Redox 1. - Fun Program

Oxidation Numbers

Oxidation numbers (or oxidation states) are numbers assigned to atoms in elements or compound, according to a set of rules. These oxidation numbers are used to determine whether or not a substance is oxidised or reduced in a reaction.

The rules for determining the oxidation number of an atom are:

i) Atoms of <u>elementary</u> substances have an oxidation number of zero. e.g. the oxidation number of each of the atoms in Cl_2 is 0, and in sodium is 0.

ii) The oxidation number of atoms that make up <u>monatomic ions</u> is equal to the charge on the ion e.g. the oxidation number of Na in Na^+ is 1, and of S in S^{2-} is -2.

(Question 1)

iii) In compounds, <u>hydrogen</u> atoms normally have an oxidation number of +1. Exception - for metal hydrides e.g. MgH_2, the oxidation number of hydrogen is -1. For example in H_2O, NH_3, CH_4 and C_2H_4, the oxidation number of all the hydrogen atoms is +1.

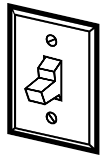
iv) In compounds, <u>oxygen</u> atoms normally have an oxidation number of -2. Exceptions - for the peroxide ion, O_2^{2-} the oxidation number of oxygen is -1 and in F_2O, the oxidation number of O is +2 (see vi) below For example in H_2O, CO_2, SiO_2 and CH_3OH, the oxidation number of all the oxygen atoms is -2.

v) The oxidation numbers of other atoms in a molecule or ion are determined by knowing that the oxidation numbers of atoms given in the formula must add up to the charge of the species. For example, for SO_3^{2-}, S must have an oxidation number of +4 (+4 + (3 x -2) = -2).

vi) In its compounds, F always has an oxidation number of -1. (Normally in compounds not containing H, the most electronegative atom has the negative oxidation number)

(Question 2)

e



Question 1. What are the oxidation numbers of each of the atoms in the following substances?

Br_2	magnesium, Mg	P^{3-}
N_2	S_8	Al^{3+}
$PbBr_2$	MgO	Fe_2S_3

Question 2. Calculate the oxidation number of each atom in the following substances:

a)	SiH_4	H_2S	PH_4^+	KH	CaH_2
b)	SO_3	SO_4^{2-}	NO_3^-	Na_2O_2	H_2O_2
c)	H_2	NaBr	O_2	SO_2	PO_4^{3-}
	HSO_3^-	P_4	Al_2S_3	BaH_2	K_2O_2
	Fe	MnO_4^-	H_2SO_4	$Cr_2O_7^{2-}$	$S_2O_3^{2-}$

d)	$CaCO_3$	BaC_2O_4	Na_2HPO_4	$Al(HSO_4)_3$
	MgO_2	CO	H_3PO_3	P_4O_{10}
	$Mg(BrO_3)_2$	$HClO_4$	SCl_6	HCN
	$Ag(NH_3)_2^+$	HgS	SiF_6^{2-}	PCl_4^+

Oxidation and Reduction Reactions

Oxidation and reduction (redox) reactions involve a transfer of electrons from one species to another.

i) When a substance loses <u>electrons</u>, it is said to have been <u>oxidised</u>, and when a substance gains electrons, it is said to have been <u>reduced</u>.

(Leo says Ger / Oil Rig)

For example, in the following oxidation and reduction reaction

$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

Cl_2 has gained electrons to form Cl^-, that is, it has been reduced, and Br^- has lost electrons to form Br_2, and so it has been oxidised.

ii) <u>Oxidation numbers</u> can also be used to determine which reactant has been oxidised and which has been reduced.

If the oxidation number of an atom in a species is increased, then the species is said to have undergone <u>oxidation</u>, but if the oxidation number is decreased, then the species is said to have undergone <u>eduction</u>.

For example, in the reaction

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$

The oxidation number of S has increased from -2 (in PbS) to +4 in SO_2. The oxidation number of oxygen has decreased from 0 (in O_2) to -2 (in PbO and SO_2). That is, the PbS has been oxidised and the O_2 has been reduced.

(Questions 3 & 4)

Oxidants and Reductants

In a redox reaction, the reactant that is oxidised (loses/donates electrons) is called the <u>reductant</u> (because it reduces the other reactant). The reactant that is reduced (gains/accepts electrons) is called the <u>oxidant</u>.

