Electrochemistry

Section 104 – Review of Redox Chemistry

104-1 Assign oxidation numbers to each element in the following substances:

(a) H_2O
(b) CO_2
(c) NH_4Cl
(d) Na_2SO_4
(e) H_3PO_4

Solution:

(a) The formal oxidation state for **O is -2; for H is +1**.

(b) Since O is -2, the C can be determined to be +4 as follows:

C + 2(-2) = 0
C -4 = 0
C = +4

Thus the oxidation states are as follows: O is -2, C is +4.

(c) Cl is -1; the ammonium ion is NH_4^{+1} to balance. H is +1 (unless bonded to a metal), so the oxidation state of N in the ammonium ion can be determined as follows:

N + 4(+1) = +1
N +4 = +1
N = +1 -4 = -3

Thus the oxidation states are as follows: Cl is -1, H is +1 and N is -3.

(d) Since sulfate (SO_4^{-2}) has an overall charge of -2, the two sodium ions must each be +1 (which is consistent with what would be expected for a Group 1 metal). Oxygen is normally -2, so the oxidation state of sulfur can be determined as follows:

S + 4(-2) = -2
S = -2 +8 = +6.

Thus the oxidation numbers are as follows: Na is +1, S is +6, O is -2.

(e) The oxidation state of H is +1; of O is -2. The phosphorus in the phosphate (PO_4^{-3}) can be determined as follows:

P + 4(-2) = -3
P -8 = -3
P = -3+8 = +5.

Thus the oxidation numbers are as follows: H is +1, O is -2, P is +5.

104-2 Assign oxidation numbers to each element in the following substances:

(a) NaOCl,
(b) ClF_3
(c) KH
(d) I_2
(e) Na

Solution:

(a) Na (a group 1 element) is +1; the hypochlorite ion OCl- has an overall charge of -1. Since O is -2, the oxidation state of Cl can be determined as follows:
Cl + (-2) = -1.
Cl = -1 +2 = +1.
Thus the oxidation states are Na +1; O -2; Cl +1.
(b) In ClF_3, F is -1 since it is the most electronegative element. Thus the Cl must be +3 since the overall charge is 0. Thus the oxidation states are as follows: F is -1; Cl is +3.
(c) Since potassium is a group I metal, K has an oxidation state of +1 while H is -1.
(d) In I_2 the oxidation state of iodine is 0.
(e) In Na the oxidation state of Na is 0 (since the overall charge is 0, it is not in ionic form).

104-3 Identify each half-reaction below as either oxidation or reduction.

(a) $Fe^{3+} + 3e^- \longrightarrow Fe$

(b) $Cr \longrightarrow Cr^{3+} + 3e^-$

(c) $MnO_4{}^{2-} \longrightarrow MnO_4{}^- + e^-$

(d) $Li^+ + e^- \longrightarrow Li$

Solution
(a) reduction
(b) oxidation
(c) oxidation
(d) reduction

104-4 Identify each half-reaction below as either oxidation or reduction.

(a) $Cl^- \longrightarrow Cl_2$

(b) $Mn^{2+} \longrightarrow MnO_2$

(c) $H_2 \longrightarrow H^+$

(d) $NO_3{}^- \longrightarrow NO$

Solution
(a) oxidation
(b) oxidation
(c) oxidation
(d) reduction

104-5 Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.

(a) $Ca \longrightarrow Ca^{2+} + 2e^-$, $F_2 + 2e^- \longrightarrow 2F^-$

(b) $Li \longrightarrow Li^+ + e^-$, $Cl_2 + 2e^- \longrightarrow 2Cl^-$

(c) $Fe \longrightarrow Fe^{3+} + 3e^-$, $Br_2 + 2e^- \longrightarrow 2Br^-$

(d) $Ag \longrightarrow Ag^+ + e^-$, $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

Solution

(a)

oxidation: $Ca \longrightarrow Ca^{2+} + 2e^-$

reduction: $F_2 + 2e^- \longrightarrow 2F^-$

overall: $F_2 + Ca \longrightarrow 2F^- + Ca^{2+}$

acidic solution: $F_2 + Ca \longrightarrow 2F^- + Ca^{2+}$

(b)

oxidation: $2 \times (Li \longrightarrow Li^+ + e^-)$

reduction: $Cl_2 + 2e^- \longrightarrow 2Cl^-$

overall: $Cl_2 + 2Li \longrightarrow 2Li^+ + 2Cl^-$

acidic solution: $Cl_2 + 2Li \longrightarrow 2Li^+ + 2Cl^-$

(c)

oxidation: $2 \times (Fe \longrightarrow Fe^{3+} + 3e^-)$

reduction: $3 \times (Br_2 + 2e^- \longrightarrow 2Br^-)$

overall: $3Br + 2Fe \longrightarrow 2Fe^{3+} + 6Br^-$

acidic solution: $3Br_2 + 2Fe \longrightarrow 2Fe^{3+} + 6Br^-$

(d)

oxidation: $3 \times (Ag \longrightarrow Ag^+ + e^-)$

reduction: $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

overall: $MnO_4^- + 4H^+ + 3Ag \longrightarrow 3Ag^+ + MnO_2 + 2H_2O$

acidic solution: $MnO_4^- + 4H^+ + 3Ag \longrightarrow 3Ag^+ + MnO_2 + 2H_2O$

104-6 Balance the equations below assuming they occur in an acidic solution.

