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Premium IB tuition — Physics, Chemistry, Maths

IB DIPLOMA CHEMISTRY · FIRST ASSESSMENT 2025

Structure 3.1 The Periodic Table

Booklet 2 · Understandings 3.1.6 – 3.1.7

Oxidation states: what they mean, how to assign them, naming with Roman numerals and spotting redox reactions; HL discontinuities in first ionization energy as evidence for sublevels

Complete revision notes & memory points · Standard Level & Higher Level

How the level tags work in this booklet

SL + HL Core material. Understanding **3.1.6 (oxidation states)** is common to both levels. Every student must know it.

HL Additional higher level material: **3.1.7 (discontinuities in first ionization energy)** in section 7, and the oxidation states of metals in complex ions (section 3.5). SL students can skip these and the questions marked HL.

Inside this booklet

1. What the syllabus actually asks of you
2. 3.1.6 — What an oxidation state is
3. 3.1.6 — Assigning oxidation states
4. 3.1.6 — Oxidation states and the periodic table
5. 3.1.6 — Naming compounds with oxidation numbers
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1 What the syllabus actually asks of you

Oxidation states are a piece of book-keeping: a way of keeping track of electrons. They are introduced here, in the periodic table topic, because the oxidation states an element can show depend on its position in the table. You will use them constantly in **Reactivity 3.2** (redox reactions, half-equations, electrochemical cells) and in naming inorganic compounds. The HL understanding 3.1.7 returns to the first ionization energy graph and asks you to explain its small dips, which are evidence that energy levels are divided into sublevels.

Understanding	What it says	What you must be able to do	Level
3.1.6 Oxidation states	The oxidation state is a number assigned to an atom to show the number of electrons transferred in forming a bond. It is the charge the atom would have if the compound were composed of ions.	Deduce the oxidation states of an atom in an ion or a compound. Explain why the oxidation state of an element is zero. Write oxidation states as a sign followed by a number (+2, −1). Include hydrogen in metal hydrides (−1) and oxygen in peroxides (−1). "Oxidation number" and "oxidation state" are both accepted. Roman numerals are used in names, but generic names (nitrate, nitrite, sulfate, sulfite) are also acceptable.	SL+HL
3.1.7 Discontinuities in first IE	Discontinuities occur in the trend of increasing first ionization energy across a period.	Explain how these discontinuities provide evidence for the existence of energy sublevels. Explanations must be based on the **energy of the electron removed**, not on the "special stability" of filled or half-filled sublevels.	HL

Linking questions and connections for 3.1.6 – 3.1.7

- **Reactivity 3.2:** how can oxidation states be used to analyse redox reactions? → section 6
- **Structure 2.2:** electronegativity decides which atom "gets" the bonding electrons when you assign oxidation states. → section 2.3
- **Structure 3.1.5 (Booklet 1):** the highest oxidation state of a period 3 element in its oxide equals its number of valence electrons; the acids in acid rain are named with oxidation numbers. → sections 4 and 5
- **Structure 1.3 (HL):** orbital diagrams, Hund's rule and ionization energies. → section 7
- **Structure 3.1.8 – 3.1.10 (HL, Booklet 3):** variable oxidation states of the transition elements.

What the data booklet gives you — and what it does not

The data booklet gives **electronegativity values** (Section 9), which tell you which atom in a bond is treated as negative, and **first ionization energies** (Section 9) for the HL section. It does **not** give rules for assigning oxidation states, the exceptions for hydrides and peroxides, or the names of oxyanions. All of these must be learned.

2 Structure 3.1.6 — What an oxidation state is SL + HL

2.1 Oxidation is more than adding oxygen

The word *oxidation* first meant combining with oxygen. When magnesium burns, it forms magnesium oxide, an ionic compound: each magnesium atom has **lost two electrons** to become Mg^{2+}.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \quad Mg \rightarrow Mg^{2+} + 2e^-$$

But magnesium loses electrons in exactly the same way when it reacts with chlorine, where no oxygen is involved: $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$. So chemists extended the idea. Any process in which an atom **loses electrons** is an oxidation, and any process in which an atom gains electrons is a reduction. Oxidation states turn this into numbers.

Definition based on	Oxidation	Reduction
oxygen	gain of oxygen	loss of oxygen
hydrogen	loss of hydrogen	gain of hydrogen
electrons	**loss of electrons**	**gain of electrons**
oxidation state	**increase in oxidation state**	**decrease in oxidation state**

The last two rows are the most general and the ones you will use. A helpful memory aid is **OIL RIG**: **O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain (of electrons).

2.2 The definition

> **Definition to learn**
>
> The **oxidation state** of an atom is a number that shows how many electrons it has lost or gained, or has partly lost or gained, in forming its bonds. It is the charge the atom **would have if the compound were made of ions**. It is written as a sign followed by a number: +2, −1, 0.

In an **ionic** compound this is easy: the oxidation state is the real charge on the ion. In NaCl, sodium is +1 and chlorine is −1. In MgO, magnesium is +2 and oxygen is −2.

2.3 Covalent compounds: pretend they are ionic

In a covalent bond the electrons are shared, not transferred, so we have to **pretend**. The bonding electrons are given entirely to the **more electronegative** atom, which is the one that already pulls them closer. Each atom then gets the "charge" it would have if that were true.

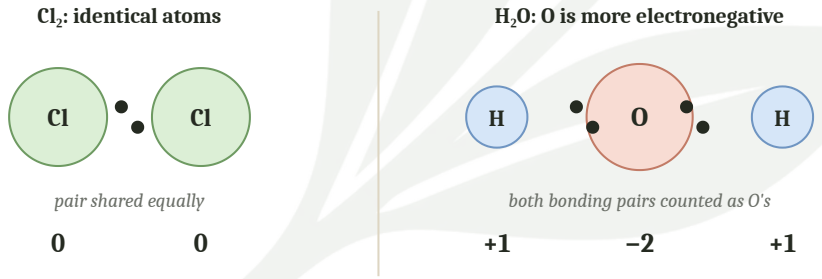


Figure 1 — In Cl_2 both atoms are identical, so neither gains control of the shared pair: both are 0. In water, oxygen is more electronegative (3.4 compared with 2.2), so both bonding pairs are counted as oxygen's: O is −2 and each H is +1.