For example, in the following redox reaction:

$$PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$$

PbO is reduced and so it is the oxidant, and CO is oxidised, so it is the reductant.

(Question 5)

Question 3. In the following equations, which reactant undergoes oxidation?

a) $Cu^{2+} + Mg \rightarrow Mg^{2+} + Cu$

b) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

c) $Cu + Cl_2 \rightarrow CuCl_2$

d) $Cu + 4H^+ + SO_4^{2-} \rightarrow Cu^{2+} + SO_2 + 2H_2O$

e) $H_2S + O_2 \rightarrow SO_2 + H_2O$

f) $H_2O_2 + NO_2^- \rightarrow H_2O + NO_3^-$

Question 4. Which of the following equations do not represent a redox reaction?

a) $CaCO_3 + 2H^+ \rightarrow CO_2 + H_2O + Ca^{2+}$

b) $2Al + 3Br_2 \rightarrow 2AlBr_3$

c) $Ag^+ + Br^- \rightarrow AgBr$

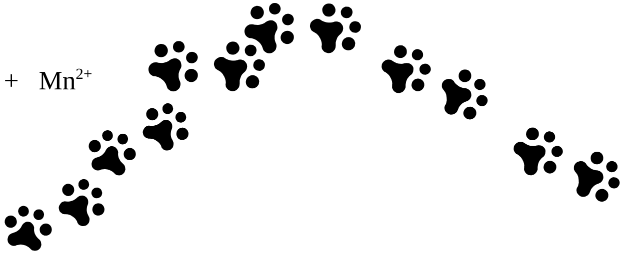
d) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

Question 5. Identify the reductant and oxidant in the following reactions:

a) $SiCl_4 + 2Mg \rightarrow 2MgCl_2 + Si$

b) $5Fe^{2+} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + 4H_2O + Mn^{2+}$

c) $Cl_2 + H_2O \rightarrow H^+ + Cl^- + HClO$



$Mg(s) + Cl_2(aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$
$2Fe^{2+}(aq) + Sn^{4+}(aq)$

Half Equations

For redox reactions, it is sometime useful to separate the equation into two half-equations, one involving the oxidation and the other the reductions. These half equations show how the electrons are gained or lost, that is, electrons (e^-) are shown as a reactant or a product.

The reduction half equation is written in the following general form:

$$X + e^- \rightarrow X^-$$

and the oxidation half equation in the general form of

$$Y \rightarrow Y^+ + e^-$$

These equations must be balanced in terms of both atoms and charge.

For example, the redox reaction

$$Mg(s) + Cl_2(aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

can be broken up into the following two half equations:

oxidation half equation: $Mg \rightarrow Mg^{2+}(aq) + 2e^-$

reduction half equation: $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$

(Questions 6 & 7)

Redox reactions carried out in acidic aqueous solutions sometimes involve half equations that are difficult to write. The following steps can be used to determine these half equations:

i) Write the formula of the reactant being oxidised or reduce and its product

ii) Balance all atoms except H and O

iii) Balance O atoms using H_2O

iv) Balance H atoms using H^+

v) Balance charge using electrons

For example, balancing the skeleton equation $Cr_2O_7^{2-} \rightarrow Cr^{3+}$:

step ii) $Cr_2O_7^{2-} \rightarrow \mathbf{2}Cr^{3+}$

step iii) $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + \mathbf{7H_2O}$

step iv) $Cr_2O_7^{2-} + \mathbf{14H^+} \rightarrow 2Cr^{3+} + 7H_2O$

step v) $Cr_2O_7^{2-} + 14H^+ + \mathbf{6e^-} \rightarrow 2Cr^{2+} + 7H_2O$

(Question 8)

Question 6. Give the half equations for the following:

a) the oxidation of Na to form Na^+

b) the reduction of F_2 to form F^-

c) the oxidation of Fe^{3+} to form Fe^{3+}

Question 7. Write the reduction and oxidation half equations for the following redox reactions:

a) $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$

b) $2Fe^{2+}(aq) + Sn^{4+}(aq) \rightarrow Sn^{2+}(aq) + 2Fe^{3+}(aq)$

c) $2K(s) + 2H_2O(l) \rightarrow 2K^+(aq) + 2OH^- + H_2(g)$

Question 8. Balance the following skeleton half equations using the method described on the left (assume they are carried out in acidic aqueous solutions).

a) $MnO_4^-(aq) \rightarrow MnO_2(s)$

b) $SO_4^{2-}(aq) \rightarrow H_2SO_3(g)$

c) $C_2H_5OH(aq) \rightarrow CO_2(g)$

d) $IO_3^-(aq) \rightarrow I_2(aq)$

e) $N_2O(g) \rightarrow NO(g)$

Balancing Redox Equations

Some redox equations are more easily balanced if they are first broken up into their two half equations and then these two half equations are added together so that the electrons cancel out.

