

## Thermodynamics of electrodes and Galvanic cells

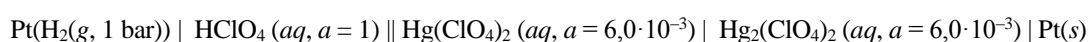
P57. Calculate the mean activity coefficient of a  $0.50 \text{ mol dm}^{-3}$  aqueous lead(II) nitrate solution from the fact that the electrode potential of a lead electrode immersed into this solution is  $-0.158 \text{ V}$  at  $25.0 \text{ }^\circ\text{C}$  and  $E^\ominus(\text{Pb}^{2+}/\text{Pb}) = -0.130 \text{ V}$ .  $[\gamma_{\pm} = 0.226]$

P58. The cell potential of the following galvanic cell is  $0.2848 \text{ V}$  at  $20.0 \text{ }^\circ\text{C}$ :



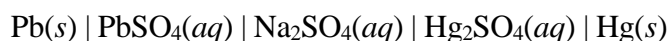
The mean activity coefficient in the right-hand side solution is  $\gamma_{\pm} = 0.896$ . Calculate the net stability constant of the following reaction:  $\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$ .  $[K = 1.37 \times 10^7]$

P59. The cell potential of the following galvanic cell is  $0.8356 \text{ V}$  at  $25.0 \text{ }^\circ\text{C}$ :



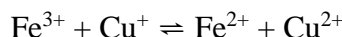
Calculate the standard electrode potential of the  $\text{Hg}^{2+}/\text{Hg}_2^{2+}$  half reaction.  $[E^\ominus = 0.901 \text{ V}]$

P60. The cell potential of the following galvanic cell is  $0.9647 \text{ V}$  at  $25.0 \text{ }^\circ\text{C}$ :



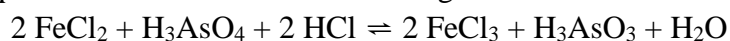
The temperature coefficient of the cell potential is  $1.74 \cdot 10^{-4} \text{ V K}^{-1}$ . Give the chemical reaction responsible for the production of electricity, and calculate its reaction heat and reaction Gibbs free energy.  $[\text{Pb}(s) + \text{Hg}_2\text{SO}_4(aq) \rightarrow \text{PbSO}_4(aq) + 2\text{Hg}(s); \Delta_r G = -186.2 \text{ kJ/mol}; \Delta_r H = -176.1 \text{ kJ/mol}]$

P61. Calculate the equilibrium constant of the following reaction at  $25.0 \text{ }^\circ\text{C}$ :



$E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V}$  and  $E^\ominus(\text{Cu}^{2+}/\text{Cu}^+) = 0.17 \text{ V}$ .  $[K = 1.39 \times 10^{10}]$

P62. Calculate the equilibrium constant of the following reaction at  $20.0 \text{ }^\circ\text{C}$ :



$E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.772 \text{ V}$  and  $E^\ominus(\text{AsO}_4^{3-}/\text{AsO}_3^{3-}) = 0.630 \text{ V}$  (the electrode half-reaction in the second case is as follows:  $\text{AsO}_4^{3-} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{AsO}_3^{3-} + \text{H}_2\text{O}$ ).  $[K = 1.31 \times 10^{-5}]$

P63. Using the fact that the Gibbs free energy is a state function, calculate  $E^\ominus(\text{Cu}^+/\text{Cu})$  from the following standard electrode potential values:  $E^\ominus(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$  and  $E^\ominus(\text{Cu}^{2+}/\text{Cu}^+) = 0.16 \text{ V}$ .  $[E^\ominus(\text{Cu}^+/\text{Cu}) = 0.52 \text{ V}]$