Electrochemistry

Section 105 – Galvanic Cells

105-1 Write a balanced net equation for each for the following cell reactions.

(a) $Mg(s) + Ni^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Ni(s)$

(b) $2Ag^{+}(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

(c) $Mn(s) + Sn(NO_3)_2(aq) \longrightarrow Mn(NO_3)_2(aq) + Sn(s)$

(d) $CuNO_3(aq) + Au(NO_3)_3(aq) \longrightarrow Cu(NO_3)_2(aq) + Au(s)$

Solution

(a) $Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$;

(b) $2Ag^{+}(aq) + Ni(s) \longrightarrow Ni^{2+}(aq) + 2Ag(s)$

(c) $Mn(s) + Sn^{+2}(aq) \longrightarrow Mn^{+2}(aq) + Sn(s)$

(d) $3Cu^{+1}(aq) + Au^{+3}(aq) \longrightarrow 3Cu^{+2}(aq) + Au(s)$

105-2 Write balanced net ionic equations for each of the following cell reactions. Indicate which half reaction is occurring at the anode and at the cathode.

(a) $Al(s) + Zr^{4+}(aq) \longrightarrow Al^{3+}(aq) + Zr(s)$

(b) $Ag^{+}(aq) + NO(g) \longrightarrow Ag(s) + NO_3^{-}(aq)$ (acidic solution)

(c) $SiO_3^{2-}(aq) + Mg(s) \longrightarrow Si(s) + Mg(OH)_2(s)$ (basic solution)

(d) $ClO_3^{-}(aq) + MnO_2(s) \longrightarrow Cl^{-}(aq) + MnO_4^{-}(aq)$ (basic solution)

Solution

(a)

anode: $4 \times (Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-})$

cathode: $3 \times (Zr^{4+}(aq) + 4e^{-} \longrightarrow Zr(s))$

overall: $3Zr^{4+}(aq) + 4Al(s) \longrightarrow 3Zr(s) + 4Al^{3+}(aq)$

(b)

anode: $NO(g) + 2\,H_2O(l) \longrightarrow NO_3^{-}(aq) + 4H^{+}(aq) + 3e^{-}$

cathode: $3 \times \left(Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)\right)$

overall: $3Ag^{+}(aq) + NO(g) + 2H_2O(l) \longrightarrow 3Ag(s) + NO_3^{-}(aq) + 4H^{+}(aq)$

(c) In acidic solution:

anode: $2 \times (Mg(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(s) + 2H^+(aq) + 2e^-)$
cathode: $SiO_3^{2-}(aq) + 6H^+(aq) + 4e^- \longrightarrow Si(s) + 3H_2O(l)$

overall: $2Mg(s) + SiO_3^{2-}(aq) + H_2O(l) + 2H^+(aq) \longrightarrow 2Mg(OH)_2(s) + Si(s)$

Adding six hydroxide ions to each side and simplifying:

overall: $2Mg(s) + SiO_3^{2-}(aq) + 3H_2O(l) \longrightarrow 2Mg(OH)_2(s) + Si(s) + 2OH^-(aq)$

(d) In acidic solution:

anode: $2 \times (MnO_2(s) + 2H_2O(l) \longrightarrow MnO_4^-(aq) + 4H^+(aq) + 3e^-$
cathode: $ClO_3^-(aq) + 6H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3H_2O(l)$

overall: $2MnO_2(s) + ClO_3^-(aq) + H_2O(l) \longrightarrow 2MnO_4^-(aq) + 2H^+(aq) + Cl^-(aq)$

Adding two hydroxide ions to each side and simplifying:

overall: $2MnO_2(s) + ClO_3^-(aq) + 2OH^-(aq) \longrightarrow 2MnO_4^-(aq) + H_2O(l) + Cl^-(aq)$

105-3 Identify the oxidant and reductant in each reaction of the previous exercise.
Solution
Species oxidized = reducing agent: (a) Al(*s*); (b) NO(*g*); (c) Mg(*s*) and (d) $MnO_2(s)$.
Species reduced = oxidizing agent: (a) $Zr^{4+}(aq)$; (b) $Ag^+(aq)$; (c) SiO_3^{2-} (*aq*); and (d) ClO_3^- (*aq*).

105-4 Why is a salt bridge necessary in galvanic cells like the one in Figure 17.3?
Solution
Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.

105-5 An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.
Solution
Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would gain mass if metal ions in solution were reduced to metal atoms and deposited on the electrode. Reduction occurs at the cathode.

105-6 An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.
Solution
Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would lose mass if metal atoms in the electrode were to oxidize and go into solution. Oxidation occurs at the anode.