For example: to balance the following equation:

$$MnO_4^- + HNO_2 + H^+ \rightarrow Mn^{2+} + NO_3^- + H_2O$$

it can be first broken up into its two balanced half equations

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O \qquad \times 2$$
$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e \qquad \times 5$$

then these two half equations are multiplied by the appropriate number/s and added together so that the electrons will cancel out

$$2MnO_4^- + 16H^+ + 5HNO_2 + 5H_2O \rightarrow 2Mn^{2+} + 8H_2O + 5NO_3^- + 15H^+$$

H^+ and H_2O are adjusted to give the final balanced equation:

$$2MnO_4^- + H^+ + 5HNO_2 \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$$

(Question 9)

Redox equations carried out in <u>basic conditions</u> can also be balanced using the method described above together with an additional final step to convert the equation showing H^+ into an equation showing OH^-.

For example, the equation can be balanced as following

$$Cr + CrO_4^- + H_2O \rightarrow Cr(OH)_3 + OH$$

<u>Step 1</u>. First write the balanced equation in acidic conditions:

$$Cr + 3H_2O \rightarrow Cr(OH)_3 + 3H^+ + 3e \qquad \times 4$$
$$CrO_4^- + 5H^+ + 4e \rightarrow Cr(OH)_3 + H_2O \qquad \times 3$$

add:

$$4Cr + 12H_2O + 3CrO_4^- + 15H^+ \rightarrow 4Cr(OH)_3 + 12H^+ + 3Cr(OH)_3 + 3H_2O$$

adjust H_2O and H^+, to give

$$4Cr + 9H_2O + 3CrO_4^- + 3H^+ \rightarrow 7Cr(OH)_3$$

<u>Step 2</u>. add same number of OH^-, as there are H^+, to both sides

$$4Cr + 9H_2O + 3CrO_4^- + 3H^+ + 3OH^- \rightarrow 7Cr(OH)_3 + 3OH^-$$

<u>Step 3.</u> replace $H^+ + OH^-$ with H_2O

$$4Cr + 9H_2O + 3CrO_4^- + 3H_2O \rightarrow 7Cr(OH)_3 + 3OH^-$$

to give $4Cr + 12H_2O + 3CrO_4^- \rightarrow 7Cr(OH)_3 + 3OH^-$

Question 9. Balance the following equations by first writing the two half equations:

a) $SO_2 + Cr_2O_7^{2-} + H^+ \rightarrow SO_4^{2-} + Cr^{3+} + H_2O$

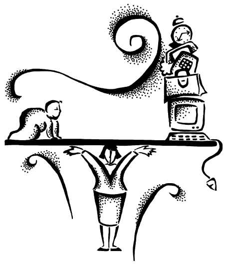
b) $HNO_2 \rightarrow N_2O + N_2O_4 + H_2O$

c) $H_2O_2 + NO_3^- + H^+ \rightarrow O_2 + NO + H_2O$

d) $CH_3CHO + MnO_4^- + H^+ \rightarrow CH_3COOH + Mn^{2+} + H_2O$

e) $CN^- + MnO_4^- + H_2O \rightarrow CNO^- + MnO_2 + OH^-$

f) $NO_2^- + Al + OH^- + H_2O \rightarrow NH_3 + AlO_2^-$



Redox Titrations

Just as a base is used to determine the concentration of an acid (or vice versa) in an acid-base titration, a known concentration of a solution of an oxidising agent can be used to determine the unknown concentration of a solution of a reducing agent (or vice versa) in a redox titration.

Commonly used primary standards used in redox titrations include oxalic acid dihydrate, $H_2C_2O_4.2H_2O$, salts containing the oxalate ion, $C_2O_4^{2-}$ and ammonium iron(II) sulfate hexahydrate, $(NH_4)_2SO_4.FeSO_4.6H_2O$.