> **The idea in one line**
>
> A **positive** oxidation state means the atom has lost some control of its electrons to a more electronegative partner. A **negative** oxidation state means it has gained control of electrons. An **increase** in oxidation state is oxidation; a **decrease** is reduction.

2.4 Why the oxidation state of an element is zero

In an uncombined element, such as Na, Fe, O_2, Cl_2, S_8 or diamond, every atom is bonded only to identical atoms (or to nothing at all). Identical atoms have the **same electronegativity**, so any shared electrons are shared **equally**; no atom gains or loses control of electrons, and no electrons are transferred. The oxidation state of every atom in an element is therefore **0**.

Model answer: "Explain why the oxidation state of chlorine in Cl_2 is zero." (2 marks)

Both atoms in the Cl–Cl bond are identical and have the same electronegativity, so the bonding pair is shared equally **[1]**. Neither atom gains or loses electrons (no electron transfer), so neither has a charge, and the oxidation state is zero **[1]**.

3 Structure 3.1.6 — Assigning oxidation states SL + HL

3.1 The rules

Apply the rules in this order. When two rules seem to clash, the one higher in the list wins.

#	Rule	Examples
1	Atoms in an **element** are 0.	Na, Fe, H_2, O_2, O_3, P_4, S_8, Ar: all 0
2	In a **simple ion**, the oxidation state equals the charge.	Fe^{3+} +3; Cl^- −1; N^{3-} −3
3	The oxidation states in a **neutral compound** add up to **0**; in a **polyatomic ion** they add up to the **charge on the ion**.	H_2SO_4: sum = 0; SO_4^{2-}: sum = −2
4	**Fluorine** is always −1 in compounds (it is the most electronegative element).	HF, OF_2, SF_6: F is −1
5	**Group 1** metals are +1, **group 2** metals +2, and **aluminium** +3 in compounds.	Na_2SO_4: Na +1; $CaCO_3$: Ca +2
6	**Hydrogen** is +1, **except in metal hydrides**, where it is −1 (hydrogen is more electronegative than the metal).	H_2O, NH_3: +1; NaH, CaH_2, $LiAlH_4$: −1
7	**Oxygen** is −2, **except in peroxides** (−1) and when bonded to fluorine (positive).	H_2O_2, Na_2O_2, BaO_2: −1; OF_2: +2
8	**Chlorine, bromine and iodine** are −1, except when bonded to oxygen or to a more electronegative halogen.	NaCl: −1; ClO^-: +1; ClF: +1; ClO_4^-: +7
9	Any other element: work it out from the others using rule 3.	see the worked examples below

3.2 Method

1. Write down the oxidation states you **know** from the rules (F, group 1, group 2, H, O, halogens).
2. Multiply each one by the **number of those atoms** in the formula.
3. Set the total equal to **0** for a neutral compound, or to the **charge** for an ion. Solve for the unknown.
4. If there are two atoms of the unknown element, divide by 2 at the end. Give the answer **per atom**, with its sign.

Worked examples — five species

Species	Working	Answer
HNO_3	$(+1) + N + 3(-2) = 0 \Rightarrow N = +6 - 1$	N = **+5**
NH_4^+	$N + 4(+1) = +1 \Rightarrow N = +1 - 4$	N = **−3**
$K_2Cr_2O_7$	$2(+1) + 2Cr + 7(-2) = 0 \Rightarrow 2Cr = +12$	Cr = **+6** (each)
ClO_3^-	$Cl + 3(-2) = -1 \Rightarrow Cl = -1 + 6$	Cl = **+5**
H_2O_2	peroxide, so O is −1: $2(+1) + 2(-1) = 0$ ✓	O = **−1**

Worked example — carbon changes its oxidation state as it is oxidized

Carbon is more electronegative than hydrogen (2.6 compared with 2.2) but less than oxygen (3.4). Each C–H bond therefore counts −1 towards carbon, and each bond to oxygen counts +1. Follow carbon as methane is oxidized step by step:

Compound	CH_4	CH_3OH	HCHO	HCOOH	CO_2
Oxidation state of C	−4	−2	0	+2	+4

Each step (gain of O or loss of H) increases the oxidation state of carbon by 2, which is exactly what "oxidation" means. Note that carbon is 0 in methanal even though methanal is a compound: a zero oxidation state does not always mean an element.

3.3 When the answer is a fraction

Sometimes the rules give a fraction, for example S in the tetrathionate ion $S_4O_6^{2-}$: $4S + 6(-2) = -2$, so S = +2.5. An atom cannot lose half an electron. A fractional answer is an **average** over atoms that are in different environments: in $S_4O_6^{2-}$, the two central sulfur atoms are bonded only to sulfur (0) and the two outer ones are +5. Similarly, Fe_3O_4 gives an average of +8/3 because it contains one Fe^{2+} and two Fe^{3+} ions. If a question gives a fractional answer, quote the average.

3.4 Writing oxidation states correctly

Oxidation state

Sign **first**, then the number, written as an Arabic numeral: **+2**, **−1**. Always include the sign, even for positive values. It refers to **one atom**.

Ionic charge

Number **first**, then the sign, written as a superscript: Mg^{2+}, Cl^-. It refers to the **whole ion**: the charge on $Cr_2O_7^{2-}$ is 2−, but each Cr is +6.

3.5 HL Oxidation states of metals in complex ions

Work back from the charges of the ligands

A complex ion contains a central metal ion bonded to **ligands** (Structure 2.2 and Booklet 3). Use the overall charge of the complex and the charges of the ligands. Neutral ligands such as H_2O and NH_3 contribute 0; anionic ligands such as Cl^-, CN^- and OH^- contribute −1 each.

