CHEMISTRY 135 BALANCING REDOX EQUATIONS

Writing balanced ionic equations for redox reactions is often rather difficult unless a step-wise approach is taken. This involves writing balanced half-equations and then combining them in such a way as to eliminate electrons. Take the example of the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ by the action of acidified potassium permanganate. The active ion in the potassium permanganate is $MnO_4^{-}(aq)$ and it is reduced to Mn^{2+} .

The half equation for the Fe^{2+} is easy to write. We start by writing:

$$Fe^{2+} \rightarrow Fe^{3}$$

and then balancing the charge in this half equation with electrons:

$$\mathrm{Fe}^{2+} \to \mathrm{Fe}^{3+} + \mathrm{e}^{-} \tag{1}$$

The half equation for the MnO_4^- is a little more difficult. First we write:

$$MnO_4^- \rightarrow Mn^{2+}$$

which is already balanced as far as the Mn goes, but not anything else. We then balance oxygen by adding water molecules:

$$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$$

We next balance hydrogen by adding hydrogen ions:

$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

Finally we balance charge by adding electrons:

$$5e^{-} + MnO_{4}^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_{2}O$$
 (2)

and this is our second balanced half equation.

To construct the balanced ionic equation required, we equalise the number of electrons in equations (1) and (2) by multiplying equation (1) by 5, giving:

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^{-}$$
 (3)

and then adding this new equation to (2):

$$5e^{-} + MnO_{4}^{-} + 8H^{+} + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_{2}O + 5Fe^{3+} + 5e^{-}$$
(4)

Electrons (and anything else that appears on both sides of the equation) may then be cancelled, giving:

$$MnO_{4}(aq) + 8H^{+}(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_{2}O(l) + 5Fe^{3+}(aq)$$
(5)

as the final balanced ionic equation. States must be included at this stage.

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Note that the presence of hydrogen ions amongst the reactants tells us that the reaction can only proceed in the presence of acid. For a reaction which occurs in alkaline solution, OH^- ions must be added to both sides in the same number as the hydrogen ions. For the above equation (5), $8OH^-$ ions would be added to each side. Where OH^- and H^+ ions occur together (on the left in the modified equation (5)) they are combined to give water molecules according to:

$$\mathrm{H}^{\scriptscriptstyle +}(\mathrm{aq}) + \mathrm{OH}^{\scriptscriptstyle -}(\mathrm{aq}) \twoheadrightarrow \mathrm{H}_2\mathrm{O}(\mathrm{l})$$

In this way equation (5) becomes:

$$MnO_{4}^{-} + 8H_{2}O + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_{2}O + 8OH^{-} + 5Fe^{3+}$$
(6)

Some further adjustments are required to make a reasonable equation. 4 water molecules should be cancelled to give:

$$MnO_{4}^{-} + 4H_{2}O + 5Fe^{2+} \rightarrow Mn^{2+} + 8OH^{-} + 5Fe^{3+}$$
(7)

and it must be realised that Mn^{2+} , Fe^{2+} and Fe^{3+} will be precipitated as $Mn(OH)_2(s)$, $Fe(OH)_2(s)$ and $Fe(OH)_3(s)$ in alkaline solution, requiring the addition of 17OH⁻ to both sides, giving:

 $MnO_{4}^{-} + 4H_{2}O + 5Fe^{2+} + 17OH^{-} \rightarrow Mn^{2+} + 8OH^{-} + 5Fe^{3+} + 17OH^{-}$ (8)

followed by a rearrangement to give:

$$MnO_{4}(s) + 4H_{2}O(l) + 5Fe(OH)_{2}(s) + 7OH(aq) - Mn(OH)_{2}(s) + 8OH(aq) + 5Fe(OH)_{3}(s)$$
(9)

and then a cancellation:

$$MnO_{4}(s) + 4H_{2}O(l) + 5Fe(OH)_{2}(s) \rightarrow Mn(OH)_{2}(s) + OH(aq) + 5Fe(OH)_{3}(s)$$
(10)

Although equation (10) looks reasonable and is balanced, it may not actually take place to any significant extent. In practice, in alkaline solution MnO_4^- is usually reduced to MnO_2 , so we should arrive at a more probable result by starting with:

$$MnO_4^- \rightarrow MnO_2$$
 and
Fe²⁺ → Fe³⁺, or better, Fe(OH)₂ → Fe(OH)₃

The student is left to complete this exercise by a series of logical steps to give:

$$MnO_{4}(aq) + 3Fe(OH)_{2}(s) + 2H_{2}O(l) \rightarrow MnO_{2}(s) + 3Fe(OH)_{3}(s) + OH(aq)$$

Exercises

- 1) a) Write ionic half-equations, including states for:
 - a) the conversion of Fe^{2+} to Fe^{3+} .
 - b) the conversion of Al to Al^{3+} .
 - c) the conversion of Cu^{2+} to Cu.
 - d) the conversion of Cu to Cu^{2+} .
 - e) the conversion of Fe to Fe^{2+} .
 - f) the conversion of Ag to Ag^+ .
 - g) the conversion of Pb to Pb^{2+} .
 - h) the conversion of Mg to Mg^{2+} .
 - i) the conversion of NO_3^- in the presence of acid to NO.
 - j) the conversion of NO_3^- in the presence of acid to NO_2^- .
 - k) the conversion of H_2 to H^+ .
 - 1) the conversion of MnO_4^- in the presence of acid to Mn^{2+} and water.
 - m) the conversion of $Cr_2O_7^{2-}$ in the presence of acid to Cr^{3+} and
 - i) The addition of metallic aluminium to a copper(II) nitrate solution results in the precipitation of copper and the formation of Al^{3+} in solution.
 - ii) When metallic copper is added to a dilute solution of nitric acid, gaseous NO is evolved and the solution becomes pale blue.
 - iii) Potassium permanganate solution is decolorised by

 H_2O .

- n) the conversion of H_2S to S and H^+ .
- o) the conversion of OH^- to O_2 and H_2O .
- b) In each of the above cases write down the appropriate E value.
- c) Classify each of the above halfequations as either an oxidation or a reduction reaction. Rank the oxidation equations in order of reducing power (since an oxidation process has the power to cause reduction elsewhere) and the reduction equations in order of oxidising power. In each case write the strongest first.

2) a) Write balanced overall ionic equations for the following reactions. You may combine some of the half equations you have written in question (1).

acidified iron(II) sulphate solution.

b) In each of the above cases calculate the E^{e} value for the ionic equation from the E^{e} values for the half-equations. (Look them up in published tables.)