Balancing Complex Oxidation - Reduction Equations

Example: $KMnO_4 + NaCl + H_2SO_4 \rightarrow MnCl_2 + Cl_2 + K_2SO_4 + Na_2SO_4 + H_2O$

Step 1: Remove spectator ions; leave only ions which undergo oxidation state changes.

- Spectator ion: ions that do not take part directly in chemical change, but are present in the system. In this case: K^+, Na^+, Cl^- (of $MnCl_2$), and SO_4^{2-} do not change oxidation state and are thus removed
- Metal cations in the first two columns of the periodic table (Li, Na, K, Rb. Cs, Be, Mg, Ca, Sr, Ba) are usually present as ions that do not change oxidation state and are thus removed.
- Certain polyatomic ions to not ionize apart, and must be treated in tact. A partial list:

CN^-	cyanide	SiO_4^{4-}	silicate
CNO^-	cyanate	PO_4^{3-}	phosphate
SCN^-	thiocyanate	HPO_4^{2-}	hydrogenphosphate
MnO_4^-	permanganate	$H_2PO_4^-$	dihydrogenphosphate
CrO_4^{2-}	chromate	SO_3^{2-}	sulfite
$Cr_2O_7^{2-}$	dichromate	SO_4^{2-}	sulfate
CO_3^{2-}	carbonate	HSO_4^-	hydrogensulfate
HCO^{3-}	hydrogencarbonate	ClO^-	chlorite
NO_2^-	nitrite	ClO_3^-	chlorate
NO_3^-	nitrate	ClO_4^-	perchlorate

This table will be provided on an exam if needed. It does not need to be memorized.

- Organic compounds are always treated in tact.
- Also remove all H^+, H_3O^+, H_2O, and HO^- (these are returned during balancing process)

$$MnO_4^- + Cl^- \rightarrow Mn^{2+} + Cl_2$$

Step 2: Write two unbalanced half-equations: One for the oxidation reaction, and one for the reduction reaction.

Half-reaction: A hypothetical oxidation or reduction reaction, pictured in isolation, to emphasize e^- gain or e^- loss.

Reduction half-reaction: $MnO_4^- \rightarrow Mn^{2+}$ (Mn^{7+} to Mn^{2+} = reduction)

Oxidation half-reaction: $Cl^- \rightarrow Cl_2$ (Cl^- to Cl^0 = oxidation)

Step 3: Insert coefficients to balance all elements except O and H.

Reduction half-reaction: $MnO_4^- \rightarrow Mn^{2+}$ *no adjustment needed*

Oxidation half-reaction: $\underline{\mathbf{2}}\ Cl^- \rightarrow Cl_2$

Step 4: Balance oxygen: Add water molecules to one side as needed.

Reduction half-reaction: $MnO_4^- \rightarrow Mn^{2+}\ \underline{\mathbf{+\ 4\ H_2O}}$

Oxidation half-reaction: $2\ Cl^- \rightarrow Cl_2$ *no adjustment needed*

Step 5: Balance hydrogen.

- Acidic solution: Add H_3O^+ to side which is hydrogen deficient, and an equal number of H_2O to other side. Each H_3O^+/H_2O pair adds one H to the H_3O^+ side.
- Basic solution: Add H_2O to side that is hydrogen deficient, and an equal number of HO^- to the other side. Each HO^-/H_2O pair adds one H to H_2O side.

Reduction half-reaction: $MnO_4^-\ \underline{\mathbf{+\ 8\ H_3O^+}} \rightarrow Mn^{2+} + 4\ H_2O\ \underline{\mathbf{+\ 8\ H_2O}}$

$MnO_4^-\ \underline{\mathbf{+\ 8\ H_3O^+}} \rightarrow Mn^{2+}\ \underline{\mathbf{+\ 12\ H_2O}}$ (H_2O combined)

Oxidation half-reaction: $2\ Cl^- \rightarrow Cl_2$ *no adjustment needed*

Step 6: Balance charge: Add electrons (e^-) as needed to balance total charge on each half-reaction.

Reduction half-reaction: $MnO_4^- + 8\ H_3O^+ \rightarrow Mn^{2+} + 12\ H_2O$

$(1^-) + (8^+) \rightarrow (2^+) + (0)$ therefore add 5 e^- to left:

$MnO_4^- + 8\ H_3O^+\ \underline{\mathbf{+\ 5\ e^-}} \rightarrow Mn^{2+} + 12\ H_2O$

Oxidation half-reaction: $2\ Cl^- \rightarrow Cl_2$

$2^- \rightarrow 0$ therefore add 2 e^- to right:

$2\ Cl^- \rightarrow Cl_2\ \underline{\mathbf{+\ 2\ e^-}}$

Step 7: Balance electrons transferred: Multiply the two half-reactions so that the number of electrons gained or lost is equal for the two half-reactions.

Reduction half-reaction: $MnO_4^- + 8\ H_3O^+ + 5\ e^- \rightarrow Mn^{2+} + 12\ H_2O$

2 x (2 e^- lost in other half reaction): $\underline{\mathbf{2}}\ MnO_4^- + \underline{\mathbf{16}}\ H_3O^+ + \underline{\mathbf{10}}\ e^- \rightarrow \underline{\mathbf{2}}\ Mn^{2+} + \underline{\mathbf{24}}\ H_2O$

Oxidation half-reaction: $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$

5 x (5 e^- gained in other half-reaction): $\underline{\mathbf{10}}\ Cl^- \rightarrow \underline{\mathbf{5}}\ Cl_2 + \underline{\mathbf{10}}\ e^-$

Step 8: Add the half-reactions. Cancel out species that are the same on each side.

Reduction: $2\ MnO_4^- + 16\ H_3O^+ + 10\ e^- \rightarrow 2\ Mn^{2+} + 24\ H_2O$

Oxidation: $10\ Cl^- \rightarrow 5\ Cl_2 + 10\ e^-$

Total: $2\ MnO_4^- + 16\ H_3O^+ \underline{\mathbf{+\ 10\ e^-}} + 10\ Cl^- \rightarrow 2\ Mn^{2+} + 24\ H_2O + 5\ Cl_2 \underline{\mathbf{+\ 10\ e^-}}$

Canceling out gives the balanced equation:

$$2\ MnO_4^- + 16\ H_3O^+ + 10\ Cl^- \rightarrow 2\ Mn^{2+} + 24\ H_2O + 5\ Cl_2$$

Step 9: Check the atom balance.

Left	Right
Mn - 2	Mn - 2
O - 24	O - 24
H - 48	H - 48
Cl -10	Cl - 10

The reduction and oxidation portion of the equation is now balanced. Spectator ions are next added and balanced, if required.