9701 CHEMISTRY · TOPIC 6 · AS LEVEL

Redox and Electrolysis — AS

01 · OXIDATION AND REDUCTION

Oxidation — loss of electrons, oxidation number rises. **Reduction** — gain of electrons, oxidation number falls. **OIL RIG.**

The **oxidising agent** is itself reduced; the **reducing agent** is itself oxidised. Name the agent, not the process, when asked which is which.

02 · OXIDATION NUMBER RULES

Species	O.N.
uncombined element	0
simple ion	the charge
Group 1 / 2	+1 / +2
H	+1 (−1 in hydrides)
O	−2 (−1 in peroxides, +2 in OF_2)
F	always −1

Sum = 0 for a neutral compound, = charge for an ion. Roman numerals in a name give the oxidation number: manganate(VII), iron(III).

03 · BUILDING REDOX EQUATIONS

Half-equation method

1 · balance the main element
2 · balance O with H_2O
3 · balance H with H^+
4 · balance charge with e^-
5 · scale so electrons cancel, then add

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

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

04 · DISPROPORTIONATION

One element is simultaneously oxidised and reduced in the same reaction.

$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$ — chlorine goes from 0 to −1 and to +1. Also $2H_2O_2 \rightarrow 2H_2O + O_2$ and Cu^+ in acid.

05 · ELECTROLYSIS

Cathode (−) attracts cations, which are **reduced**. **Anode (+)** attracts anions, which are **oxidised**. Current flows only when ions are mobile — molten or in solution.

In aqueous solution the water can discharge instead: H_2 at the cathode for reactive metals, O_2 at the anode unless a halide is concentrated.

06 · FARADAY CALCULATIONS

$$Q = It \cdot n(e^-) = Q \div F$$
$$F = 96\,500\ C\ mol^{-1}$$

2.00 A for 30.0 min through $CuSO_4(aq)$.
$Q = 2.00 \times 1800 = 3600$ C
$n(e^-) = 3600 \div 96\,500 = 0.0373$ mol
$Cu^{2+} + 2e^- \rightarrow Cu$, so $n(Cu) = 0.0187$ mol
$m = 0.0187 \times 63.5 =$ **1.19 g**

07 · COMMON OXIDISING AND REDUCING AGENTS

Reagent	Becomes	Colour change
MnO_4^- / H^+	Mn^{2+}	purple → colourless
$Cr_2O_7^{2-}$ / H^+	Cr^{3+}	orange → green
I_2	I^-	brown → colourless
Fe^{2+}	Fe^{3+}	pale green → yellow
$S_2O_3^{2-}$	$S_4O_6^{2-}$	used in iodine titrations

Manganate(VII) titrations are self-indicating — the first permanent pink is the end point. Use dilute H_2SO_4, never HCl (chloride is oxidised) and never HNO_3 (itself an oxidising agent).

08 · ELECTROLYSIS PRODUCTS IN SOLUTION

Electrolyte	Cathode	Anode
conc. NaCl(aq)	H_2	Cl_2
dilute NaCl(aq)	H_2	O_2
$CuSO_4$(aq), Pt	Cu	O_2
molten NaCl	Na	Cl_2

A metal below hydrogen in reactivity is deposited; a more reactive one leaves H_2 instead. With copper electrodes in $CuSO_4$ the anode dissolves — the basis of electroplating and purification.

09 · ELECTRODE HALF-EQUATIONS

Cathode (reduction)
$Cu^{2+} + 2e^- \rightarrow Cu$
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode (oxidation)
$2Cl^- \rightarrow Cl_2 + 2e^-$
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

The same quantity of charge passes through both electrodes, so the mole ratio of products follows the electrons in each half-equation.