Complex ion	Working	Metal
$[Cu(H_2O)_6]^{2+}$	Cu + 6(0) = +2	+2
$[Fe(CN)_6]^{3-}$	Fe + 6(−1) = −3 ⇒ Fe = +3	+3
$[CoCl_4]^{2-}$	Co + 4(−1) = −2 ⇒ Co = +2	+2
$[Cr(NH_3)_4Cl_2]^{+}$	Cr + 4(0) + 2(−1) = +1 ⇒ Cr = +3	+3

Examiner traps in assigning oxidation states

- Write **+2**, not 2+ and not "2". A missing sign usually loses the mark.
- Give the oxidation state **per atom**. In $Cr_2O_7^{2-}$, chromium is +6, not +12.
- Remember to multiply: in H_2SO_4 there are four oxygens (−8) and two hydrogens (+2).
- For an ion, the total equals the **charge**, not zero. Forgetting this is the most common error.
- Learn the exceptions: H is −1 in metal hydrides; O is −1 in peroxides and +2 in OF_2.
- An oxidation state of 0 does not prove that a substance is an element (carbon in HCHO is 0), but every element is 0.

4 Structure 3.1.6 — Oxidation states and the periodic table SL + HL

An element's position in the table limits the oxidation states it can have. Atoms lose or gain electrons until the next change would mean breaking into a full inner shell, which needs far too much energy.

- **Highest positive oxidation state** = the number of valence electrons (all of them used in bonding). For main-group elements this is the group number for groups 1 and 2, and the group number minus 10 for groups 13 to 17.
- **Most negative oxidation state** (non-metals only) = number of valence electrons − 8. This is the number of electrons needed to reach a noble gas configuration.
- **Metals** have positive oxidation states only in their compounds. Group 1 metals are always +1 and group 2 metals always +2: removing a further electron would mean breaking into a full inner shell, which needs a very large amount of energy.

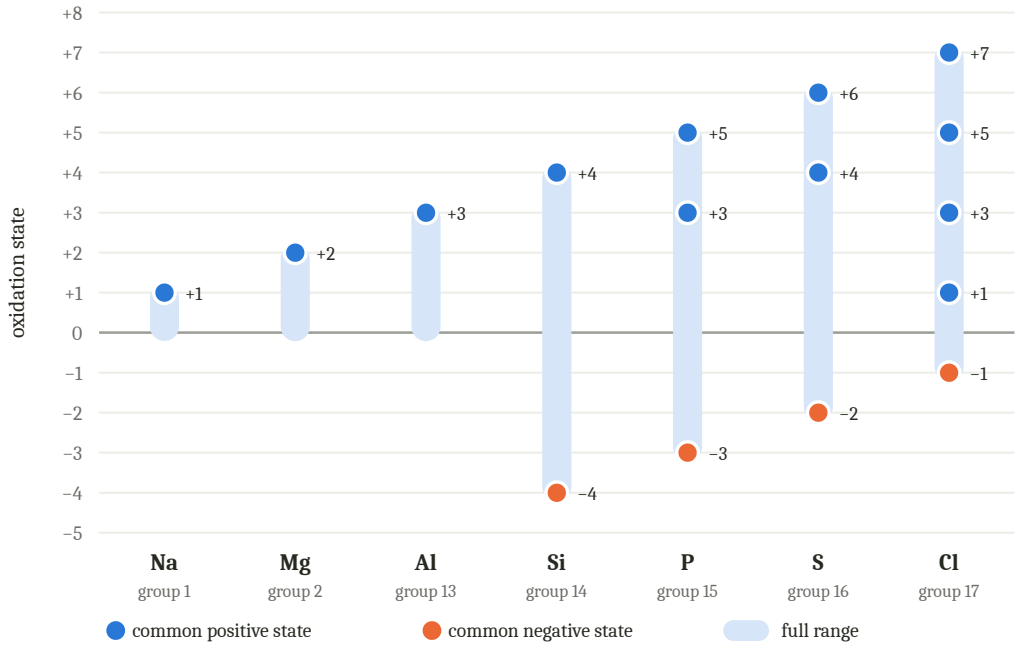


Figure 2 — Oxidation states of the period 3 elements. The highest positive state rises by one each step from +1 (Na) to +7 (Cl). Non-metals can also have negative states, down to −4 for Si, −3 for P, −2 for S and −1 for Cl. These are the oxidation states found in the oxides in Booklet 1 (Na_2O +1 to Cl_2O_7 +7).

Non-metals in the middle of the p block show the widest range. **Nitrogen** (five valence electrons) can be anything from +5, when all five are counted as lost to oxygen, to −3, when it gains three to complete its octet. This range is why nitrogen chemistry includes ammonia, the nitrogen oxides in acid rain and nitric acid.

HL Transition elements also show variable oxidation states, because their 3d and 4s electrons are close in energy. The highest states rise from Sc (+3) to Mn (+7), the total number of 3d and 4s electrons. This is developed in Booklet 3.

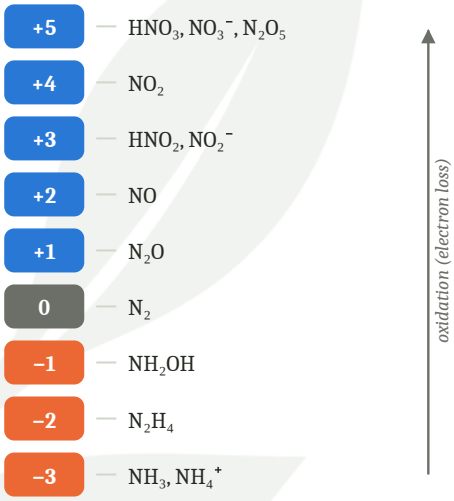


Figure 3 — Nitrogen from −3 to +5.

Model answer: "Explain why sulfur can have an oxidation state of +6 but not +7, and why its most negative oxidation state is −2." (3 marks)

Sulfur has six valence electrons ($3s^2\ 3p^4$) **[1]**. When bonded to more electronegative atoms such as oxygen, all six can be counted as lost, giving +6; a seventh electron would have to come from the full inner second shell, which needs far too much energy **[1]**. Sulfur needs only two more electrons to reach the configuration of argon, so its most negative state is −2 **[1]**.

