

ES4103: Geochemistry
End Semester (Autumn) Examination, 2018
Department of Earth Sciences, IISER-Kolkata

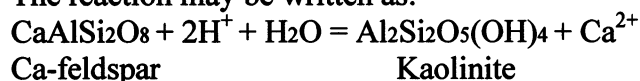
Total marks: 50

Time: 3 hours

Questions are printed on both sides of the paper

1. The breakdown of the silicate mineral Ca-feldspar (anorthite) to form kaolinite clay is an important weathering reaction, particularly in humid climate soils.

The reaction may be written as:



a). Calculate the equilibrium constant for this reaction at 25°C given the following free energies of formation and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. [3]

Ca-feldspar	-4001.4 kJ/mol
H ⁺	0
H ₂ O (l)	-237.14 kJ/mol
kaolinite	-3799.4 kJ/mol
Ca ²⁺	-553.54 kJ/mol

b) Assuming that soil moisture contains concentrations of $[\text{Ca}^{2+}] = 2 \times 10^{-4} \text{ mol/l}$, and behaves as an ideal solution ($a = m$), at what pH would anorthite be in equilibrium with the kaolinite and, therefore not react further (weather)? [4]

2. The REE patterns are typically used as tracers of sediment provenance. Explain why REEs of parent rocks generally retain their normalized abundance patterns during weathering and transport. [5]

3. Pure water is brought into equilibrium with barite (BaSO_4 , solubility product $K_{s1} = 10^{-10}$), anhydrite (CaSO_4 , solubility product $K_{s2} = 10^{-4.5}$), anglesite (PbSO_4 , solubility product $K_{s3} = 10^{-7.8}$) and celestite (SrSO_4 , $K_{s4} = 10^{-6.5}$). What is the composition of the solution? Ignore activity coefficients. [6]

4. It is often observed that experimentally measured rates of dissolution appear to decrease with time after the start of the experiment. Explain why. [4]

5. Explain why the sorption affinity of Cs^+ is greater than that of Li^+ . [4]

6. Derive the following relationship that describes the variation of calcium concentration in water, which is in equilibrium with calcite, as a function of partial pressure of CO_2 . Clearly state your assumptions. [7]

$$[\text{Ca}^{2+}]^3 = P_{\text{CO}_2} \frac{K_1 K_{\text{CO}_2} K_{\text{cal}}}{4K_2 \gamma_{\text{Ca}} \gamma_{\text{HCO}_3}^2}$$

7. Using chemical reactions and equilibrium expressions show that solubility of silica in waters is a function of pH. State your assumptions. [6]

8. Determine the concentrations of carbonate, bicarbonate and carbonic acid in a water supply if the total amount of inorganic carbon dissolved in it is $85 \mu\text{g/mL}$ and its pH is 7.9. What is the partial pressure of CO_2 which would be in equilibrium with this water? The water also contains $6 \mu\text{g/mL}$ of Ca^{2+} . Is the water saturated with respect to calcite? (Given $K_1 = 10^{-6.35}$, $K_2 = 10^{-10.3}$, $K_{\text{CO}_2} = 10^{-1.5}$, $K_{\text{cal}} = 10^{-8.35}$). Assume $a = m$. [6+2+3]

TS