Chem Factsheet

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Balancing Redox Equations in Acidic Solution

Introduction

Redox is a portmanteau, i.e., a word blending the sounds and combining the meanings of two words; reduction and oxidation. Redox is defined as the loss of electrons by one chemical species (oxidation), and the gain of electrons by another chemical species (reduction).

e.g.

reduction

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

oxidation

This is illustrated using ionic half-equations:

$Zn \rightarrow Zn^{2+} + 2e^-$ **(oxidation)**

$Cu^{2+} + 2e^- \rightarrow Cu$ **(reduction)**

Half-Equations

When completing equations for redox reactions, the oxidation and reduction processes are treated individually using separate ionic half-equations. These describe; (i) the oxidised chemical species, and, (ii) the reduced chemical species.

Example 1:

Silver ions (in aqueous solution) oxidise metallic zinc.

The ionic half-equation for the reduction of silver ions:

$Ag^+(aq) + e^- \rightarrow Ag(s)$

The ionic half-equation for the oxidation of zinc:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Comparing the two half-equations reveals an inconsistency in the number of electrons involved. Before combining the half-equations, determine the correct factor to ensure the number of electrons gained by silver ions is equivalent to the number of electrons released by zinc atoms. In this example the factor is 2.

$\mathbf{2}Ag^+(aq) + \mathbf{2}e^- \rightarrow \mathbf{2}Ag(s)$

Combining the two half-equations provides a correctly balanced redox equation. When combining two half-equations, the number of electrons on both sides of the equation are omitted, i.e. they cancel out:

$2Ag^+(aq) + \cancel{2e^-} + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq) + \cancel{2e^-}$

Giving the completed equation:

$2Ag^+(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$

> *Ionic equations are used to complete redox equations. Only chemical species undergoing a change in the reaction are included. Chemical species that remain unchanged in solution are called spectator ions.*

Half-equations involving oxyanions, i.e., anions consisting of a chemical element and oxygen, are more complicated. Typically, oxyanion oxygen atoms combine with hydrogen ions, H^+, present in the reaction mixture, forming water, H_2O. The hydrogen ions, H^+, are usually provided by adding an excess of a strong acid to the reaction, for example, sulphuric acid, H_2SO_4, or nitric acid, HNO_3.

REDOX REACTIONS IN ACIDIC SOLUTIONS

Potassium manganate(VII), $KMnO_4$, is a strong oxidising agent and a common reagent in redox reactions. In acidic conditions, manganese atoms in the +7 oxidation state gain five electrons and are reduced to the +2 oxidation state. The four oxyanion oxygens involved combine with eight hydrogen ions, H^+, producing four water molecules.

Example 2:

The manganate(VII) ion, MnO_4^-, is reduced to the manganese(II) ion, Mn^{2+}.

$MnO_4^- + \mathbf{5e^-} \rightarrow Mn^{2+}$	**manganese gains 5 electrons**
$Mn\mathbf{O_4}^- + 5e^- \rightarrow Mn^{2+} + \mathbf{4}H_2\mathbf{O}$	**4 oxyanion oxygens produce 4 waters**
$MnO_4^- + \mathbf{8H^+} + 5e^- \rightarrow Mn^{2+} + \mathbf{4H_2}O$	**4 waters require 8 hydrogen ions, H^+**

Giving the completed half-equation:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Balancing Redox Reactions In Acidic Solutions

When balancing redox equations, ascertain the reaction taking place, identifying the chemical species; (1) oxidised, and (2) reduced. Complete ionic half-equations, following the steps provided:

1. Confirm oxidation states/changes in oxidation states.
2. Ensure all non-oxygen/hydrogen atoms are balanced in the half-equation.
3. Determine the number of electrons; (1) lost through oxidation, and, (2) gained through reduction.
4. Accommodate any required oxygen atoms (present in oxyanions) by adding the required number of water molecules.
5. Accommodate any required hydrogen atoms by adding the required number of hydrogen ions.

Example 3a:

Potassium dichromate(VI), $K_2Cr_2O_7$, oxidises iron(II) ions to iron(III) ions under acidic conditions; dichromate(VI) ions are reduced to chromium(III).

Iron(II) is oxidised to iron(III) – losing one electron.

Completed ionic half-equation for the oxidation of iron(II) ions:

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

The dichromate(VI) ion, $Cr_2O_7^{2-}$, is reduced to the chromium(III) ion, $2Cr^{3+}$.

