Topic 4.9: Introduction to Oxidation-Reduction Reactions

Revision Notes · AP Chemistry

UNIT 4 · CHEMICAL REACTIONS

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Redox Means Electrons Change Hands

Oxidation is the loss of electrons. Reduction is the gain of electrons. The memory hook is OIL RIG: Oxidation Is Loss, Reduction Is Gain.

The two never happen alone. Electrons lost by one species must be gained by another, so every oxidation is matched by a reduction; together, the process is a redox reaction.

Oxidation numbers track the transfer: the number increases in oxidation and decreases in reduction.

In $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, zinc moves from 0 to +2, losing two electrons per atom: oxidised. Copper moves from +2 to 0, gaining them: reduced.

Oxidation Numbers: The Bookkeeping Rules

Free elements are 0. Na, O_2 and Cl_2 are all 0.

A monatomic ion takes its charge. Na^+ is +1, Cl^- is −1, Al^{3+} is +3.

Fluorine is always −1, the most electronegative element, so it takes the negative value in every compound.

Oxygen is usually −2. In peroxides, such as H_2O_2, it is −1, because the two oxygens are bonded to each other. Bonded to fluorine it is positive: in OF_2 oxygen is +2.

Hydrogen is usually +1 with nonmetals. In metal hydrides, such as NaH, the metal is less electronegative than hydrogen, so hydrogen is −1.

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The sum rule ties it together. Oxidation numbers add up to 0 in a neutral compound and to the charge on a polyatomic ion. Fixed values help: Group 1 metals are +1, Group 2 metals +2, aluminium +3.

Oxidation numbers are bookkeeping, not real charges: carbon is +4 in CO_2, but no C^{4+} ion exists there.

Finding an Unknown Oxidation Number

Use the sum rule as an equation: insert the unknown, fill in the known values, solve.

Sulfur in H_2SO_4: $2(+1) + S + 4(-2) = 0$, so S = +6.

Nitrogen in NO_3^-: $N + 3(-2) = -1$, so N = +5.

Chromium in $Cr_2O_7^{2-}$: $2Cr + 7(-2) = -2$, so $2Cr = +12$ and Cr = +6.

The Agents Do the Opposite of Their Names

The oxidising agent takes electrons from its partner, causing oxidation, and is itself reduced in the process.

The reducing agent gives electrons to its partner, causing reduction, and is itself oxidised.

In $2Na + Cl_2 \rightarrow 2NaCl$, chlorine gains electrons, falling from 0 to −1: chlorine is reduced, so Cl_2 is the oxidising agent. Sodium loses electrons and is oxidised, so Na is the reducing agent.

The strongest oxidising agent is the species most readily reduced: the one that takes electrons most eagerly, and so oxidises its partners most powerfully.

Half-Reactions: Balancing in Acidic Solution

Splitting an equation into an oxidation half and a reduction half shows the electrons explicitly and makes balancing systematic.

In each half, balance the atoms other than oxygen and hydrogen first. Balance oxygen by adding H_2O, hydrogen by adding H^+, which acidic solution supplies freely. Then balance charge by adding electrons: on the right of an oxidation half, on the left of a reduction half.

Multiply the halves so electrons lost equal electrons gained, add them, and the electrons cancel. Finish by checking atoms and total charge.

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For basic solutions, balance as for acid first, then add OH^- to both sides to convert H^+ into H_2O, and cancel duplicated water.

Disproportionation: One Species, Both Jobs

In a disproportionation reaction, the same species is both oxidised and reduced: part of it climbs to a higher oxidation number, part falls to a lower one. The element must start in an intermediate state, able to move both ways.

Decomposing hydrogen peroxide, $2H_2O_2 \rightarrow 2H_2O + O_2$: oxygen starts at -1, falls to -2 in H_2O (reduced) and rises to 0 in O_2 (oxidised). Chlorine in alkali does the same: $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$, chlorine moving from 0 to both -1 and $+1$.

Redox Titrations

A redox titration spends the electron transfer itself as the measurement. The balanced equation gives the mole ratio between titrant and analyte, and the titre at the endpoint converts that ratio into the unknown concentration, as in Topic 4.6 but with the ratio set by electrons, not protons.

Permanganate is self-indicating: MnO_4^- is purple, its product Mn^{2+} colourless, so no separate indicator is needed; the endpoint is the first permanent purple tinge.