The half equations for the reactions these substances undergo in titrations are:

oxalic acid $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e$

oxalate ions $C_2O_4^{2-} \rightarrow 2CO_2 + 2e$

ammonium iron(II) sulfate hexahydrate $Fe^{2+} \rightarrow Fe^{3+} + e$

Potassium permanganate is often used in primary titrations because it is a strong oxidising agent and its solution is intensely coloured (purple). However, it cannot be used as a primary standard because its solution is not very stable. It decomposes in the presence of air, to form brown deposits of manganese dioxide, MnO_2.

In a titration, the permanganate ion undergoes the following reaction

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

In the titration, the purple permanganate ion reacts to form the very pale pink Mn^{2+} ion to give a sharp end-point, without the use of a redox indicator (unlike acid-base indicator, not many redox indicator exist).

The acid normally used to acidify the solution is sulfuric acid. If hydrochloric acid is used, the Cl^- could possibly be oxidised by the MnO_4^-. If acid is not present, or if insufficient acid is present, an alternative oxidation reaction occurs to form MnO_2 (a brown substance) rather than Mn^{2+}.

Because the permanganate solution is dark purple, it is difficult to read the volume using the bottom of the meniscus in a burette, so the top of the meniscus is normally used.

(Questions 10 and 11)

Question 10. The following procedure was used to determine the concentration of calcium ions in milk. A 2.50 mL sample of milk was treated with an excess of sodium oxalate to precipitate the calcium ions as calcium oxalate:

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$$

The precipitate was filtered off, dissolved in dilute H_2SO_4 and made up to a final volume of 10.00 mL. This solution was then titrated with 0.00456 mol L^{-1} $KMnO_4$. 6.53 mL of the permanganate solution was required to reach the end point.

a) Write the balance ionic equation for the reaction between the MnO_4^- and $C_2O_4^{2-}$ ions. Mn^{2+} and CO_2 are formed in this reaction.

b) Calculate the concentration, in mol L^{-1} of Ca^{2+} in the milk.

Question 11. A chemical engineer determines the percentage by mass of iron in an ore sample by converting the Fe to Fe^{2+} in acid, and then titrating the Fe^{2+} with MnO_4^-. A 11.081 g sample of the iron containing ore was dissolved in dilute sulfuric acid and after filtering, the solution was made up to 250 mL with distilled water. 25.00 mL of this solution was then titrated with 0.03190 mol L^{-1} $KMnO_4$. 39.92 mL of the permanganate solution was required to reach the end point.

a) Give the ionic equation for the reaction between MnO_4^- and Fe^{2+} (Mn^{2+} and Fe^{3+} are formed).

b) Calculate the percentage, by mass of iron in the ore.

ANSWERS

Question 1.

0	0	-3	0	0	+3
Br_2	Mg	P^{3-}	N_2	S_8	Al^{3+}

+2 -1	+2 -2	+3 -2
$PbBr_2$	MgO	Fe_2S_3

Question 2.

	-4 +1	+1 -2	-3 +1	+1 -1	+2 -1
a)	SiH_4	H_2S	PH_4^+	KH	CaH_2
	+6 -2	+6 -2	+5 -2	+1 -1	+1 -1
b)	SO_3	SO_4^{2-}	NO_3^-	Na_2O_2	H_2O_2
	0	+1 -1	0	+4 -2	+5 -2
c)	H_2	NaBr	O_2	SO_2	PO_4^{3-}
	+1 +4 -2	0	+3 -2	+2 -1	+1 -1
	$H\ S\ O_3^-$	P_4	Al_2S_3	BaH_2	K_2O_2
	0	+7 -2	+1 +6 -2	+6 -2	+2 -2
	Fe	MnO_4^-	$H_2\ S\ O_4$	$Cr_2O_7^{2-}$	$S_2O_3^{2-}$

	+2 +4 -2	+2 +3 -2	+1 +1 +5 -2	+3 +1 +6 -2
d)	$Ca\ C\ O_3$	$Ba\ C_2\ O_4$	$Na_2\ H\ P\ O_4$	$Al\ (H\ S\ O_4)_3$
	+2 -1	+2 -2	+1 +3 -2	+5 -2
	MgO_2	C O	$H_3\ P\ O_3$	$P_4\ O_{10}$
	+2 +5 -2	+1 +7 -2	+6 -6	+1 +2 -3
	$Mg(BrO_3)_2$	$H\ Cl\ O_4$	$S\ Cl_6$	H C N
	+1 -3 +1	+2 -2	+4 -1	+5 -1
	$Ag(N\ H_3)_2^+$	HgS	$Si\ F_6^{2-}$	PCl_4^+