5 Structure 3.1.6 — Naming compounds with oxidation numbers SL + HL

Many elements can have more than one oxidation state, so a name such as "iron chloride" is ambiguous: $FeCl_2$ or $FeCl_3$? IUPAC names solve this by putting the oxidation state as a **Roman numeral in brackets** directly after the name of the element, with no space. The terms **oxidation number** and **oxidation state** are used interchangeably, and both are accepted by the IB.

Two ways of writing the same idea

In a **formula or a calculation**, write the oxidation state with a sign and an Arabic numeral: Fe is +3 in $FeCl_3$. In a **name**, write it as a Roman numeral in brackets with no sign: iron(III) chloride. A negative value is never shown in a name.

5.1 Metals with variable oxidation states

Formula	Name	Formula	Name
$FeCl_2$	iron(II) chloride	$FeCl_3$	iron(III) chloride
Cu_2O	copper(I) oxide	CuO	copper(II) oxide
$SnCl_2$	tin(II) chloride	PbO_2	lead(IV) oxide
MnO_2	manganese(IV) oxide	Fe_2O_3	iron(III) oxide

Group 1 and group 2 metals, aluminium and zinc have only one oxidation state, so no numeral is used: sodium chloride, not sodium(I) chloride.

5.2 Oxyanions and oxoacids

The ending **-ide** means a simple anion with no oxygen (chloride, Cl^-). The ending **-ate** means an oxyanion (chlorate, ClO_3^-). The Roman numeral tells you the oxidation state of the central atom, so the systematic name tells you exactly which oxyanion is meant. Traditional names are still accepted.

Ion or acid	Oxidation state	Systematic name	Traditional name (accepted)
SO_4^{2-}	S +6	sulfate(VI)	sulfate
SO_3^{2-}	S +4	sulfate(IV)	sulfite
NO_3^-	N +5	nitrate(V)	nitrate
NO_2^-	N +3	nitrate(III)	nitrite
ClO^-	Cl +1	chlorate(I)	hypochlorite
ClO_3^-	Cl +5	chlorate(V)	chlorate
ClO_4^-	Cl +7	chlorate(VII)	perchlorate
MnO_4^-	Mn +7	manganate(VII)	permanganate
$Cr_2O_7^{2-}$	Cr +6	dichromate(VI)	dichromate
H_2SO_4 / H_2SO_3	S +6 / +4	sulfuric(VI) acid / sulfuric(IV) acid	sulfuric acid / sulfurous acid

Ion or acid	Oxidation state	Systematic name	Traditional name (accepted)
HNO_3 / HNO_2	N +5 / +3	nitric(V) acid / nitric(III) acid	nitric acid / nitrous acid
H_3PO_4	P +5	phosphoric(V) acid	phosphoric acid

Non-metal oxides can also be named in this way: NO_2 is nitrogen(IV) oxide, N_2O_5 is nitrogen(V) oxide and SO_3 is sulfur(VI) oxide (sulfur trioxide).

Worked example — from name to formula: sodium bromate(V) and iron(III) sulfate

Sodium bromate(V). "-ate" means an oxyanion of bromine; Br is +5. With O = −2, the ion BrO_3 has a charge of +5 + 3(−2) = −1, so it is BrO_3^-. Sodium is +1, so the formula is **$NaBrO_3$**.

Iron(III) sulfate. Fe^{3+} and SO_4^{2-}. To balance the charges you need 2 × (+3) = +6 and 3 × (−2) = −6, so the formula is **$Fe_2(SO_4)_3$**.

6 Structure 3.1.6 — Using oxidation states to analyse reactions SL + HL

6.1 Is it a redox reaction?

A **redox reaction** is one in which oxidation and reduction happen together: the electrons lost by one species are gained by another. To decide whether a reaction is redox, assign oxidation states to every element on both sides. If any element changes its oxidation state, the reaction is redox; if none do, it is not.

Definitions to learn

- **Oxidizing agent** (oxidant): a species that oxidizes another species by removing electrons from it. The oxidizing agent is itself **reduced**; its oxidation state decreases.
- **Reducing agent** (reductant): a species that reduces another species by giving electrons to it. The reducing agent is itself **oxidized**; its oxidation state increases.

Worked example — iron oxide in the blast furnace: $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$

Element	Reactant	Product	Change
Fe	+3 (in Fe_2O_3)	0 (element)	decreases: **reduced**
C	+2 (in CO)	+4 (in CO_2)	increases: **oxidized**
O	−2	−2	no change

This is a redox reaction. Fe_2O_3 is the **oxidizing agent** (it oxidizes CO and is itself reduced). CO is the **reducing agent** (it reduces Fe_2O_3 and is itself oxidized). Check the electrons: 2 Fe each gain 3 (6 in total); 3 C each lose 2 (6 in total) ✓.

Worked example — redox or not?

Reaction	Oxidation state changes	Verdict
$Cl_2 + 2KI \rightarrow 2KCl + I_2$	Cl 0 → −1; I −1 → 0	**redox**
$2SO_2 + O_2 \rightarrow 2SO_3$	S +4 → +6; O 0 → −2	**redox**
$Na_2O + H_2O \rightarrow 2NaOH$	Na +1, O −2, H +1 throughout	not redox
$HCl + NaOH \rightarrow NaCl + H_2O$	no changes (neutralization)	not redox
$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$	no changes (precipitation)	not redox
$CaCO_3 \rightarrow CaO + CO_2$	Ca +2, C +4, O −2 throughout	not redox

Shortcut: if an **element** appears on one side of the equation but not the other (Cl_2, I_2, O_2), the reaction must be redox, because that element changes from 0. Neutralization and precipitation reactions are never redox.

6.2 Disproportionation

Definition

Disproportionation is a redox reaction in which the **same element** is both oxidized and reduced: some of its atoms increase their oxidation state while others decrease.