105-7 The masses of three electrodes (A, B, and C), each from three different galvanic cells, were measured before and after the cells were allowed to pass current for a while. The mass of electrode A increased, that of electrode B was unchanged, and that of electrode C decreased. Identify each electrode as active or inert, and note (if possible) whether it functioned as anode or cathode.

Solution
Active electrodes will gain or lose mass during reactions, while inert electrodes will not. Active electrodes: A and C; inert electrode: B. Reduction occurs at the cathode and often involves converting metal ions in solution into metal atoms on the electrode; the electrode mass tends to increase. Oxidation occurs at the anode and often involves converting metal atoms from the electrode into metal ion in solution; the mass of the electrode tends to decrease. Therefore, A was probably a cathode (involved in the reduction half-reaction) and C was probably an anode (involved in the oxidation half-reaction). The inert electrode, B, could have been *either* the anode or the cathode because it only provided a way for current to flow through the cell.

105-8 Write cell schematics for the following cell reactions, using platinum as an inert electrode as needed.

(a) $Mg(s) + Ni^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Ni(s)$

(b) $2Ag^{+}(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

(c) $Mn(s) + Sn(NO_3)_2(aq) \longrightarrow Mn(NO_3)_2(aq) + Sn(s)$

(d) $3CuNO_3(aq) + Au(NO_3)_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + Au(s)$

Solution
(a) $Mg(s) \mid Mg^{2+}(aq) \parallel Ni^{+}(aq) \mid Ni(s)$;
(b) Stoichiometric coefficients do not appear in cell notation $Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$;
(c) Spectator ions do not appear in cell notation $Mn(s) \mid Mn^{2+}(aq) \parallel Sn^{2+}(aq) \mid Sn(s)$
(d) Neither stoichiometric coefficients nor spectator ions appear in cell notation. Platinum electrode needed $Pt(s) \mid Cu^{+}(aq), Cu^{2+}(aq) \parallel Au^{3+}(aq) \mid Au(s)$

105-9 Assuming the schematics below represent galvanic cells as written, identify the half-cell reactions occurring in each.

(a) $Mg(s) \mid Mg^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

(b) $Ni(s) \mid Ni^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$

Solution
(a) species oxidized: Mg(*s*); species reduced: $Cu^{2+}(aq)$; oxidizing agent: $Cu^{2+}(aq)$; reducing agent: Mg(*s*);
(b) species oxidized: Ni(*s*); species reduced: $Ag^{+}(aq)$; oxidizing agent: $Ag^{+}(aq)$; reducing agent: Ni(*s*)

105-10 From the information provided, use cell notation to describe the following systems:
(a) In one half-cell, a solution of $Pt(NO_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $Cu(NO_3)_2$ solution with all solute concentrations 1 *M*.
(b) The cathode consists of a gold electrode in a 0.55 *M* $Au(NO_3)_3$ solution and the anode is a magnesium electrode in 0.75 *M* $Mg(NO_3)_2$ solution.

(c) One half-cell consists of a silver electrode in a 1 *M* $AgNO_3$ solution, and in the other half-cell, a copper electrode in 1 *M* $Cu(NO_3)_2$ is oxidized.

Solution

(a) Copper is oxidized at the anode and platinum reduced at the cathode, so

$$\text{anode: } Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$
$$\text{cathode: } Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$$

$$\text{overall: } Cu(s) + Pt^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Pt(s)$$
$$Cu(s) \,\big|\, Cu^{2+}(aq, 1\ M) \,\|\, Pt^{2+}(aq, 1\ M) \,\big|\, Pt(s)$$

(b) Oxidation occurs at the anode and reduction at the cathode

$$\text{anode: } 3 \times (Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-)$$
$$\text{cathode: } 2 \times (Au^{3+}(aq) + 3e^- \longrightarrow Au(s))$$

$$\text{overall: } 3Mg(s) + 2Au^{3+}(aq) \longrightarrow 2Au(s) + 3Mg^{2+}(s)$$
$$Mg(s) \,\big|\, Mg^{2+}(aq, 0.75\ M) \,\|\, Au^{3+}(aq, 0.75\ M) \,\big|\, Au(s)$$

(c) Oxidation occurs at the anode and reduction at the cathode:

$$\text{anode: } Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$
$$\text{cathode: } 2 \times (Ag^+(aq) + e^- \longrightarrow Ag(s))$$

$$\text{overall: } Cu(s) + 2\ Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$
$$Cu(s) \,\big|\, Cu^{2+}(aq, 1\ M) \,\|\, Ag^+(aq, 1\ M) \,\big|\, Ag(s)$$