

Determine the ionic strength in solution based on TDS

$$I = (2.5 \times 10^{-5}) \times \text{TDS}(\text{mg/L})$$
$$I = 0.00448$$

Determine activity coefficient for HCO_3^-

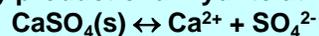
$$\log \gamma_i = -\frac{0.5(z_i)^2 I^{1/2}}{1 + I^{1/2}}$$
$$\log \gamma_{\text{HCO}_3^-} = -\frac{0.5(-1)^2 (0.00448)^{1/2}}{1 + (0.00448)^{1/2}} = -0.0313$$
$$\gamma_{\text{HCO}_3^-} = 0.93$$

Determine activity coefficient for Ca^{+2}

$$\log \gamma_{\text{Ca}^{+2}} = -\frac{0.5(+2)^2 (0.00448)^{1/2}}{1 + (0.00448)^{1/2}} = -0.125$$
$$\gamma_{\text{Ca}^{+2}} = 0.75$$

SOLUBILITY PRODUCT

Calculate the solubility product of anhydrite at 25°C



Look up:

http://inside.mines.edu/~epoeter/_GW19WaterChem3/GibbsFreeEnergyValues.xls

$$\Delta_f G^\circ_{\text{Ca}^{2+}} = -553.6 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ_{\text{SO}_4^{2-}} = -744.0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ_{\text{CaSO}_4(\text{s})} = -1321.8 \text{ kJ mol}^{-1}$$

$$R \text{ (gas constant)} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

so: $\Delta_r G^\circ = -553.6 + (-744.0) - (-1321.8) = 24.2 \text{ kJ mol}^{-1}$

$$\log K_{\text{SP}} = \frac{-\Delta_r G^\circ}{2.303RT} = \frac{-24,200 \text{ J mol}^{-1}}{2.303 (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})} = -4.24$$

$$K_{\text{SP}} = 10^{-4.24} = 5.75 \times 10^{-5}$$

assume Kelvin for thermodynamic expressions, unless noted otherwise

Suppose a groundwater analysis indicates
 5×10^{-2} mol/L Ca^{2+} and 7×10^{-3} mol/L SO_4^{2-} (assume TDS = 300 mg/L)
 Is this water saturated with respect to anhydrite?

Determine the ionic strength in solution based on TDS

$$I = (2.5 \times 10^{-5}) \times \text{TDS}(\text{mg/L})$$

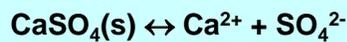
$$I = 0.0075$$

Determine activity coefficient for both Ca^{+2} and SO_4^{-2}

$$\log \gamma_{\text{Ca}^{+2}} = \log \gamma_{\text{SO}_4^{-2}} = -\frac{0.5(+2)^2(0.0075)^{1/2}}{1 + (0.0075)^{1/2}} = -0.16$$

$$\gamma_{\text{Ca}^{+2}} = \gamma_{\text{SO}_4^{-2}} = 0.69$$

Suppose a groundwater is analysis indicates
 5×10^{-2} mol/L Ca^{2+} and 7×10^{-3} mol/L SO_4^{2-} (assume TDS = 300 mg/L)
 Is this water saturated with respect to anhydrite?



$$\text{SI} = \log\left(\frac{\text{IAP}}{K_{\text{SP}}}\right) = \log\left(\frac{(\text{Ca}^{2+})_{\text{act}}(\text{SO}_4^{2-})_{\text{act}}}{K_{\text{SP}}}\right)$$

$$= \log\left(\frac{\gamma_{\text{Ca}}[\text{Ca}^{2+}]\gamma_{\text{SO}_4}[\text{SO}_4^{2-}]}{K_{\text{SP}}}\right)$$

$$\text{IAP} = 0.69(5 \times 10^{-2})0.69(7 \times 10^{-3}) = 1.68 \times 10^{-4} = 10^{-3.77} \text{ mol}^2 \text{ L}^{-2}$$

$$K_{\text{SP}} = 10^{-4.24} \text{ mol}^2 \text{ L}^{-2}$$

$$\text{SI} = \log\left(\frac{\text{IAP}}{K_{\text{SP}}}\right) = \log\left(\frac{10^{-3.77}}{10^{-4.24}}\right) = 0.47$$

In this case, $\text{SI} > 0$, i.e., $\text{IAP} > K_{\text{SP}}$, so the solution is supersaturated and anhydrite should precipitate

Consider the acid-base reaction



$$K = 10^{-6.35}$$

Which way should the reaction go if

$$\text{pH} = 7 \quad a_{\text{H}_2\text{CO}_3} = 10^{-4} \quad a_{\text{HCO}_3^-} = 10^{-3}?$$

First, calculate the *IAP*

Recall $\text{pH} = -\log a_{\text{H}^+}$ so $a_{\text{H}^+} = 10^{-7}$

$$IAP = \frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{H}_2\text{CO}_3}} = \frac{(10^{-3})(10^{-7})}{(10^{-4})} = 10^{-6}$$

$$IAP > K \quad (10^{-6} > 10^{-6.35})$$

The reaction will shift to the left until $IAP = K$

so more H_2CO_3 will be formed

ALKALINITY

A 100 mL sample with a pH of 8 is titrated to the methyl-orange-end-point (which goes from yellow at pH 4.4 to red at pH 3.1) with 2 mL of 0.5 N H_2SO_4

What is the total alkalinity in mg L^{-1} as CaCO_3 and what is the concentration of HCO_3^- in mg L^{-1} ?

The total alkalinity in mg L^{-1} as CaCO_3 is given by:

$$\begin{aligned} \text{Alk}_T &= \frac{2 \text{ mL} \times 0.5 \text{ eq/L} \times 50 \text{ g/eq} \times (1000 \text{ mg/g})}{100 \text{ mL}} \\ &= 500 \text{ mg/L as CaCO}_3 \end{aligned}$$

The concentration of HCO_3^- is given as:

$$\begin{aligned} \text{HCO}_3^- \text{ (mg/L)} &= \frac{2 \text{ mL} \times 0.5 \text{ eq/L} \times 61 \text{ g/eq} \times (1000 \text{ mg/g})}{100 \text{ mL}} \\ &= 610 \text{ mg/L} \end{aligned}$$

**CORRECTION on Check Correctness of Analysis:
Calculate TDS**

Solute	Measured Conc (mg/L)
Ca ²⁺	92.0
Mg ²⁺	34.0
Na ⁺	8.2
K ⁺	1.4
Fe(III)	0.1
HCO ₃ ⁻	325.0
SO ₄ ²⁻	84.0
Cl ⁻	9.6
NO ₃ ⁻	13.0

Calculated TDS =
 $0.6 \text{Alkalinity} + \text{Na} + \text{K} + \text{Ca} + \text{Mg} + \text{Cl} + \text{SO}_4 + \text{SiO}_2 + \text{NO}_3\text{-N} + \text{F}$

0.6Alkalinity because CO₃ 60% of CaCO₃ by weight

Reported Alkalinity OR
 $[\text{HCO}_3^-] * \frac{50\text{g/eq CaCO}_3}{61\text{g/eq HCO}_3^-} = 266.4\text{mg/L}$

What is the Calculated TDS?

Measured TDS > Calculated TDS because some species not included in the calculation (e.g. Fe⁺³)

acceptable range: $1.0 < \frac{\text{measured TDS}}{\text{calculated TDS}} < 1.2$

If the ratio is out of the range, reanalyze

**Measured value in this case 603.5 mg/L
What is the ratio? Is it acceptable?**