { Different reported values of ε at different T and $P_{\text{H}_2\text{O}}$ [3]: $\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.625\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.6\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.583\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.48\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.15\text{H}_2\text{O}$ etc.

Experimental methods

- TGA of synthetic dehydrated $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under controlled T and $P_{\text{H}_2\text{O}}$
- Symmetrical thermobalance (TAG 16 Setaram) and water vapor generator (Wetsys Setaram)
- Δm by TGA used to calculate the water content ε (using a dry reference of anhydrous CaSO_4)
- Morphological characterizations (SEM, Optical microscopy)

3 Experimental results

Water content after dehydration of gypsum: $\varepsilon\text{-T-}P_{\text{H}_2\text{O}}$ diagrams

3 zones:

- 2 zones of divariance (lower and upper): continuous variation of ε with T and $P_{\text{H}_2\text{O}}$
- 1 zone of univariant transitions (middle)

Hypotheses:

- 1 zone of univariant transition between AIII- CaSO_4 and $\beta\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$
- 2 zones of divariance (lower and upper): water vapor adsorption models

$\varepsilon = n_{\text{structure}} + n_{\text{ads}}$

4 $P_{\text{H}_2\text{O}}\text{-T}$ diagram

Law of mass action:

$$K_{eq}(T) = P_{eq}^{0.5} = K_0 \exp\left(-\frac{\Delta_r H}{RT}\right)$$

$\Delta_r H = 35.3 \text{ kJ/mol}$

Comparison with literature [4]:

$\Delta_r H = 34.4 \text{ kJ/mol}$; $\Delta_r H = 31.9 \text{ kJ/mol}$; $\Delta_r H = 33.0 \text{ kJ/mol}$ (different products, natural samples with unknowns composition)

5 Modeling of water vapor adsorption

Water vapor adsorption on AIII- CaSO_4

Monolayer adsorption (Langmuir model) [5]

$$\theta = \frac{n_a}{n_m} = \frac{K_{eq}P}{1 + K_{eq}P}$$

Average monolayer capacity
 $n_m = (0.121 \pm 0.008) \text{ mol H}_2\text{O/mol CaSO}_4$

Surface area (SA) ($\sigma_{\text{H}_2\text{O}} = 0.125 \text{ nm}^2$) **VS.** SA using N_2 (BET theory, $\sigma_{\text{N}_2} = 0.162 \text{ nm}^2$):
 $S_{\text{H}_2\text{O}} = (66 \pm 5) \text{ m}^2/\text{g}$ $S_{\text{N}_2} = (14 \pm 1) \text{ m}^2/\text{g}$

$K_{eq}(T) = K_0 \exp\left(-\frac{E_{ads}}{RT}\right)$ $E_{ads} = -14.3 \text{ kJ/mol}$
 $K_0 = 1.13$

K_{eq} follows Van't Hoff law **Physisorption**

6 Conclusions and Perspectives

- Experimental measurements of $\varepsilon(T, P_{\text{H}_2\text{O}})$
- Interpretation of results by water adsorption models
- PT diagram (for highly pure synthetic material)

Next steps:

- Kinetic modeling of dehydration reactions (*Oral presentation OP2.23 Thursday 30th August, 3:30pm*)

References

- [1] Kuntze, R. A., Gypsum: Connecting science and technology, ASTM (2009).
- [2] Crangle, R. D., USGS Mineral Commodities Summaries, January 2017.
- [3] Schmidt H., et al., Acta Cryst. B 67 (2011) 467-475
- [4] Kelley, K., et al., US. Bur. Mines Tech. Paper 625 (1941).
- [5] Rouquerol, F., Rouquerol, J., Sing, K., Adsorption by Powder and Porous Solids: Principles, Methodology and Applications, Academic Press (1999)

Water vapor adsorption on $\beta\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$

Multilayer adsorption (BET theory) [5]

$$\frac{1}{n_a(P_0/P_{\text{H}_2\text{O}} - 1)} = \frac{C_{\text{BET}} - 1}{n_m C_{\text{BET}}} \left(\frac{P_{\text{H}_2\text{O}}}{P_0}\right) + \frac{1}{n_m C_{\text{BET}}}$$

T(°C)	S _{H₂O} (m ² /g)	C _{BET}
45	46	140
50	45	140
60	51	110
70	61	77

- SA by water vapor adsorption is larger than for N_2 adsorption ($S_{\text{N}_2} = (14 \pm 1) \text{ m}^2/\text{g}$)
- Hypothesis: Shifts between model and experimental points for low pressures explained by the **presence of micropores**

ESTAC12 European Symposium of Thermal Analysis and Calorimetry – 27-30 August 2018 – Brasov, Romania (PS1.021)