$\mathbf{Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+}}$ **6 electrons gained**

Ensure chromium atoms are balanced in the half-equation. There are **2** chromium atoms and each gains **3** electrons. Therefore, a total of **6 electrons** are required.

$Cr_2\mathbf{O}_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + \mathbf{7}H_2\mathbf{O}$

7 oxyanion oxygens produce 7 waters

$Cr_2O_7^{2-} + \mathbf{14H^+} + 6e^- \rightarrow 2Cr^{3+} + \mathbf{7H_2}O$

7 waters require 14 hydrogen ions, H^+

Completed ionic half-equation for the reduction of chromium:

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

The above example demonstrates the importance in ensuring non-oxygen/hydrogen atoms are correctly balanced. A common error occurs when this step is ignored and two half-equations are subsequently merged with incorrect stoichiometry.

To confirm equations are correctly balanced, check that the net charge on both sides of the equation is equal. For example, in:
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
The net charge on both sides of the equation is 6+.

To correctly merge and complete the full redox equation:

6. Determine the correct factor to balance the equations so the number of electrons is equal.
7. Merge (add) the two half-equations together.
8. Cancel the electrons (appearing on both sides of the merged equation).
9. If required, cancel any excess water molecules and/or hydrogen ions appearing on both sides of the merged equation (see **Example 4**).

Example 3b:

Compare the two redox half-equations completed above (see **Example 3a**), and factor the stoichiometric ratio to ensure the number of electrons gained in the reduction process matches the electrons released through oxidation.

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

Oxidation process requires the loss of 6 electrons, i.e., a factor of 6 is required:

Oxidation: $\mathbf{6}Fe^{2+}(aq) \rightarrow \mathbf{6}Fe^{3+}(aq) + \mathbf{6}e^-$

Adding/merging both half-equations completes the fully balanced ionic equation:

$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

As before, the electrons 'cancel out' and are not included in the final equation.

Example 4 demonstrates how the number of hydrogen ions, H^+, and/or water molecules, H_2O, appearing on both sides of the combined equation are cancelled in the full equation.

Example 4:

Acidified potassium dichromate oxidises manganese(II) ions, Mn^{2+}, to manganese(IV), MnO_2; dichromate(VI), $Cr_2O_7^{2-}$, is reduced to chromium(III), Cr^{3+}.

Refer back to **Example 3a** to complete the reduction half-equation:

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

Manganese(II) is oxidised to manganese(IV):

$Mn^{2+} \rightarrow MnO_2 + \mathbf{2e^-}$ **2 electrons released.**

$Mn^{2+} + \mathbf{2H_2O} \rightarrow Mn\mathbf{O_2} + 2e^-$ **2 oxygen/oxide atoms are produced from 2 water molecules.**

$Mn^{2+} + \mathbf{2H_2}O \rightarrow MnO_2 + \mathbf{4H^+} + 2e^-$ **4 hydrogen ions are produced from 2 water molecules.**

Completed ionic half-equation for the oxidation of manganese(II):

$Mn^{2+} + \mathbf{2H_2}O \rightarrow MnO_2 + \mathbf{4H^+} + 2e^-$

Factor the stoichiometry for both half-equations: 6 electrons gained by chromium atoms require 6 electrons released by manganese atoms, i.e., a factor of 3:

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

$\mathbf{3}Mn^{2+} + \mathbf{6}H_2O \rightarrow \mathbf{3}MnO_2 + \mathbf{12}H^+ + \mathbf{6e^-}$

Merging both half-equations completes the fully balanced ionic equation:

$Cr_2O_7^{2-}(aq) + 3Mn^{2+}(aq) + 14H^+(aq) + 6H_2O(l) \rightarrow 2Cr^{3+}(aq) + 3MnO_2(s) + 12H^+(aq) + 7H_2O(l)$

The above equation contains hydrogen ions, H^+, and water molecules, H_2O, on both sides of the equation. The equation is simplified by cancelling excess hydrogen ions, H^+, and water molecules, H_2O:

$Cr_2O_7^{2-}(aq) + 3Mn^{2+}(aq) + 1\underset{2}{\cancel{4}}H^+(aq) + 6\cancel{H}_2O(l) \rightarrow 2Cr^{3+}(aq) + 3MnO_2(s) + 12\cancel{H}^+(aq) + \cancel{7}H_2O(l)$

Completed equation: $Cr_2O_7^{2-}(aq) + 3Mn^{2+}(aq) + 2H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3MnO_2(s) + H_2O(l)$

When determining the stoichiometric ratio/factor, apply simple whole-numbers, i.e., use the lowest common multiple to correctly balance half-equations. See **Example 5**.