Worked example — chlorine in water (how chlorine disinfects drinking water)

$$Cl_2(aq) + H_2O(l) \rightleftharpoons HCl(aq) + HClO(aq)$$

Chlorine starts at 0. In HCl it is −1 (reduced); in HClO, chloric(I) acid, it is +1 (oxidized). H stays at +1 and O at −2. One chlorine atom is reduced and the other oxidized, so this is a **disproportionation**. The same happens in cold sodium hydroxide, which is how household bleach (sodium chlorate(I)) is made: $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$.

Other examples: the decomposition of hydrogen peroxide, $2H_2O_2 \rightarrow 2H_2O + O_2$ (O goes from −1 to −2 and to 0), and the reaction of nitrogen dioxide with water in acid rain, $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$ (N goes from +4 to +3 and to +5).

Looking ahead to Reactivity 3.2: oxidation states and half-equations

A redox reaction can be split into two **half-equations**, one for oxidation and one for reduction. The change in oxidation state tells you how many electrons each one involves. For the reaction of acidified manganate(VII) with iron(II):

$$\text{reduction: } MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad (\text{Mn } +7 \rightarrow +2\text{: gains 5 electrons})$$

$$\text{oxidation: } Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (\text{Fe } +2 \rightarrow +3\text{: loses 1 electron})$$

$$\text{overall (oxidation} \times 5\text{): } MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Writing and balancing half-equations is assessed in Reactivity 3.2, not in Structure 3.1. It is shown here so you can see why oxidation states matter.

Model answer: "Deduce, with reference to oxidation states, whether the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$ is a redox reaction, and identify its type." (3 marks)

Oxygen is −1 in H_2O_2, −2 in H_2O and 0 in O_2; hydrogen is +1 throughout **[1]**. Some oxygen atoms are reduced (−1 to −2) while others are oxidized (−1 to 0), so it is a redox reaction **[1]**. The same element is both oxidized and reduced, so it is a disproportionation reaction **[1]**.

Examiner traps in using oxidation states

- The **oxidizing agent is reduced** and the **reducing agent is oxidized**. Students often swap them.
- Name the oxidizing or reducing agent as the whole **species** (Fe_2O_3, CO, Cl_2), but say which **element** changes its oxidation state.
- Spectator ions do not change oxidation state. In Cl_2 + 2KI, potassium is +1 on both sides.
- In the name of a compound, use a Roman numeral with no sign and no space: iron(III) chloride, not iron (+3) chloride.
- Do not call a reaction redox just because it involves oxygen or water: $Na_2O + H_2O$ is not redox.

7 Structure 3.1.7 — Discontinuities in first ionization energy HL

7.1 The general trend and the two dips

Booklet 1 explained the **general increase** in first ionization energy across a period: the nuclear charge increases, the electrons enter the same principal energy level, so Z_{eff} increases and the outer electron is held more strongly. The increase is not smooth, however. There are two small drops in every period.

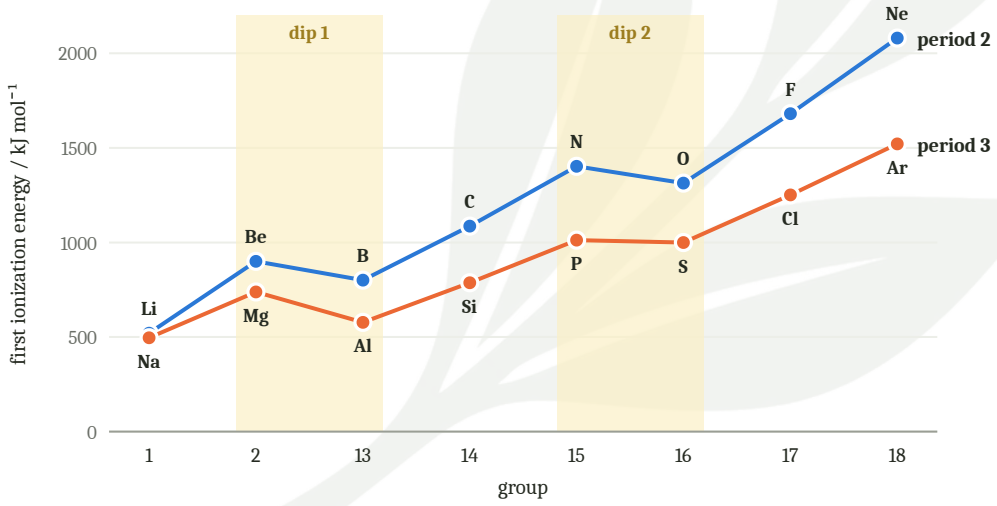


Figure 4 — First ionization energies of periods 2 and 3, lined up by group. Both periods show the same pattern: a drop from group 2 to group 13 (dip 1) and a smaller drop from group 15 to group 16 (dip 2).

How the IB wants these explained

Base the explanation on the **energy of the electron being removed**. If the electron removed is in a **higher-energy** orbital, or has its energy **raised** by repulsion, less energy is needed to remove it. Do **not** argue from the "special stability" of a full or half-full sublevel: the guide says this is not the basis for the explanation.

7.2 Dip 1: group 2 to group 13 (Be → B and Mg → Al)

Be $1s^2\ 2s^2$



red electron removed from 2s

B $1s^2\ 2s^2\ 2p^1$



red electron removed from 2p (higher in energy)

In beryllium the electron removed is a **2s** electron. In boron it is the single **2p** electron. A 2p orbital is at a **higher energy** than the 2s orbital of the same level: on average it is further from the nucleus, and it is partly shielded by the 2s electrons. So, even though boron has one more proton, its outer electron is easier to remove, and its first ionization energy is lower (B 801 kJ mol^{-1}, Be 900 kJ mol^{-1}). The same happens from Mg ($3s^2$, 738) to Al ($3s^2\ 3p^1$, 578).

