

Chapter 8 Problems

1. Consider crystalline A to be in equilibrium with water saturated with A at a pressure of 1234.0 bars and a temperature of 567.0°C. A is very slightly soluble (0.001 moles/Kg H₂O) so that $P_{\text{H}_2\text{O}} = P_{\text{total}}$. The vapor pressure of crystalline A varies with temperature according to the relation

$$\log P(\text{bars}) = (-19,130/T(\text{K})) + 7.65$$

Its molar volume is 22.7 cm³ mol⁻¹ and is essentially constant in the pressure range under consideration. The fugacity coefficient for water at this P and T is 0.541.

- (a) What is the activity of crystalline A, using the following standard states:
- pure A(s) at T , P .
 - pure A(s) at T and a pressure of 1 bar.
 - pure A(s) at T and under its own vapor pressure.
 - pure ideal gaseous A at T and one bar.
- (b) What is the activity of water, using the following standard states:
- pure water at T and P .
 - pure water at T and a pressure of 500 bars (fugacity coefficient is 0.747).
 - ideal gaseous water at T and a pressure of 123.456 bars.
 - Hypothetical ice at T and a pressure of 1 bar. (Suggest how this could be done, without performing any calculations).
- (c) What is the activity of A(aq) (with $\gamma_{\text{A}}(\text{aq})$ assumed to be 1.0) using the following standard states:
- an ideal one molal solution of A at T and P .
 - a 17.2 molal solution of A having an activity coefficient of 0.123, at T and P .
- (d)
- Under what conditions is $\mu_{\text{A}(s)} = \mu_{\text{A}(\text{aq})}$?
 - Under what conditions is $\mu_{\text{A}(s)}^\circ = \mu_{\text{A}(\text{aq})}^\circ$?
- (e) Calculate the difference in chemical potential between dissolved A at T and P and dissolved A in standard state (1(c)i).
- (f) Experiments show that at 9.7 Kb, 1080°C, the system SiO₂-H₂O shows a second critical end point at which quartz and a supercritical fluid of composition 75 wt. % SiO₂, 25 wt. % H₂O coexist at equilibrium. What is the activity of SiO₂ in this fluid, referred to a standard state of quartz at 1080°C and one bar?
2. How would you modify equation (8.17) if you wished to have a constant T standard state?

3. According to Wellman (1969)¹, the fugacity of NaCl in equilibrium with nepheline (NaAlSiO_4) and sodalite ($3\text{NaAlSiO}_4 \cdot \text{NaCl}$) at 600°C , 1 bar, is $10^{-10.566}$ bars, and the fugacity of pure halite at the same T, P is $10^{-5.780}$ bars. Thus the activity of NaCl at nepheline–sodalite equilibrium at these conditions is $10^{-4.786}$ bars, using a pure halite at T, P standard state. If $\Delta_f G_{\text{NaCl}(aq)}^\circ$ is $-393133 \text{ J mol}^{-1}$ (ideal 1 m standard state), and $\Delta_f G_{\text{NaCl, Halite}}^\circ$ is $-384138 \text{ J mol}^{-1}$, what is the activity of NaCl at nepheline–sodalite equilibrium using the ideal one molal standard state?

¹Geochim. Cosmochim. Acta, v. 33, pp. 1302–1304.