The snow line

There are large pressures (up to 1 kbar) in the deep ocean. One scenario is that calcium carbonate forms at the surface and sinks to depths where it redissolves because of effect of pressure on the dissolution reaction:

$$CaCO_3(s) \longrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$$

Given that the density of $CaCO_3$(s) is 2.3 gm/cm^3 and the density of the solvated ions is 7.2 gm/cm^3 calculate the change in the solubility of $CaCO_3$ in the ocean at a depth where the pressure is 500 atm. This depth is known as the snow line since solid $CaCO_3$ particle “melt” at this depth just like snow flakes melt before they reach the ground if the air is warm enough.

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Solution: First we should calculate the solubility of $CaCO_3$ as well as its free energy. Given that $K_{sp} = 4.92 \times 10^{-9}$, we can obtain the solubility as follows

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]$$

$$K_{sp} = x^2$$

$$x = \sqrt{K_{sp}} = \sqrt{4.92\ x\ 10^{-9}}$$

Therefore, $[Ca^{2+}] = [CO_3^{2-}] = 7\ x\ 10^{-5}\ M$

And the free energy is

$$\Delta G^o = -RT \ln K_{sp}$$

$$\Delta G^o = -\left(8.31 \frac{J}{molK}\right)(298\ K) \ln(4.92\ x\ 10^{-9})$$

$$\Delta G^o = 47{,}690\ J/mol$$

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The difference in the densities of the two forms of $CaCO_3$ will cause a shift in K_{sp} according to:

$$\Delta G^o(500\ atm) = \Delta G^o(1\ atm) + \Delta V_m \Delta P$$

$$\Delta V_m = \frac{M_m}{\rho_{aq}} - \frac{M_m}{\rho_s}$$

$$\Delta V_m = \frac{0.1\ kg/mol}{7200\ kg/m^3} - \frac{0.1\ kg/mol}{2300\ kg/m^3}$$

$$\Delta V_m = -29.5\ x\ 10^{-6}\ m^3/mol$$

$$\Delta G^o(500\ atm) = 47{,}690 + (-29.5\ x\ 10^{-6})(5\ x 10^7)$$

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At 500 atm of pressure the solubility free energy is

$$\Delta G^{o}(500\ atm) = 46{,}215\ J/mol$$

and the value of K_{sp} is:

$$K_{sp}(500\ atm) = exp\left\{-\frac{\Delta G^{o}}{RT}\right\}$$

$$K_{sp}(500\ atm) = exp\left\{-\frac{46215}{8.31(298)}\right\}$$

$$K_{sp}(500\ atm) = 8.85\ x\ 10^{-9}$$

The solubility increases to 8.8 x 10^{-5} M. The change in solubility is +1.8 x 10^{-5} M.