

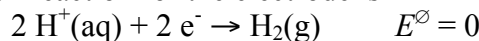
Solutions 10

1. The Nernst equation applies to half-cells as well as cells

Initially, $E_i = E^\ominus - (RT/\nu F) \ln Q_i = E^\ominus - (25.7 \text{ mV} / \nu) \ln Q_i$

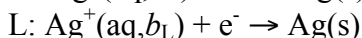
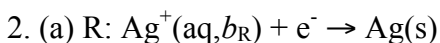
Finally, $E_f = E^\ominus - (25.7 \text{ mV} / \nu) \ln Q_f$

The half reaction for the electrode is

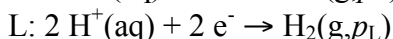
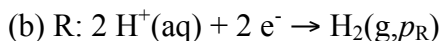


$$Q = p_{\text{H}_2}/[\text{H}^+]^2 = 1.45/[\text{H}^+]^2$$

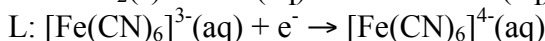
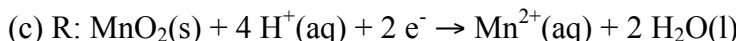
$$\Delta E = E_f - E_i = (-25.7 \text{ mV} / 2) \ln(Q_f/Q_i) = (-25.7 \text{ mV}) \ln([\text{H}^+]_i/[\text{H}^+]_f) = (-25.7 \text{ mV}) \ln(5.0/25.0) = 41.36 \text{ mV}$$



R - L: $\text{Ag}^+(\text{aq}, b_R) \rightarrow \text{Ag}^+(\text{aq}, b_L) \quad E = E^\ominus - (RT/F) \ln(b_L/b_R) = -(RT/F) \ln(b_L/b_R)$

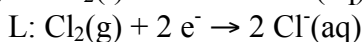
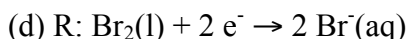


R - L: $\text{H}_2(\text{g}, p_L) \rightarrow \text{H}_2(\text{g}, p_R) \quad E = E^\ominus - (RT/2F) \ln(p_R/p_L) = -(RT/2F) \ln(p_R/p_L)$

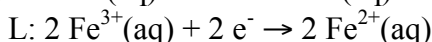
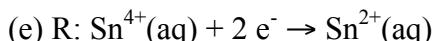


R - L: $\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 [\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 2 [\text{Fe}(\text{CN})_6]^{3-}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$
 $E = E^\ominus - (RT/2F) \ln \{ ([\text{Mn}^{2+}][\text{Fe}(\text{CN})_6]^{3-})^2 / ([\text{Fe}(\text{CN})_6]^{4-})^2 [\text{H}^+]^4 \}$

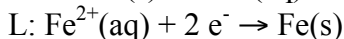
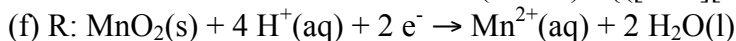
(Here and below in Nernst equations involving ions in aqueous solution we replace activities with molar concentrations).



R - L: $\text{Br}_2(\text{l}) + 2 \text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2 \text{Br}^-(\text{aq}) \quad E = E^\ominus - (RT/2F) \ln(p_{\text{Cl}_2} [\text{Br}^-]^2 / [\text{Cl}^-]^2)$

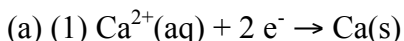


R - L: $\text{Sn}^{4+}(\text{aq}) + 2 \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2 \text{Fe}^{3+}(\text{aq})$
 $E = E^\ominus - (RT/2F) \ln \{ ([\text{Sn}^{2+}][\text{Fe}^{3+}]^2) / ([\text{Sn}^{4+}][\text{Fe}^{2+}]^2) \}$

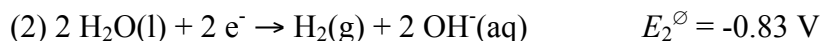


R - L: $\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$
 $E = E^\ominus - (RT/2F) \ln \{ [\text{Mn}^{2+}][\text{Fe}^{2+}] / [\text{H}^+]^4 \}$

