Solubility and saturation

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Often we need to know if a water sample, with some measured activity values, is undersaturated or oversaturated with respect to a particular mineral. Will the mineral dissolve on contact with the solution? Or is the water oversaturated? If so, the mineral is liable to precipitate, which could reduce porosity in an aquifer or clog up pipes. This can be important in groundwater chemistry, dispersal of contaminants, geothermal power extraction, and so on.

Consider our generic reaction:

$$aA + bB \rightleftharpoons cC + dD \tag{1}$$

With arbitrary activities of the products and reactants, we can write:

$$\Delta G = \Delta G^0 + RT\ ln(\frac{a_C^c.a_D^d}{a_A^a.a_B^b}) \tag{2}$$

The term $(\frac{a_C^c.a_D^d}{a_A^a.a_B^b})$ is called the *Ion Activity Product* or *IAP*.

For a dissolution reaction such as $CaSO_4.2H_2O \rightleftharpoons Ca^{2+}+SO_4^{2-}+2\ H_2O$, the *IAP* is $(a_{Ca^{2+}}\ .\ a_{SO_4^{2-}})$.

In contrast, at equilibrium, $\Delta G = 0$, and

$$\Delta G^0 = -RT\ ln(K_{eq}) \tag{3}$$

For a dissolution reaction, this would describe the case of a saturated solution, where activities of the dissolved ions are fixed by an excess of the solid phase.

Now we can go back to the general case of equation (2) and re-write it as:

$$\Delta G = -RT\ ln(K_{eq}) + RT\ ln(IAP) = RT\ ln(\frac{IAP}{K_{eq}}) \tag{4}$$

Then depending on the activities in solution, we can distinguish three possibilities:

- If $IAP = K_{eq}$, $\Delta G = 0$; the solution is at equilibrium.
- If $IAP < K_{eq}$, $\Delta G < 0$; reaction goes to the right and the mineral dissolves.
- If $IAP > K_{eq}$, $\Delta G > 0$; reaction goes to the left; the solution is supersaturated and the mineral should precipitate.

For example, suppose a groundwater sample contains 160 ppm Ca^{2+} and 550 ppm SO_4^{2-}. Assuming ideality, the activities (in mol/kg) are $a_{Ca^{2+}} = 4.0 \times 10^{-3}$ and $a_{SO_4^{2-}} = 5.7 \times 10^{-3}$. Hence the *IAP* $= 2.3 \times 10^{-5} = 10^{-4.6} = K_{eq}$. The solution is saturated with respect to gypsum.