7.3 Dip 2: group 15 to group 16 (N → O and P → S)

N $1s^2\ 2s^2\ 2p^3$



red electron: from a singly occupied 2p orbital

O $1s^2\ 2s^2\ 2p^4$



red electron: from a doubly occupied 2p orbital

In nitrogen the three 2p electrons occupy **separate** 2p orbitals (Hund's rule). In oxygen the fourth 2p electron has to **pair up** in an orbital that is already occupied. The two electrons in the same orbital **repel** each other strongly, which raises the energy of the paired electron. Removing one of the paired electrons therefore needs less energy, even though oxygen has a greater nuclear charge (O 1314 kJ mol^{-1}, N 1402 kJ mol^{-1}). The same happens from P (1012) to S (1000).

7.4 Why this is evidence for sublevels

If all the electrons in the second energy level had the **same energy**, the first ionization energy would rise steadily from lithium to neon as the nuclear charge increases. It does not. The dips occur at exactly the elements where a new sublevel (2p) starts to be filled (boron) and where electrons in that sublevel start to pair (oxygen). The pattern 2 + 3 + 3 (two elements up, a drop, three up, a drop, three up) matches one s orbital and three p orbitals in each level. So the discontinuities are experimental evidence that each principal energy level is divided into **sublevels** of different energy, and that the p sublevel has **three orbitals**.

Model answer: "Explain why the first ionization energy of aluminium is lower than that of magnesium." (2 marks)

The electron removed from aluminium is in a 3p orbital, while that removed from magnesium is in a 3s orbital **[1]**. The 3p orbital is higher in energy (further from the nucleus and shielded by the 3s electrons), so less energy is needed to remove the aluminium electron, despite its greater nuclear charge **[1]**.

Model answer: "Explain why the first ionization energy of sulfur is lower than that of phosphorus." (2 marks)

In sulfur ($3p^4$) the electron is removed from a 3p orbital that contains two electrons, whereas in phosphorus ($3p^3$) each 3p orbital contains one electron **[1]**. Repulsion between the paired electrons in sulfur raises the energy of the electron removed, so less energy is needed to remove it **[1]**.

7.5 Period 4

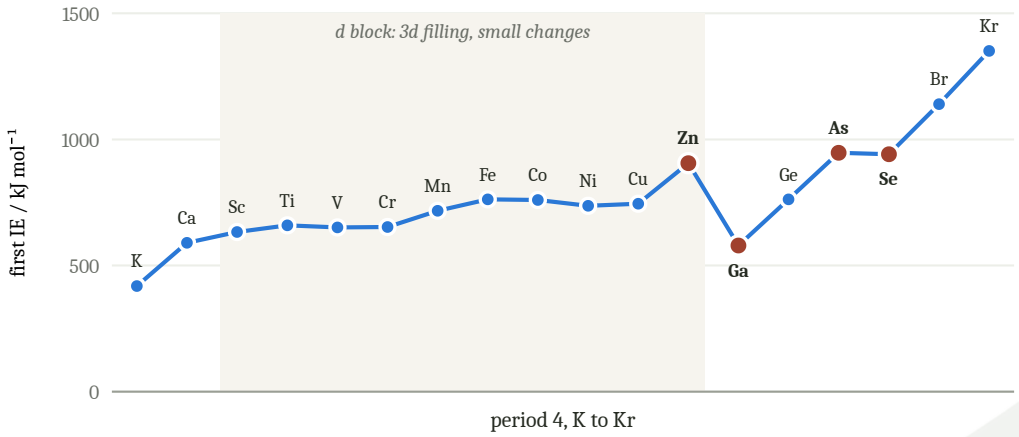


Figure 5 — First ionization energies across period 4. The d block changes little; the two p-block dips appear again at Zn → Ga and As → Se.

- **Across the d block** (Sc to Zn) the first ionization energy rises only slightly. The electrons are being added to the inner **3d** sublevel, while the electron removed is a **4s** electron. The extra 3d electrons shield the 4s electrons quite well, so Z_{eff} for the 4s electron increases only a little.
- **Zn → Ga** (906 → 579 kJ mol^{-1}): the electron removed from gallium is in a **4p** orbital, higher in energy than the 4s electron removed from zinc. This is dip 1 again.
- **As → Se** (947 → 941 kJ mol^{-1}): selenium's electron is removed from a doubly occupied 4p orbital. This is dip 2 again.

Reminder from Structure 1.3: d-block atoms lose their 4s electrons first

Although 4s fills before 3d, once the 3d sublevel is occupied the 4s electrons are the outermost and are removed first when ions form. So V^{2+} is [Ar] $3d^3$ (not [Ar] $3d^1$ $4s^2$), Fe^{3+} is [Ar] $3d^5$, Ti^{4+} is [Ar], and Cu^{2+} is [Ar] $3d^9$. You will need this in Booklet 3.

Model answer: "Explain how the variation in first ionization energy across period 2 provides evidence for the existence of sublevels." (3 marks)

The general increase across the period is interrupted by a decrease from Be to B and from N to O **[1]**. The drop from Be to B shows that the electron removed from B is in a higher-energy sublevel (2p) than the 2s electron removed from Be **[1]**. The drop from N to O shows that the 2p sublevel consists of separate orbitals: in O the electron removed is paired, and electron–electron repulsion raises its energy **[1]**.

Examiner traps in 3.1.7

- "Oxygen has a lower IE because nitrogen's half-filled p sublevel is especially stable" will not score. Explain using the **energy of the electron removed** in oxygen: it is paired, so it is repelled and easier to remove.
- For dip 1, compare the **sublevels** of the electrons removed (s versus p). "Boron has one more electron" is not an explanation.
- Always acknowledge that the nuclear charge is **greater** for the second element; the dip happens **despite** this.
- The dips are small departures from the trend. They do not reverse the general increase across the period: Ne still has the highest value in period 2.
- Use orbital diagrams if they help, but label the electron removed and its sublevel.

8 Key points to memorise

Everything below is either wording that examiners look for, or knowledge you must carry into the exam yourself.