Example 5:

The oxidation of hydrogen peroxide, H_2O_2, by potassium manganate(VII), $KMnO_4$, gives the following redox half-equations:

Reduction: $MnO_4^-(aq) + 8H^+(aq) + \mathbf{5e^-} \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Oxidation: $H_2O_2(aq) \rightarrow 2H^+(aq) + O_2(g) + \mathbf{2e^-}$

The ratio observed is 2½ : 1. For simplicity, find the lowest common multiple and use whole-numbers, i.e., 10; (2 × 5), (5 × 2):

Reduction: $\mathbf{2}MnO_4^-(aq) + \mathbf{16}H^+(aq) + \mathbf{10e^-} \rightarrow \mathbf{2}Mn^{2+}(aq) + \mathbf{8}H_2O(l)$

Oxidation: $\mathbf{5}H_2O_2(aq) \rightarrow \mathbf{10}H^+(aq) + \mathbf{5}O_2(g) + \mathbf{10e^-}$

Merging the half-equations, cancelling electrons and excess hydrogen ions, H^+, gives:

$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$

Redox Reactions In Alkaline Solutions

Redox reactions occur in alkaline solutions. The principles for balancing redox equations in alkaline conditions are like those used completing in acidic conditions. The method is more complicated due to the required manipulation of equations using hydroxide ions, OH^-.

Example 6:

The oxidation of chromium(III) hydroxide, $Cr(OH)_3$, to potassium chromate(VI), K_2CrO_4, is achieved using the oxidizing agent potassium chlorate(V), $KClO_3$. In the reaction, chlorate(V) is reduced to the chloride ion, Cl^-. This reaction is completed in alkaline conditions. Chromium(III) is oxidised to chromate(VI) – releasing 3 electrons.

$Cr(OH)_3 \rightarrow CrO_4^{2-} + \mathbf{3e^-}$

chromium loses 3 electrons.

$Cr(\mathbf{O}H)_3 + \mathbf{H_2O} \rightarrow Cr\mathbf{O_4}^{2-} + 3e^-$

balance oxygen atoms by adding H_2O.

$Cr(O\mathbf{H})_3 + \mathbf{H_2}O \rightarrow CrO_4^{2-} + \mathbf{5H^+} + 3e^-$

balance hydrogen atoms by adding $5H^+$.

The reaction is completed in alkaline conditions. Any hydrogen ions, H^+, need to be countered by hydroxide ions, OH^-. It is necessary to add required hydroxide ions, OH^-, to both sides of the equation:

$Cr(OH)_3 + H_2O + \mathbf{5OH^-} \rightarrow CrO_4^{2-} + 5H^+ + \mathbf{5OH^-} + 3e^-$

Hydrogen ions and hydroxide ions combine to form water:

$H^+ + OH^- \rightarrow H_2O$

$Cr(OH)_3 + H_2O + 5OH^- \rightarrow CrO_4^{2-} + \mathbf{5H_2O} + 3e^-$

Cancel water molecules, H_2O, present on both sides of the equation. This completes the oxidation half-equation:

$Cr(OH)_3 + 5OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-$

Chlorate(V) is reduced to chloride (-1) – gaining 6 electrons.

$ClO_3^- + 6e^- \rightarrow Cl^-$ **chlorine gains 6 electrons.**

$Cl\mathbf{O_3}^- + 6e^- \rightarrow Cl^- + \mathbf{3}H_2\mathbf{O}$ **3 oxyanion oxygens produce 3 waters.**

$ClO_3^- + \mathbf{6H^+} + 6e^- \rightarrow Cl^- + \mathbf{3H_2}O$ **3 waters require 6 hydrogen ions.**

Add hydroxide ions, OH^-, to counter the hydrogen ions, H^+, on the left-side of the equation. Then, cancel excess water molecules appearing on both sides of the equation:

$ClO_3^- + 3H_2O + 6e^- \rightarrow Cl^- + 6OH^-$

Balance the two half-equations. The factor in this example is 2.