3. Each reaction has to be broken down into the two half-reactions from which it is formed. The standard potential for the cell is then calculated from the standard electrode potentials in Data Section. The standard Gibbs energies of the reaction are then calculated from $\Delta_r G^\ominus = -\nu F E^\ominus$.



$$E_1^\ominus = -2.87 \text{ V}$$

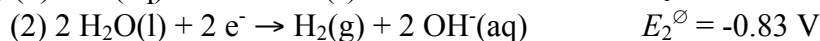


The overall reaction is then obtained from (2) – (1) and the $E^\ominus$ value for the cell reaction is obtained as

$$E^\ominus = E_2^\ominus - E_1^\ominus = -0.83 \text{ V} - (-2.87 \text{ V}) = +2.04 \text{ V}$$

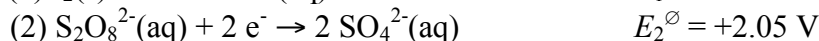
$$\Delta_r G^\ominus = -\nu F E^\ominus = -2 \times 96.485 \text{ kC mol}^{-1} \times 2.04 \text{ V} = -393.66 \text{ kJ mol}^{-1}$$

(b) Same as above.



$$E^\ominus = E_2^\ominus - E_1^\ominus = -0.83 \text{ V} - (-0.44 \text{ V}) = -0.39 \text{ V}$$

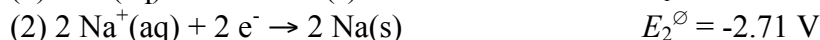
$$\Delta_r G^\ominus = -\nu F E^\ominus = -2 \times 96.485 \text{ kC mol}^{-1} \times (-0.39 \text{ V}) = +75.26 \text{ kJ mol}^{-1}$$



$$E^\ominus = E_2^\ominus - E_1^\ominus = 2.05 \text{ V} - 0.54 \text{ V} = +1.51 \text{ V}$$

$$\Delta_r G^\ominus = -\nu F E^\ominus = -2 \times 96.485 \text{ kC mol}^{-1} \times (1.51 \text{ V}) = -291.38 \text{ kJ mol}^{-1}$$

(e) Same as above.

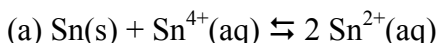


$$E^\ominus = E_2^\ominus - E_1^\ominus = -2.71 \text{ V} - (-0.13 \text{ V}) = -2.58 \text{ V}$$

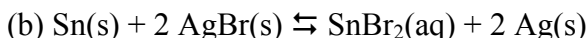
$$\Delta_r G^\ominus = -\nu F E^\ominus = -2 \times 96.485 \text{ kC mol}^{-1} \times (-2.58 \text{ V}) = +497.86 \text{ kJ mol}^{-1}$$

4. In each case we use $\ln K = \nu F E^\ominus / RT$. Also, note that at 25°C (298 K),

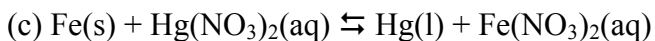
$$RT/F = (8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) / 96485 \text{ C mol}^{-1} = 25.69 \times 10^{-3} \text{ V}$$



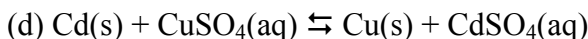
$$E^\ominus = +0.29 \text{ V} \quad \ln K = 2 \times 0.29 \text{ V} / 25.69 \times 10^{-3} \text{ V} = +22.6 \quad K = 6.5 \times 10^9$$