A Definitions — near-verbatim

- **Oxidation state:** the charge an atom would have if the compound were composed of ions; it shows the number of electrons transferred in forming a bond.
- **Oxidation:** loss of electrons, or increase in oxidation state. **Reduction:** gain of electrons, or decrease in oxidation state.
- **Oxidizing agent:** removes electrons from another species and is itself reduced. **Reducing agent:** gives electrons to another species and is itself oxidized.
- **Disproportionation:** a redox reaction in which the same element is both oxidized and reduced.
- **Element = 0:** identical atoms, equal electronegativity, electrons shared equally, no transfer.

B The rules and their exceptions

- Sum = 0 for a compound; sum = charge for an ion. F always −1. Group 1 +1, group 2 +2, Al +3.
- H +1, but **−1 in metal hydrides** (NaH, CaH_2). O −2, but **−1 in peroxides** (H_2O_2) and +2 in OF_2.
- Cl, Br, I −1, except when bonded to O or a more electronegative halogen.
- Highest state = number of valence electrons; most negative (non-metals) = valence electrons − 8.
- Write +2 for an oxidation state, 2+ for an ionic charge, and (II) in a name.

C Names to know

- sulfate(VI) SO_4^{2-}; sulfate(IV) SO_3^{2-}; nitrate(V) NO_3^-; nitrate(III) NO_2^-; chlorate(I) ClO^-; chlorate(V) ClO_3^-; manganate(VII) MnO_4^-; dichromate(VI) $Cr_2O_7^{2-}$.
- sulfuric(VI) acid H_2SO_4; sulfuric(IV) acid H_2SO_3; nitric(V) acid HNO_3; nitric(III) acid HNO_2.

D HL **Discontinuities in first ionization energy**

- Group 2 → 13 (Be → B, Mg → Al): electron removed from a p orbital, higher in energy than s.
- Group 15 → 16 (N → O, P → S): electron removed from a doubly occupied p orbital; repulsion raises its energy.
- Explain from the energy of the electron removed, never from "stability of half-filled sublevels". The dips are evidence for s and p sublevels.
- Complex ions: metal oxidation state = overall charge − sum of ligand charges (H_2O, NH_3 0; Cl^-, CN^-, OH^- −1).

E Command terms — what each one is actually asking for

- **Deduce** (an oxidation state) — show the sum: the known values, the number of each atom, and the total (0 or the charge).
- **Explain** (why an element is zero) — identical atoms, equal electronegativity, equal sharing, no electron transfer.
- **Identify** (the oxidizing agent) — name the species; no explanation needed unless asked.
- **State** (whether a reaction is redox) — a short answer, ideally supported by the oxidation state changes.
- HL **Explain** (a discontinuity) — name the orbital the electron is removed from in both atoms, and link it to the energy of that electron.

9 Check yourself

Cover the answers on the next pages. Marks are shown in brackets where a question is written in exam style. Questions marked HL are for Higher Level students.

1. What is the oxidation state of chromium in $K_2Cr_2O_7$?

   A +3 B +6 C +7 D +12

2. Deduce the oxidation state of: (a) N in NO_2^- (b) S in $S_2O_3^{2-}$ (c) Mn in MnO_4^{2-} (d) C in $C_2O_4^{2-}$ (e) P in H_3PO_4 (f) Cl in Cl_2O_3. **[6]**

3. Explain why the oxidation state of oxygen in O_2 is zero. **[2]**

4. State the oxidation state of: (a) hydrogen in CaH_2 (b) oxygen in Na_2O_2 (c) oxygen in OF_2. **[3]**

5. In which species does sulfur have the lowest oxidation state?

   A SO_2 B H_2S C SO_4^{2-} D S_8

6. In which pair does manganese have the same oxidation state?

   A MnO_2 and MnO_4^- B MnO_4^{2-} and MnO_4^- C Mn_2O_7 and $KMnO_4$ D $MnCl_2$ and Mn_2O_3

7. Deduce the oxidation state of sulfur in $Na_2S_4O_6$, and comment on your answer. **[2]**

8. Name the following using oxidation numbers: (a) Cu_2O (b) PbO_2 (c) HNO_2 (d) $KClO_3$. **[4]**

9. Deduce the formulas of: (a) iron(III) oxide (b) tin(II) chloride (c) sodium chlorate(I) (d) potassium manganate(VII). **[4]**

10. State the highest and the lowest oxidation states expected for (a) phosphorus, (b) silicon and (c) iodine. Explain the values for phosphorus. **[4]**

11. Suggest why potassium never has an oxidation state of +2 in its compounds. **[2]**

12. Which is **not** a redox reaction?

A $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$ B $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$ C $2Mg + O_2 \rightarrow 2MgO$

D $Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$

13. For the reaction $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$, deduce the oxidation state changes, and identify the oxidizing agent and the reducing agent. **[4]**

14. State, with reasons, which of these are redox reactions: (a) $SO_3 + H_2O \rightarrow H_2SO_4$ (b) $2Na + 2H_2O \rightarrow 2NaOH + H_2$ (c) $MgO + 2HCl \rightarrow MgCl_2 + H_2O$ (d) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$. **[4]**

15. Nitrogen dioxide reacts with water: $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$. Deduce the oxidation state of nitrogen in each species and identify the type of reaction. **[3]**

16. Which statement about $2H_2O_2 \rightarrow 2H_2O + O_2$ is correct?

A Oxygen is oxidized only. B Oxygen is reduced only. C Oxygen is both oxidized and reduced.

D Hydrogen is reduced.