10 · WORKED EXAMPLE — OXIDATION NUMBERS

Cr in $Cr_2O_7^{2-}$: $2x + 7(-2) = -2 \rightarrow x =$ **+6**

S in H_2SO_4: $2(+1) + x + 4(-2) = 0 \rightarrow x =$ **+6**

N in NH_4^+: $x + 4(+1) = +1 \rightarrow x =$ **−3**

Cl in ClO_3^-: $x + 3(-2) = -1 \rightarrow x =$ **+5**

11 · USES OF ELECTROLYSIS

Extraction of aluminium — molten Al_2O_3 in cryolite, which lowers the melting point and cuts the energy cost. Carbon anodes burn away as CO_2 and must be replaced.

Purification of copper — impure Cu anode dissolves, pure Cu deposits on the cathode; the impurities drop as anode sludge.

Electroplating — the object is the cathode and the plating metal the anode, in a solution of that metal's salt.

12 · WORKED EXAMPLE — TWO CELLS IN SERIES

The same current passes through $AgNO_3$(aq) and $CuSO_4$(aq). 1.08 g of Ag is deposited.

$Ag^+ + e^- \rightarrow Ag$: $n(Ag) = 1.08 \div 107.9 = 0.0100$ mol
$n(e^-) = 0.0100$ mol — the same in both cells
$Cu^{2+} + 2e^- \rightarrow Cu$: $n(Cu) = 0.00500$ mol
$m(Cu) = 0.00500 \times 63.5 =$ **0.318 g**

13 · WORKED EXAMPLE — REDOX TITRATION

25.0 cm^3 of Fe^{2+} solution needs 21.5 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$ in excess dilute H_2SO_4.

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

$n(MnO_4^-) = 0.0200 \times 0.0215 = 4.30 \times 10^{-4}$ mol
$n(Fe^{2+}) = 5 \times 4.30 \times 10^{-4} = 2.15 \times 10^{-3}$ mol
$c(Fe^{2+}) = 2.15 \times 10^{-3} \div 0.0250 =$ **0.0860 mol dm^{-3}**

End point: the first permanent pale pink.

MARKS LOST HERE

— Naming the oxidising agent as the species that is oxidised.

— Leaving time in minutes inside Q = It.

— Forgetting the electron ratio from the half-equation before converting to mass.

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Electrode Potentials — A2

14 · STANDARD CONDITIONS

All solutions 1 mol dm^{-3}, gases at 100 kPa, temperature 298 K, measured against the **standard hydrogen electrode** which is defined as 0.00 V.

A platinum electrode is used where no solid metal is involved — it is inert and provides a surface for electron transfer. The salt bridge (KNO_3) completes the circuit and balances charge without mixing the solutions.

15 · READING E° VALUES

Data-booklet half-equations are written as **reductions**. A **more positive E°** means a greater tendency to be reduced, so that species is the better oxidising agent.

A **more negative E°** means the reduced form is the better reducing agent. The more negative half-cell runs backwards and forms the negative electrode.

16 · CELL E.M.F.

$$E^\circ_{cell} = E^\circ(\text{reduced, +ve}) - E^\circ(\text{oxidised, −ve})$$

Zn^{2+}/Zn $E^\circ = -0.76$ V, Cu^{2+}/Cu $E^\circ = +0.34$ V

$E^\circ_{cell} = +0.34 - (-0.76) =$ **+1.10 V**
Zn is oxidised (negative electrode), Cu^{2+} reduced.
$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Cell diagram: $Zn \mid Zn^{2+} \vdots\vdots Cu^{2+} \mid Cu$

Positive E°_{cell} → the reaction is feasible.

Feasible does not mean fast: a large E_a can still make it immeasurably slow.

17 · EFFECT OF CONCENTRATION

Apply Le Chatelier to the half-equation. Raising the concentration of the **oxidised** species drives the reduction forward and makes E° **more positive**; raising the reduced species makes it more negative.

For MnO_4^-/Mn^{2+}, raising $[H^+]$ makes E more positive — which is why acidified manganate(VII) is the stronger oxidising agent.

18 · ΔG AND E°

$$\Delta G^\circ = -n\,F\,E^\circ_{cell}$$

n = moles of electrons transferred, F = 96 500 C mol^{-1}. Answer in J mol^{-1} — divide by 1000 for kJ mol^{-1}. A positive E°_{cell} gives a negative ΔG°, the same feasibility test seen twice.

