

(22.6) What will be the ratio of [Pu(III)]/Pu[(IV)] in a groundwater containing small concentrations of iron in the relation Fe(II) 99% and Fe(III) 1%? E° for Fe(II)/Fe(III) = 0.743 V. Neglect hydrolysis.

Assume that data for Pu(III)/Pu(IV) from Fig. 22.5 at pH 8 are valid and that water temperature is 10°C.

$$E0_{Fe} := 0.743 \cdot \text{volt}$$

$$E0_{Pu} := -0.39 \cdot \text{volt}$$

$$T := (273.15 + 10) \cdot K$$

$$R := 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

$$n := 1 \quad \text{for both Fe and Pu in this example.}$$

$$N_A := 6.022137 \cdot 10^{23} \cdot \text{mole}^{-1}$$

$$q_e := 1.6021773 \cdot 10^{-19} \cdot \text{coul}$$

$$F := q_e \cdot N_A$$

$$x_{Fe2} := 99 \cdot \%$$

$$x_{Fe3} := 1 \cdot \%$$

$$E_{Fe} := E0_{Fe} + \frac{R \cdot T}{n \cdot F} \cdot \ln\left(\frac{x_{Fe3}}{x_{Fe2}}\right)$$

$$E_{Pu} = E0_{Pu} + \frac{R \cdot T}{n \cdot F} \cdot \ln(r_{Pu})$$

$$E_{Fe} = 0.631 \cdot \text{volt}$$

$$E_{Pu} := E_{Fe}$$

$$r_{Pu} := \exp\left[\frac{(E_{Pu} \cdot n \cdot F - E0_{Pu} \cdot n \cdot F)}{(R \cdot T)}\right]$$

$$r_{Pu} = 1.481 \cdot 10^{18} \quad \text{and} \quad \frac{1}{r_{Pu}} = 6.753 \cdot 10^{-19}$$

Thus, the ratio Pu(IV)/Pu(III) will be $1.481 \cdot 10^{18}$, and the inverse is $6.75 \cdot 10^{-19}$ or $10^{-18.2}$.