17. Explain the difference between "2+" in Mg^{2+} and "+2" as the oxidation state of magnesium. **[2]**

18. HL Deduce the oxidation state of the metal in: (a) $[Fe(CN)_6]^{4-}$ (b) $[CuCl_4]^{2-}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[Cr(H_2O)_4Cl_2]^{+}$. **[4]**

19. HL First ionization energies increase from E1 to E2 to E3, three consecutive elements in period 2. Identify them.

A Be, B, C B B, C, N C N, O, F D Li, Be, B

20. HL Explain why the first ionization energy of boron is lower than that of beryllium. **[2]**

21. HL Explain why the first ionization energy of oxygen is lower than that of nitrogen. **[2]**

22. HL A student writes: "Nitrogen has a higher first ionization energy than oxygen because a half-filled p sublevel is extra stable." Explain why this answer would not gain credit, and rewrite it. **[2]**

23. HL Explain why the first ionization energy of gallium is much lower than that of zinc. **[2]**

24. HL Which is the electron configuration of Fe^{3+}?

A $[Ar]\ 3d^3\ 4s^2$ B $[Ar]\ 3d^5$ C $[Ar]\ 3d^6$ D $[Ar]\ 3d^4\ 4s^1$

25. HL Outline how the pattern of first ionization energies from Li to Ne provides evidence for energy sublevels. **[3]**

10 Answers

1. **B.** 2(+1) + 2Cr + 7(−2) = 0, so each Cr is +6.
2. (a) +3 (b) +2 (c) +6 (d) +3 (e) +5 (f) +3 **[1]** each.
3. The two atoms are identical and have the same electronegativity, so the bonding electrons are shared equally **[1]**; no electrons are transferred, so neither atom has a charge **[1]**.
4. (a) −1 (metal hydride) (b) −1 (peroxide) (c) +2 (fluorine is more electronegative) **[1]** each.
5. **B.** S is −2 in H_2S, +4 in SO_2, +6 in SO_4^{2-} and 0 in S_8.
6. **C.** Mn is +7 in both. (A: +4 and +7; B: +6 and +7; D: +2 and +3.)
7. 2(+1) + 4S + 6(−2) = 0, so S = +2.5 **[1]**. A fractional value is an average: the sulfur atoms are in different environments and have different oxidation states **[1]**.
8. (a) copper(I) oxide (b) lead(IV) oxide (c) nitric(III) acid (nitrous acid) (d) potassium chlorate(V) **[1]** each.
9. (a) Fe_2O_3 (b) $SnCl_2$ (c) NaClO (d) $KMnO_4$ **[1]** each.
10. (a) P: +5 and −3 (b) Si: +4 and −4 (c) I: +7 and −1 **[2]** for all three. Phosphorus has five valence electrons, which can all be counted as lost to a more electronegative atom, giving +5; it needs three more to complete its octet, giving −3 **[2]**.
11. Potassium has one valence electron ($4s^1$) **[1]**. A second electron would have to be removed from the full inner third shell, closer to the nucleus and much less shielded, which needs far too much energy **[1]**.
12. **B.** Ca +2, C +4, O −2, H +1 and Cl −1 do not change.
13. Al: 0 → +3, oxidized **[1]**; Fe: +3 → 0, reduced **[1]**. Oxidizing agent: Fe_2O_3 **[1]**; reducing agent: Al **[1]**.
14. (a) not redox: S +6, O −2, H +1 throughout (b) redox: Na 0 → +1, H +1 → 0 (c) not redox: neutralization, no changes (d) redox: N −3 → +2, O 0 → −2 **[1]** each.
15. N is +4 in NO_2, +5 in HNO_3 and +2 in NO **[2]**. Nitrogen is both oxidized and reduced: disproportionation **[1]**.
16. **C.** O goes from −1 to −2 and from −1 to 0; H stays at +1.
17. "2+" is the actual charge on the magnesium ion, written number first **[1]**. "+2" is the oxidation state of the Mg atom, written sign first; in an ionic compound the two have the same value, but oxidation states are also assigned to atoms in covalent species, where there is no real charge **[1]**.
18. (a) +2 (b) +2 (c) +3 (d) +3 **[1]** each.
19. **B.** B 801, C 1086, N 1402 kJ mol^{-1}. Each of the others contains a dip.
20. The electron removed from boron is in a 2p orbital; that removed from beryllium is in the 2s orbital **[1]**. The 2p orbital is higher in energy (further from the nucleus and shielded by the 2s electrons), so less energy is needed, despite boron's greater nuclear charge **[1]**.
21. In oxygen ($2p^4$) the electron is removed from a doubly occupied 2p orbital; in nitrogen ($2p^3$) all the 2p electrons are unpaired **[1]**. Repulsion between the paired electrons raises the energy of the electron removed from oxygen, so less energy is needed **[1]**.
22. It explains using the "stability" of a half-filled sublevel, which the guide says is not an acceptable basis; the explanation must refer to the energy of the electron removed **[1]**. Rewrite: the electron removed from oxygen is paired in a 2p orbital, so it is repelled by its partner and has a higher energy, making it easier to remove than the unpaired electron in nitrogen **[1]**.

23. The electron removed from gallium is in a 4p orbital, while that removed from zinc is in the 4s orbital **[1]**. The 4p orbital is higher in energy and further from the nucleus (and shielded by the full 3d and 4s), so less energy is needed **[1]**.

24. **B.** Iron is [Ar] $3d^6$ $4s^2$; the two 4s electrons are lost first, then one 3d electron.

25. The general increase from Li to Ne is interrupted by drops from Be to B and from N to O **[1]**. Boron's electron is removed from the higher-energy 2p sublevel rather than 2s, showing that the second level contains s and p sublevels of different energy **[1]**. Oxygen's electron is removed from a doubly occupied p orbital, showing that the p sublevel consists of separate orbitals that are first singly occupied **[1]**.

Where this fits in Structure 3.1

- **Booklet 1** — 3.1.1 to 3.1.5: the table, configuration and position, periodicity, group trends and the oxides.
- **Booklet 2** (this booklet) — 3.1.6 oxidation states and HL 3.1.7 discontinuities in first ionization energy.
- **Booklet 3** — HL 3.1.8 to 3.1.10: characteristic properties of the transition elements, their variable oxidation states, and the colour of their complexes.
- Links forward: **Reactivity 3.2** (redox, half-equations, electrochemical cells), **Structure 2.2** HL (coordination bonds in complex ions).

These notes are a free resource, shared for any IB student who finds them useful.

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