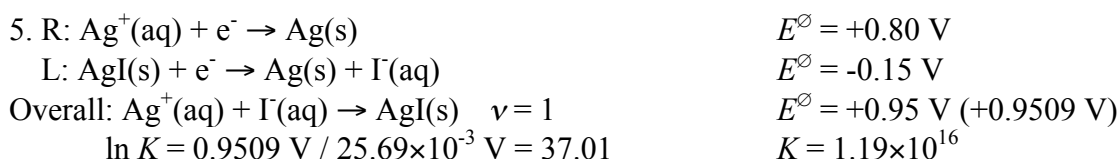
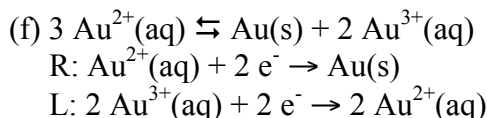
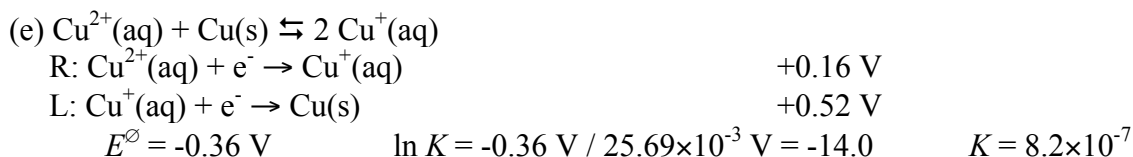
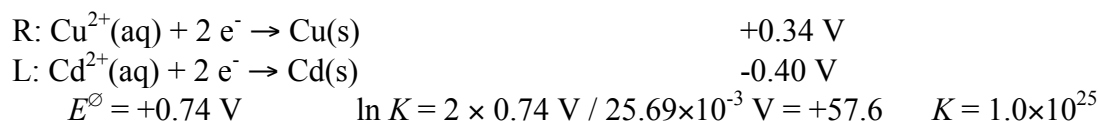


$$E^\ominus = +0.21 \text{ V} \quad \ln K = 2 \times 0.21 \text{ V} / 25.69 \times 10^{-3} \text{ V} = +16.3 \quad K = 1.2 \times 10^7$$

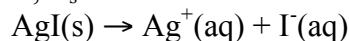


$$E^\ominus = +1.30 \text{ V} \quad \ln K = 2 \times 1.30 \text{ V} / 25.69 \times 10^{-3} \text{ V} = +101.2 \quad K = 9.0 \times 10^{43}$$





However, $K_s = 1/K$ because the solubility equilibrium is written as the reverse of the cell reaction:

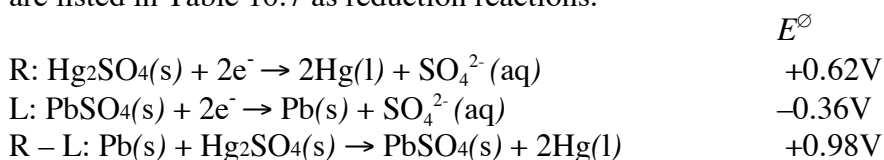


Therefore, $K_s = 8.45 \times 10^{-17}$.

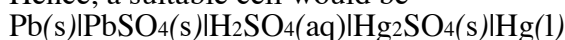
The solubility is obtained from $[\text{Ag}^{+}] = [\text{I}^{-}]$ and $S = [\text{Ag}^{+}]$.

$$K_s = [\text{Ag}^{+}]^2 = S^2 \quad S = (K_s)^{1/2} \text{ mol L}^{-1} = (8.45 \times 10^{-17})^{1/2} \text{ mol L}^{-1} = 9.19 \times 10^{-9} \text{ mol L}^{-1}$$

6. We require two half-cell reactions, which upon subtracting one (left) from the other (right), yields the given overall reaction. The half-reaction at the right electrode corresponds to reduction, that at the left electrode to oxidation, though all half-reactions are listed in Table 10.7 as reduction reactions.



