1. Consider the formation/dissolution of aragonite from calcium and carbonate:

   $CaCO_3$ (aragonite) $\leftrightarrow Ca^{2+} + CO_3^{2-}$

a. Determine the concentration of carbonate, $[CO_3^{2-}]$ in equilibrium with aragonite in surface seawater at 25°C, salinity=35, using standard free energy of formation data, ΔG_f^o.

b. If the carbonate ion concentration in the North Pacific is 150 µmol kg^{-1}, what is the value of ΔG_r? What is Q/K?

c. Is it thermodynamically possible for the above equation to proceed to the right? Explain why based on Fig 3.7 in E&H (2008), reproduced below.

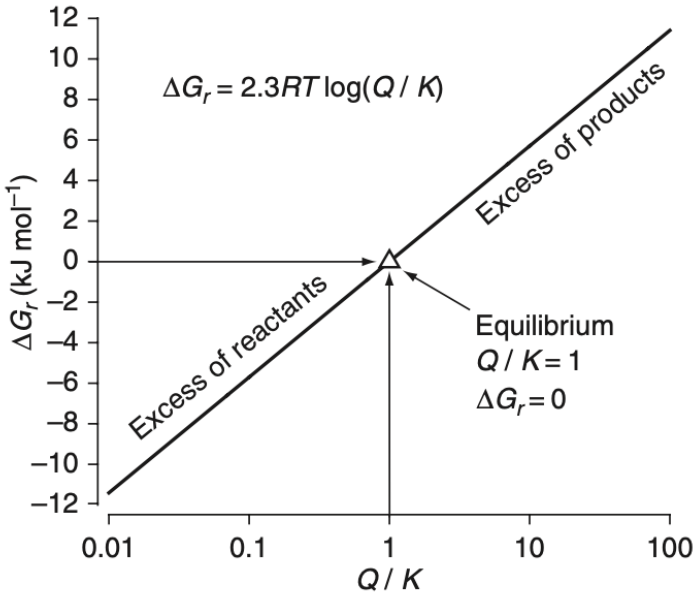


Figure 3.7. A schematic illustration of the change in free energy of a reaction, ΔG_r, as a function of the reaction progress. The *x*-axis is the quotient of the ion product, *Q*, and the equilibrium constant, *K*.

2. A marine organism, *Acantharia*, makes its test out of celestite (SrSO4), a mineral similar in some respects to calcite.

a. What would be the concentration of Sr^{2+} in equilibrium with solid celestite at 25°C in distilled water? Assume that the ionic strength is low enough that the activity coefficients are 1 ($\gamma_{Sr} = \gamma_{SO4} = 1$) and that no ion pairs form at this low ionic strength.

b. What would be the concentration of Sr^{2+} in equilibrium with solid celestite at 25°C in seawater? Assume that the total activity coefficient for Sr^{2+} is the same as that of Ca^{2+} because they have similar chemical characteristics.

c. In nature, thermodynamic equilibrium is not always a good assumption. Would you predict that celestite would spontaneously precipitate in seawater? Do you think the *Acantharia* tests will be preserved or dissolve in the sediments after the organism dies?

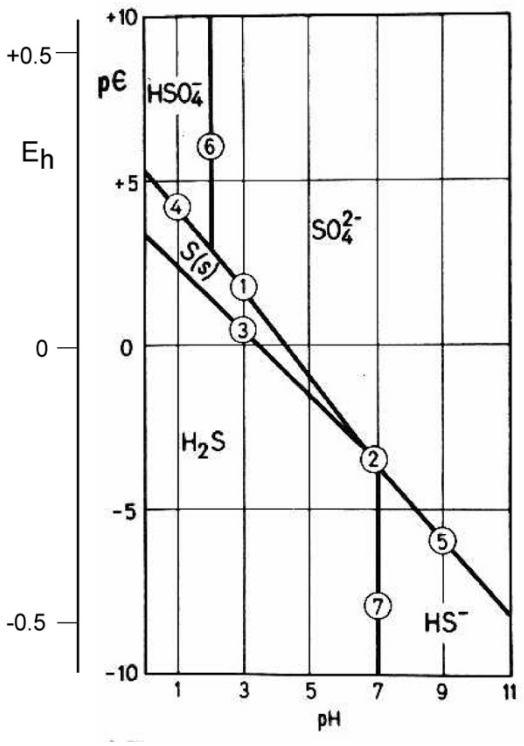
3. This question refers to the sulfur pE-pH diagram below:

a. It is commonly assumed that, in anoxic seawater containing H_2S, the pE is controlled by the sulfide-sulfate redox couple (reaction). Write the equation for this couple in terms of SO_4^{2-}, H^+, HS^-, H_2O, and electrons.

b. Calculate the E^o for this reaction from the Gibbs free energies of formation of products and reactants. (Hint: use Table 3-1 in the Snoeyink & Jenkins (1980) handout on Laulima.)

c. A seawater sample at 25°C obtained from 144 m depth in the Black Sea has pH = 7.79, $\{HS^-\} = 8.2 \times 10^{-6}$, and $\{SO_4^{2-}\} = 4.5 \times 10^{-3}$. What is the Eh of this water?

d. What is the pE of this water?



Are your results consistent with the pE-pH diagram for the sulfur system? What is the basis for your answer?