Determine the ionic strength in solution based on TDS

$$I = (2.5\times10^{-5})\times \text{TDS(mg/L)}$$

I = 0.00448

Determine activity coefficient for HCO_3^-

$$\log\gamma_i = -\frac{0.5(z_i)^2 I^{1/2}}{1+I^{1/2}}$$

$$\log\gamma_{HCO_3^-} = -\frac{0.5(-1)^2(0.00448)^{1/2}}{1+(0.00448)^{1/2}} = -0.0313$$

$$\gamma_{HCO_3^-} = 0.93$$

Determine activity coefficient for Ca^{+2}

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

$$\gamma_{Ca^{+2}} = 0.75$$

SOLUBILITY PRODUCT

Calculate the solubility product of anhydrite at 25°C

$CaSO_4(s) \leftrightarrow Ca^{2+} + SO_4^{2-}$

Look up:

http://inside.mines.edu/~epoeter/_GW\19WaterChem3/GibbsFreeEnergyValues.xls

$\Delta_f G°_{Ca2+}$ = -553.6 kJ mol^{-1}

$\Delta_f G°_{SO_4^{2-}}$ = -744.0 kJ mol^{-1}

$\Delta_f G°_{CaSO_4(s)}$ = -1321.8 kJ mol^{-1}

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

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

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

$$K_{SP} = 10^{-4.24} = 5.75x10^{-5}$$

assume Kelvin for thermodynamic expressions, unless noted otherwise

Suppose a groundwater analysis indicates
$5x10^{-2}$ mol/L Ca^{2+} and $7x10^{-3}$ 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

$$I = (2.5\times10^{-5})\times \text{TDS(mg/L)}$$

I = 0.0075

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

$$\log\gamma_{Ca^{+2}} = \log\gamma_{SO_4^{-2}} = -\frac{0.5(+2)^2(0.0075)^{1/2}}{1+(0.0075)^{1/2}} = -0.16$$

$$\gamma_{Ca^{+2}} = \gamma_{SO_4^{-2}} = 0.69$$

Suppose a groundwater is analysis indicates
$5x10^{-2}$ mol/L Ca^{2+} and $7x10^{-3}$ mol/L SO_4^{2-} (assume TDS = 300 mg/L)
Is this water saturated with respect to anhydrite?

$CaSO_4(s) \leftrightarrow Ca^{2+} + SO_4^{2-}$

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

$$= \log\left(\frac{\gamma_{Ca}\left[\text{Ca}^{2+}\right]\gamma_{SO_4}\left[\text{SO}_4^{2-}\right]}{\text{K}_{\text{SP}}}\right)$$

IAP **= 0.69(5x10^{-2})0.69(7x10^{-3}) = 1.68x10^{-4} = 10$^{-3.77}$ mol^2 L^{-2}**

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

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

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

Consider the acid-base reaction

$H_2CO_3 \leftrightarrow HCO_3^- + H^+$

$K = 10^{-6.35}$

Which way should the reaction go if

pH = 7 $a_{H_2CO_3} = 10^{-4}$ $a_{HCO_3^-} = 10^{-3}$**?**

First, calculate the *IAP*

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

$$IAP = \frac{a_{HCO_3^-} a_{H^+}}{a_{H_2CO_3}} = \frac{(10^{-3})(10^{-7})}{(10^{-4})} = 10^{-6}$$

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

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:

$$Alk_T = \frac{2\,mL \times 0.5\,eq/L \times 50\,g/eq \times (1000\,mg/g)}{100\,mL}$$
$$= 500\,mg/L\ as\ CaCO_3$$

The concentration of HCO_3^- is given as:

$$HCO_3^-\ (mg/L) = \frac{2\,mL \times 0.5\,eq/L \times 61\,g/eq \times (1000\,mg/g)}{100\,mL}$$
$$= 610\,mg/L$$

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 =
0.6Alkalinity + Na + K + Ca + Mg +
Cl + SO_4 + SiO_2 + NO_3-N + F

0.6Alkalinity because CO_3 60% of $CaCO_3$ by weight

Reported Alkalinity OR

$[HCO_3^-] * \frac{50 g/eq\ CaCO_3}{61 g/eq\ HCO_3^-} = 266.4 mg/L$

What is the Calculated TDS?

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

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

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?