The ratio is rarely 1 to 1: Fe^{2+} to MnO_4^- runs 5 to 1, and assuming equal moles would miss the answer by a factor of five.

Worked Examples

> **Example 1: Redox or not, decided by the numbers. In $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, carbon moves from -4 to $+4$: oxidised. Oxygen moves from 0 to -2: reduced. Numbers moved, so the reaction is redox. In $CaCO_3 \rightarrow CaO + CO_2$, calcium stays $+2$, carbon $+4$ and oxygen -2 on both sides: nothing moved, so this decomposition is not redox.**

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Example 2: Balancing MnO_4^- + Fe^{2+} in acid. Oxidation half: $Fe^{2+} \rightarrow Fe^{3+} + e^-$, atoms already balanced, one electron fixing the charge. Reduction half: $MnO_4^- \rightarrow Mn^{2+}$. Add $4H_2O$ on the right for the oxygens, $8H^+$ on the left for the hydrogens. The left now carries charge $-1 + 8 = +7$ against +2 on the right, so add $5e^-$ to the left: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$, matching manganese falling from +7 to +2. Multiply the oxidation half by 5 and add: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$. Check: atoms match, charge +17 on each side.

Example 3: A titration with a 5 to 1 ratio. A 25.0 mL sample of Fe^{2+} solution needs 24.0 mL of 0.0200 mol/L $KMnO_4$ to reach the endpoint. Moles of MnO_4^- = $0.0200 \times 0.0240 = 4.80 \times 10^{-4}$ mol. With Fe^{2+} : MnO_4^- at 5 : 1, moles of Fe^{2+} = $5 \times 4.80 \times 10^{-4} = 2.40 \times 10^{-3}$ mol. Concentration = $2.40 \times 10^{-3} \div 0.0250 = 0.0960$ mol/L.

Traps That Cost Marks in Topic 4.9

Naming the agent after its own fate. The oxidising agent is itself reduced; the reducing agent is itself oxidised. Find the electron flow first, then name each agent by what it does to its partner.

Treating oxidation numbers as real ionic charges. They are a counting scheme: sulfur is +6 in H_2SO_4 without any S^{6+} ion existing.

Missing the three exceptions. Free elements are 0, so oxygen in O_2 is 0, not −2; oxygen in peroxides is −1; hydrogen in metal hydrides is −1. Questions target exactly these cases.

Putting the electrons on the wrong side. Oxidation produces electrons, so they are written as products; reduction consumes them, so they are written as reactants. $MnO_4^- \rightarrow Mn^{2+}$ gains $5e^-$, and those electrons belong on the left.

Balancing the atoms and forgetting the charge. An equation is balanced only when atoms and total charge both match; the charge check is what fixes how many electrons a half-reaction needs.

Carrying the 1 to 1 habit into redox titrations. Ratios come from the balanced equation: 5 Fe^{2+} per MnO_4^-, 6 Fe^{2+} per $Cr_2O_7^{2-}$, 2 $S_2O_3^{2-}$ per I_2.

Hunting for redox in partner swapping. Double replacement and acid-base reactions change no oxidation number, so are never redox; single replacement and combustion always are.

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Key Relationships to Remember

- Oxidation is loss of electrons and the oxidation number rises; reduction is gain and the number falls; OIL RIG; the two always occur together
- Oxidising agent: gains electrons, is itself reduced, causes oxidation. Reducing agent: loses electrons, is itself oxidised, causes reduction. The strongest oxidising agent is the species most readily reduced
- Oxidation number rules: free element 0; monatomic ion equals its charge; F −1; O −2 except peroxides (−1) and with fluorine (positive); H +1 except metal hydrides (−1); sums to 0 for a neutral compound, to the charge for an ion
- Half-reaction method in acid: balance other atoms, O with H_2O, H with H^+, charge with e^-; scale so electrons cancel; check atoms and charge
- Disproportionation: one species is oxidised and reduced at once, its key element starting in an intermediate state, as oxygen does at −1 in H_2O_2
- The redox test: assign oxidation numbers before and after; any change means redox. Single replacement and combustion always qualify; double replacement and acid-base never do
- Redox titrations turn on the balanced equation's mole ratio, not on 1 to 1: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$, and purple MnO_4^- is its own indicator

Continue Revising

Topic 4.9 Quiz: Introduction to Oxidation-Reduction Reactions

Topic 4.9 Worksheet

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