Hence, a suitable cell would be



or, alternatively,



For the cell in which the only sources of electrolyte are the slightly soluble salts, PbSO_4 and Hg_2SO_4 ,

the cell would be



The potential of this cell is given by the Nernst equation

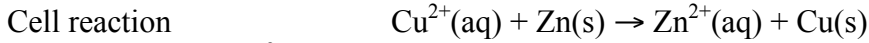
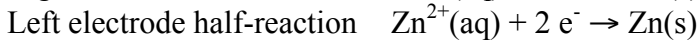
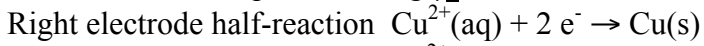
$$\begin{aligned}
 E &= E^{\circ} - (RT/\nu F) \ln Q \quad \nu = 2 \\
 Q &= \{a(\text{Pb}^{2+})a(\text{SO}_4^{2-})\} / \{a(\text{Hg}_2^{2+})a(\text{SO}_4^{2-})\} = K_s(\text{PbSO}_4)/K_s(\text{Hg}_2\text{SO}_4) \\
 E &= (0.98\text{V}) - (RT/2F) \ln \{K_s(\text{PbSO}_4)/K_s(\text{Hg}_2\text{SO}_4)\} = (0.98\text{V}) - (25.693 \times 10^{-3}\text{ V}) \times \\
 &\ln \{1.6 \times 10^{-8}/6.6 \times 10^{-7}\} = (0.98\text{V}) + (0.05\text{V}) = +1.03\text{V}
 \end{aligned}$$

$$\begin{array}{l}
 7. \text{ (a) CuSO}_4 \text{ compartment: } I = (1/2) \times \{(2)^2 \times 0.001 + (-2)^2 \times 0.001\} = 0.004 \\
 \text{ZnSO}_4 \text{ compartment: } I = (1/2) \times \{(2)^2 \times 0.003 + (-2)^2 \times 0.003\} = 0.012
 \end{array}$$

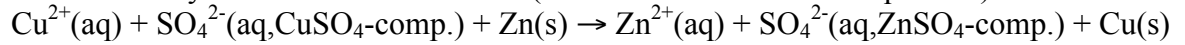
(b) CuSO_4 compartment: $\log \gamma_{\pm} = -A |z_+ z_-| I^{1/2} = -0.509 \times |2 \times (-2)| \times 0.004^{1/2} = -0.1288$

$$\gamma_{\pm} = 10^{-0.1288} = 0.7434$$

ZnSO_4 compartment: $\log \gamma_{\pm} = -0.509 \times |2 \times (-2)| \times 0.012^{1/2} = -0.2230$ $\gamma_{\pm} = 10^{-0.2230} = 0.5984$



However, since SO_4^{2-} ions are present in two different compartments with different concentrations, the more accurate way to write the cell reaction (and use it for the reaction quotient) is:



(c) The reaction quotient:

$$Q = \frac{a_{\text{Zn}^{2+}} a_{\text{SO}_4^{2-}} (\text{ZnSO}_4)}{a_{\text{Cu}^{2+}} a_{\text{SO}_4^{2-}} (\text{CuSO}_4)} = \left[\frac{b_{\text{Zn}^{2+}} / b^{\ominus}}{b_{\text{Cu}^{2+}} / b^{\ominus}} \frac{\gamma_{\pm} (\text{ZnSO}_4)}{\gamma_{\pm} (\text{CuSO}_4)} \right]^2 = \left[\frac{b_{\text{Zn}^{2+}} \gamma_{\pm} (\text{ZnSO}_4)}{b_{\text{Cu}^{2+}} \gamma_{\pm} (\text{CuSO}_4)} \right]^2$$

$$Q = [(0.003/0.001) \times (0.5984/0.7434)]^2 = 5.8309$$

(d) $E^{\ominus} = -\Delta_r G^{\ominus} / \nu F = (+212.7 \text{ kJ mol}^{-1}) / (2 \times 96.4853 \text{ kC mol}^{-1}) = 1.1022 \text{ V}$

(e) $E = E^{\ominus} - (RT / \nu F) \ln Q = (1.1022 \text{ V}) - (25.7 \times 10^{-3} \text{ V} / 2) \times \ln(5.8309) = 1.0796 \text{ V}$