(a) $H_2O_2 + Sn^{2+} \longrightarrow H_2O + Sn^{4+}$

(b) $PbO_2 + Hg \longrightarrow Hg_2^{2+} + Pb^{2+}$

(c) $Al + Cr_2O_7^{2-} \longrightarrow Al^{3+} + Cr^{3+}$

Solution

(a)

oxidation: $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-$

reduction: $H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$

overall: $H_2O_2(aq) + 2H^+(aq) + Sn^{2+}(aq) \longrightarrow 2H_2O(l) + Sn^{4+}(aq)$

(b)

oxidation: $2Hg(l) \longrightarrow Hg_2^{2+}(aq) + 2e^-$

reduction: $PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$

overall: $PbO_2(s) + 4H^+(aq) + 2Hg(l) \longrightarrow Hg_2^{2+}(aq) + Pb^{2+}(aq) + 2H_2O(l)$

(c)

reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

oxidation: $2 \times (Al(s) \longrightarrow Al^{3+}(aq) + 3e^-)$

overall: $Cr_2O_7^{2-}(aq) + 2Al(s) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 2Al^{3+}(aq) + 7H_2O(l)$

104-7 Identify the oxidant, reductant, oxidizing agent and reducing agent in each reaction of the previous exercise.

Solution
Oxidized: (a) Sn^{2+}; (b) Hg; (c) Al,
reduced: (b) H_2O_2; (b) PbO_2; (c) $Cr_2O_7^{2-}$,
oxidizing agent: (a) H_2O_2; (b) PbO_2; (c) $Cr_2O_7^{2-}$,
reducing agent: (a) Sn^{2+}; (b) Hg; (c) Al.

104-8 Balance the equations below assuming they occur in a basic solution.

(a) $SO_3^{2-}(aq) + Cu(OH)_2(s) \longrightarrow SO_4^{2-}(aq) + Cu(OH)(s)$

(b) $O_2(g) + Mn(OH)_2(s) \longrightarrow MnO_2(s)$

(c) $NO_3^-(aq) + H_2(g) \longrightarrow NO(g)$

(d) $Al(s) + CrO_4^{2-}(aq) \longrightarrow Al(OH)_3(s) + Cr(OH)_4^-(aq)$

Solution
First balance in acidic solution, then "convert" to basic solution:
(a)

reduction: $2 \times (Cu(OH)_2(s) + H^+(aq) + e^- \longrightarrow Cu(OH)(s) + H_2O(l))$

oxidation: $SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$

overall: $2Cu(OH)_2(s) + SO_3^{2-}(aq) \longrightarrow 2Cu(OH)(s) + SO_4^{2-}(aq) + H_2O(l)$

basic solution: $2Cu(OH)_2(s) + SO_3^{2-}(aq) \longrightarrow 2\,Cu(OH)(s) + SO_4^{2-}(aq) + H_2O(l)$

(b)

oxidation: $2 \times (Mn(OH)_2(s) \longrightarrow MnO_2(s) + 2H^+(aq) + 2e^-)$

reduction: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

overall: $2Mn(OH)_2(s) + O_2(g) \longrightarrow 2MnO_2(s) + 2H_2O(l)$

basic solution: $2Mn(OH)_2(s) + O_2(g) \longrightarrow 2MnO_2(s) + 2H_2O(l)$

(c)

oxidation: $3 \times (H_2(g) \longrightarrow 2\ H^+(aq) + 2e^-)$
reduction: $2 \times (NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l))$

overall: $2NO_3^-(aq) + 2H^+(aq) + 3H_2(g) \longrightarrow 2NO(g) + 4H_2O(l)$
basic solution: $2NO_3^-(aq) + 2(H^+ + OH^-) + 3H_2(g) \longrightarrow 2NO(g) + 4H_2O(l)$
$2NO_3^-(aq) + 3H_2(g) \longrightarrow 2NO(g) + 2OH^-(aq) + 2H_2O(l)$

(d)

reduction: $CrO_4^{2-}(aq) + 4H^+(aq) + 3e^- \longrightarrow Cr(OH)_4^-(aq)$
oxidation: $Al(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3H^+(aq) + 3e$

overall: $CrO_4^{2-}(aq) + Al(s) + H^+(aq) + 3H_2O(l) \longrightarrow Cr(OH)_4^-(aq) + Al(OH)_3(s)$
basic solution:
$CrO_4^{2-}(aq) + Al(s) + (H^+ + OH^-) + 3H_2O(l) \longrightarrow Cr(OH)_4^-(aq) + Al(OH)_3(s) + OH^-(aq)$
$CrO_4^{2-}(aq) + Al(s) + 4H_2O(l) \longrightarrow Cr(OH)_4^-(aq) + Al(OH)_3(s) + OH^-(aq)$

104-9 Identify the oxidant and reductant of each reaction of the previous exercise.

Solution

Oxidized = reducing agent: (a) SO_3^{2-}; (b) $Mn(OH)_2$; (c) H_2; (d) Al;
reduced = oxidizing agent: (a) $Cu(OH)_2$; (b) O_2; (c) NO_3^-; (d) CrO_4^{2-}

104-10 Why don't hydroxide ions appear in equations for half-reactions occurring in acidic solution?

Solution

In acidic solution, $[H^+] > 1 \times 10^{-7} M > [OH^-]$. Hydroxide ion cannot appear as a reactant because its concentration is essentially zero. If it were produced, it would instantly react with the excess hydrogen ion to produce water. Thus, hydroxide should *not* appear as a reactant or product in acidic solution.

104-11 Why don't hydrogen ions appear in equations for half-reactions occurring in basic solution?

Solution

In basic solution, $[OH^-] > 1 \times 10^{-7} M > [H^+]$. Hydrogen ion cannot appear as a reactant because its concentration is essentially zero. If it were produced, it would instantly react with the excess hydroxide ion to produce water. Thus, hydrogen ion should *not* appear as a reactant or product in basic solution.

104-12 Why must the charge balance in oxidation-reduction reactions?

Solution

If the charge does not balance, then there would be a different number of electrons on each side of the equation. This would violate the law of conservation of charge.