

Solutions for Potentiometry Questions

Check for Understanding 11.1

1. a) H(+1) b) H(+1) c) S(+4) d) Cr(+6) e) Hg(+1)
 Cl(+1) Cl(+5) O(-2) O(-2) Cl(-1)
 O(-2) O(-2)

Check for Understanding 11.2

1. a) $\text{NO}_3^-(\text{aq}) + \text{Cu}(\text{s}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{Cu}^{2+}(\text{aq})$ (acidic soln)
 +5 0 +4 +2

Cu is being oxidized and N is being reduced.

oxidation: $(\text{Cu} \rightleftharpoons \text{Cu}^{2+} + 2\text{e}^-)$

reduction: $(\text{NO}_3^- + \text{e}^- + 2\text{H}^+ \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O}) \times 2$



- b) $\text{MnO}_4^-(\text{aq}) + \text{Br}^-(\text{aq}) \rightleftharpoons \text{MnO}_2(\text{s}) + \text{BrO}_3^-(\text{aq})$ (basic soln)
 +7 -1 +4 +5

Br is being oxidized and Mn is being reduced.

oxidation: $(\text{Br}^- + 6\text{OH}^- \rightleftharpoons \text{BrO}_3^- + 6\text{e}^- + 3\text{H}_2\text{O})$

reduction: $(\text{MnO}_4^- + 3\text{e}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-) \times 2$



Solutions for Potentiometry Questions

Check for Understanding 11.3

1. The posted table of values are standard potentials for reduction half reactions. The value for the standard oxidation half-cell potential $E^0_{\text{Ag}/\text{AgCl}}$ is numerically equal to $E^0_{\text{AgCl}/\text{Ag}}$ with a change of mathematical sign. Thus, $E^0_{\text{Ag}/\text{AgCl}} = -(0.222 \text{ V}) = -0.222 \text{ V}$.

Check for Understanding 11.4

- 1.

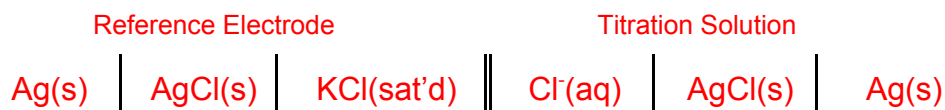
$$E_{\text{cell}} = E_{\text{ref}} + 0.771 \text{ V} - 0.05916 \log \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} = -0.197 \text{ V} + 0.771 \text{ V} - 0.05916 \log \frac{[\text{Fe}^{2+}]\gamma_{\text{Fe}^{2+}}}{[\text{Fe}^{3+}]\gamma_{\text{Fe}^{3+}}}$$

For $\mu = 0.10 \text{ M}$, $\gamma_{\text{Fe}^{2+}} = 0.405$ and $\gamma_{\text{Fe}^{3+}} = 0.18$. Thus,

$$E_{\text{cell}} = -0.197 \text{ V} + 0.771 \text{ V} - 0.05916 \log \frac{(0.035)(0.405)}{(0.035)(0.18)} = 0.553 \text{ V}$$

Check for Understanding 11.5

- 1.



2. The anode half reaction is:



The reduction reaction at the cathode is the reverse of the anode reaction.



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3. For the anode half cell, the Nernst equation is:

$$E_{ox} = E^0_{Ag/AgCl} - \frac{0.05916}{n} \log \frac{1}{a_{Cl^-}} = E_{ref}$$

The Nernst equation for the cathode is:

$$E_{red} = E^0_{AgCl/Ag} - \frac{0.05916}{n} \log a_{Cl^-} = 0.222 \text{ V} - \frac{0.05916}{1} \log a_{Cl^-}$$

The overall cell potential (E_{cell}) is the sum of the half-cell potentials. For this potentiometric chloride titration cell,

$$E_{cell} = E_{ox} + E_{red} = E_{ref} + 0.222 \text{ V} - 0.05916 \log a_{Cl^-}$$

Check for Understanding 11.6

1. In 0.100 M KCl, $[Cl^-] = 0.100 \text{ M}$ and $\mu = 0.10 \text{ M}$. Thus, $\gamma_{Cl^-} = 0.755$ and $a_{Cl^-} = [Cl^-]\gamma_{Cl^-} = (0.100)(0.755) = 0.0755$.
2. For a KCl-saturated Ag/AgCl reference electrode, $E_{ref} \sim -0.197 \text{ V}$, and $a_{Cl^-} = 0.0755$ in a 0.100 M KCl solution. Substituting these values gives $E_{cell} \sim 0.091 \text{ V}$.
3. At the equivalence point, $a_{Cl^-} \sim a_{Ag^+}$ and $K_{sp} = a_{Ag^+}a_{Cl^-} \sim a_{Cl^-}^2$. Thus, $a_{Cl^-} = (K_{sp})^{1/2} = (1.8 \times 10^{-10})^{1/2} = 1.3_4 \times 10^{-5}$.
 $E_{cell} = E_{ox} + E_{red} = -0.197 \text{ V} + 0.222 \text{ V} - 0.05916 \log (1.3_4 \times 10^{-5}) = 0.313 \text{ V}$

Check for Understanding 11.7

1. a) There is a net migration of H^+ and Cl^- to the solution of lower concentration. Since H^+ has a higher mobility than Cl^- , the solution of lower concentration is at the more positive potential.
b) There is a net migration of K^+ and Cl^- to the solution of lower concentration. Since Cl^- has a higher mobility than K^+ , the solution of higher concentration is at the more positive potential.

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2. Since the mobilities of K^+ and NO_3^- are closer than the mobilities of K^+ and Cl^- , there is less separation of charges as a result of ion migration from high concentration to low concentration. This reduces the junction potential of a KNO_3 solution interface compared with that for a KCl solution interface. Since K^+ has a higher mobility than NO_3^- but lower than that for Cl^- , the sign of the junction potential for KNO_3 will be the reverse of that for KCl .