19 · CELLS IN USE

Fuel cell (H_2/O_2, alkaline): anode $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$, cathode $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. Only product is water; efficiency is high, but storing and transporting H_2 is the difficulty.

Rechargeable cells reverse the electrode reactions on charging. Redox potentials also explain corrosion: a metal with a more negative E° protects one with a less negative E° (sacrificial protection of iron by zinc).

20 · PREDICTING REACTIONS FROM E°

Will Br_2 oxidise Fe^{2+}?

$Br_2 + 2e^- \rightarrow 2Br^-$ $E^\circ = +1.07$ V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^\circ = +0.77$ V

Br_2 has the more positive E°, so it is reduced and Fe^{2+} oxidised.
$E^\circ_{cell} = 1.07 - 0.77 =$ **+0.30 V** → feasible.

I_2 ($E^\circ = +0.54$ V) would **not** oxidise Fe^{2+}: $E^\circ_{cell} = -0.23$ V.

21 · HALF-CELL TYPES

Type	Example
metal / metal ion	$Zn(s) \mid Zn^{2+}(aq)$
gas / ion, Pt	$Pt \mid H_2(g) \mid H^+(aq)$
two ions, Pt	$Pt \mid Fe^{2+}, Fe^{3+}$
ion / solid, Pt	$Pt \mid MnO_4^-, Mn^{2+}, H^+$

In a cell diagram, | is a phase boundary and ⋮⋮ the salt bridge; the oxidised form is written next to the bridge on each side.

22 · WORKED EXAMPLE — ΔG° FROM E°

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, $E^\circ_{cell} = +1.10$ V, n = 2.

$\Delta G^\circ = -nFE^\circ$
$\Delta G^\circ = -2 \times 96\,500 \times 1.10$
$\Delta G^\circ = -212\,300$ J mol^{-1}
$\Delta G^\circ =$ **−212 kJ mol^{-1}**

Strongly negative, so the reaction is thermodynamically feasible.

23 · DISPROPORTIONATION FROM E° VALUES

A species disproportionates when its own reduction has a **more positive** E° than its own oxidation — the two half-reactions combine to give a positive E°_{cell}.

$Cu^+ + e^- \rightarrow Cu$ $E^\circ = +0.52$ V
$Cu^{2+} + e^- \rightarrow Cu^+$ $E^\circ = +0.15$ V

$E^\circ_{cell} = 0.52 - 0.15 =$ **+0.37 V**
$2Cu^+ \rightarrow Cu + Cu^{2+}$ is feasible, which is why Cu^+ is unstable in aqueous solution.

24 · E° VALUES WORTH REMEMBERING

Half-cell	E° / V
F_2 / F^-	+2.87
$MnO_4^-, H^+ / Mn^{2+}$	+1.52
$Cr_2O_7^{2-}, H^+ / Cr^{3+}$	+1.33
Fe^{3+} / Fe^{2+}	+0.77
Cu^{2+} / Cu	+0.34
$2H^+ / H_2$	0.00
Zn^{2+} / Zn	−0.76

The list is the reactivity series in another form: the most negative metals are the strongest reducing agents, the most positive non-metals the strongest oxidising agents.

25 · CORROSION AND PROTECTION

Rusting is electrochemical: $Fe \rightarrow Fe^{2+} + 2e^-$ at the anodic region, while oxygen is reduced at the cathodic region. Both water and oxygen are needed, and salt speeds it up by carrying the current.

Sacrificial protection — attach a metal with a more negative E° (Zn or Mg) so it corrodes instead. Galvanising does both: the zinc coats the surface and protects sacrificially where it is scratched.

MARKS LOST HERE

— Multiplying E° when scaling a half-equation; E° is intensive and never multiplied.

— Subtracting the wrong way round and reporting a negative E°_{cell} for a feasible cell.

— Treating "feasible" as "will actually happen quickly".

— Forgetting that the quoted values only hold under standard conditions.