$\mathbf{2}Cr(OH)_3(s) + \mathbf{10}OH^-(aq) \rightarrow \mathbf{2}CrO_4^{2-}(aq) + \mathbf{8}H_2O(l) + \mathbf{6e^-}$

$ClO_3^-(aq) + 3H_2O(l) + \mathbf{6e^-} \rightarrow Cl^-(aq) + 6OH^-(aq)$

Merge the two half-equations, cancelling electrons, hydroxide ions, OH^-, and water molecules, H_2O, appearing on both sides of the merged redox equation:

$ClO_3^-(aq) + 2Cr(OH)_3(s) + 4OH^-(aq) \rightarrow Cl^-(aq) + 2CrO_4^{2-}(aq) + 5H_2O(l)$

Questions

1. For each example provided, complete a balanced ionic half-equation:
   (a) copper is oxidised to copper(II) ions.
   (b) dioxovanadium(V) ions, VO_2^+, reduced to vanadium(II) ions, V^{2+}
   (c) aqueous bromine is reduced to bromide ions.
   (d) bromine is oxidised to bromate(V).

2. Potassium manganate(VII) is an oxidising agent. It oxidises vanadium(II), V^{2+}, to vanadate(V) ions, VO_3^-. This reaction is completed under acidic conditions.
   (a) Complete a balanced half-equation for the reduction of manganate(VII).
   (b) Complete a balanced half-equation for the oxidation of vanadium(II).
   (c) Give a balanced redox equation for this reaction.
   (d) Give the generic name used to describe the role of the potassium ions, K^+, in this reaction.
   (e) Sulphuric acid, H_2SO_4, is used to acidify the conditions for this reaction. Suggest why hydrochloric acid should NOT be used. Provide an ionic equation in support of this answer.

3. Zinc metal reduces acidified dichromate(VI) ions, $Cr_2O_7^{2-}$, to form a solution containing zinc(II) ions, Zn^{2+}, and chromium(II) ions, Cr^{2+}.
   (a) Complete a balanced half-equation for the reduction process.
   (b) Complete a balanced half-equation for the oxidation process.
   (c) Give a balanced redox equation for this reaction.

4. Aldehydes are oxidised to carboxylic acids using strong oxidising agents. For example, acidified potassium dichromate(VI) oxidises ethanal, CH_3CHO, to ethanoic acid, CH_3COOH. Typically, dichromate(VI), $Cr_2O_7^{2-}$, is reduced to chromium(III), Cr^{3+}.
   (a) Complete the half-equation for the reduction process.
   (b) Complete the incomplete half-equation describing the oxidation of ethanal: $C_2H_4O \rightarrow C_2H_4O_2$
   (c) Give a balanced redox equation for this reaction.

5. Aluminium-oxygen fuel cells are being developed that may potentially power motor vehicles. This redox reaction occurs under alkaline conditions.
   (a) Complete the incomplete half-equation describing the oxidation of aluminium: $Al(s) \rightarrow Al(OH)_4^-(aq)$
   (b) Complete the incomplete half-equation for the reduction of oxygen: $O_2(g) \rightarrow 4OH^-(aq)$
   (c) Give the overall equation for the aluminium-oxygen cell.

Answers

1. (a) $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
   (b) $VO_2^+(aq) + 4H^+(aq) + 3e^- \rightarrow V^{2+}(aq) + 2H_2O(l)$
   (c) $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$
   (d) $Br_2 + 6H_2O(l) \rightarrow 2BrO_3^- + 12H^+(aq) + 10e^-$

2. (a) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
   (b) $V^{2+}(aq) + 3H_2O \rightarrow VO_3^-(aq) + 6H^+(aq) + 3e^-$
   (c) $3MnO_4^-(aq) + 5V^{2+}(aq) + 3H_2O(l) \rightarrow 3Mn^{2+}(aq) + 5VO_3^-(aq) + 6H^+(aq)$
   (d) Spectator ion.
   (e) Toxic chlorine gas is liberated. $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$, or
   $2MnO_4^-(aq) + 10Cl^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l)$

3. (a) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 8e^- \rightarrow 2Cr^{2+}(aq) + 7H_2O(l)$
   (b) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
   (c) $Cr_2O_7^{2-}(aq) + 4Zn(s) + 14H^+(aq) \rightarrow 2Cr^{2+}(aq) + 4Zn^{2+}(aq) + 7H_2O(l)$

4. (a) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
   (b) $C_2H_4O(l) + H_2O(l) \rightarrow C_2H_4O_2(l) + 2H^+(aq) + 2e^-$
   (c) $Cr_2O_7^{2-}(aq) + 3C_2H_4O(l) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3C_2H_4O_2(l) + 4H_2O(l)$

5. (a) $Al(s) + 4OH^-(aq) \rightarrow Al(OH)_4^-(aq) + 3e^-$
   (b) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
   (c) $3O_2(g) + 4Al(s) + 4OH^-(aq) + 6H_2O(l) \rightarrow 4Al(OH)_4^-(aq)$

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