Question 3. a) Mg b) I^- c) Cu d) Cu e) H_2S f) NO_2^-

Question 4. a), c)

Question 5. a) $SiCl_4$ - oxidant Mg - reductant

b) Fe^{2+} - reductant MnO_4^- - oxidant

c) Cl_2 - oxidant and reductant

Question 6. a) $Na \rightarrow Na^+ + e^-$ b) $F_2 + 2e^- \rightarrow 2F^-$

c) $Fe^{3+} + e \rightarrow Fe^{3+}$

Question 7.

a) oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$
reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

b) oxidation: $2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 2e^-$
reduction: $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$

c) oxidation: $K(s) \rightarrow K^+(aq) + e^-$
reduction: $2H_2O(l) + 2e^- \rightarrow 2OH^- + H_2(g)$

Question 8.

a) $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$

b) $SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow H_2SO_3(g) + H_2O(l)$

c) $C_2H_5OH(aq) + 3H_2O(l) \rightarrow 2CO_2(g) + 12H^+ + 12e^-$

d) $2IO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow I_2(aq) + 6H_2O(l)$

e) $N_2O(g) + H_2O(l) \rightarrow 2NO(g) + 2H^+(aq) + 2e^-$

Question 9.

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

$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ x 3

$Cr_2O_7^{2-} + 2\ H^+ + 3SO_2 \rightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$

b) $2HNO_2 + 4H^+ + 4e^- \rightarrow N_2O + 3H_2O$

$2HNO_2 \rightarrow N_2O_4 + 2H^+ + 2e$ x 2

$6HNO_2 \rightarrow N_2O + 3H_2O + 2N_2O_4$

c) $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ x 3

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ x 2

$3H_2O_2 + 2NO_3^- + 2H^+ \rightarrow 3O_2 + 2NO + 4H_2O$

d) $CH_3CHO + H_2O \rightarrow CH_3COOH + 2H^+ + 2e^-$ x 5

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

$5CH_3CHO + 2MnO_4^- + 6\ H^+ \rightarrow 5CH_3COOH + 2Mn^{2+} + 3\ H_2O$

Question 9. (cont)

e) $CN^- + H_2O \rightarrow CNO^- + 2H^+ + 2e$ x 3

$MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O$ x 2

$3CN^- + 2MnO_4^- + 2H^+ \rightarrow 3CNO^- + 2MnO_2 + H_2O$

$3CN^- + 2MnO_4^- + H_2O \rightarrow 3CNO^- + 2MnO_2 + 2OH^-$

f) $NO_2^- + 7H^+ + 6e \rightarrow NH_3 + 2H_2O$

$Al + 2H_2O \rightarrow AlO_2^- + 4H^+ + 3e$ x 2

$NO_2^- + 2Al + 2H_2O \rightarrow NH_3 + 2AlO_2^- + H^+$

$NO_2^- + 2Al + H_2O + OH^- \rightarrow NH_3 + 2AlO_2^-$

Question 10.

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

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e$ x 5

$2MnO_4^- + 16\,H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8\,H_2O + 10CO_2$

b) moles of $KMnO_4$ used = 0.00456 x 0.00653 = 2.978×10^{-5}
= moles of MnO_4^-
moles of $C_2O_4^{2-}$ present = 5/2 x 2.978×10^{-5} = 7.444×10^{-5}
= moles of Ca^{2+} present
i.e. have 7.444×10^{-5} moles Ca^{2+} in 2.50 mL of milk
conc of Ca^{2+} in milk = 7.444×10^{-5} / 0.00250 = **0.0298 mol L^{-1}**

Question 11.

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

$Fe^{2+} \rightarrow Fe^{3+} + e$ x 5

$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

b) moles of $KMnO_4$ used = 0.03190 x 0.03992 = 0.001273
= moles of MnO_4^-
moles of Fe^{2+} present in 25.00 mL = 5 x 0.001273 = 0.006367
moles Fe^{2+} in 250 mL = 0.006367 x 250/25 = 0.06367
= moles of Fe in ore sample
mass of Fe = 0.06367 x 55.85 = 3.556 g
percentage of Fe = 3.556/ 11.081 x 100 = **32.1%**