MEGA LECTURE

IB DP CHEMISTRY

Reactivity 3 · What Are the Mechanisms of Change?

MARK SCHEME

R3.1 Proton Transfer · R3.2 Electron Transfer
R3.3 Radical Substitution · R3.4 Electron Pair Sharing

Standard and Higher Level · Syllabus 2025

Fahad H. Ahmad

+92 323 509 4443 | Megalecture.com

Original exam-style questions written for the IB Diploma Programme Chemistry course (first assessment 2025)

Section A — Multiple Choice: Answer Key (15 marks)

1. Answer: **B** — A Bronsted-Lowry base is a proton acceptor. NH_3 accepts a proton (H^+) from H_2O to form NH_4^+, so NH_3 is the base (and H_2O is the acid) in this direction of the reaction.

2. Answer: **B** — HCl is a strong acid and dissociates completely, so $[H^+] = 0.010$ mol dm^{-3}; pH = $-\log_{10}(0.010) = 2$.

3. Answer: **C** — A weak acid is one that only partially dissociates (ionizes) into ions in aqueous solution, establishing an equilibrium between the undissociated acid and its ions.

4. Answer: **C** — The salt formed (e.g. NaCl) from a strong acid and a strong base does not hydrolyse, so the solution at the equivalence point is neutral, pH ≈ 7.

5. Answer: **B** — Sn^{2+} loses two electrons to form Sn^{4+} (oxidation number increases from +2 to +4), so Sn^{2+} is oxidized; Fe^{3+} is reduced to Fe^{2+}.

6. Answer: **C** — Each oxygen is −2, and there are four oxygens, giving −8; for the overall charge to be −2, sulfur must be +6, since (+6) + (−8) = −2.

7. Answer: **D** — The species with the most positive (least negative) standard electrode potential is reduced most readily and is therefore the strongest oxidizing agent; Ag^+ has the highest E° (+0.80 V).

8. Answer: **B** — A voltaic cell uses a spontaneous redox reaction to generate an electric current, converting chemical energy into electrical energy.

9. Answer: **B** — The initiation step requires UV (or visible) light to provide enough energy for homolytic fission of the Cl-Cl bond, producing two chlorine radicals: $Cl_2 \rightarrow 2Cl\bullet$.

10. Answer: **B** — In homolytic fission, the shared pair of bonding electrons splits evenly, with one electron going to each atom, producing two neutral species each with a single unpaired electron (free radicals).

11. Answer: **B** — In each propagation step, a radical reacts with a stable molecule to produce a new radical (which can continue the chain) together with a product molecule; the number of radicals is conserved at each propagation step.

12. Answer: **B** — Primary halogenoalkanes have the least steric hindrance around the carbon bearing the halogen and cannot readily form a stable carbocation, so they react by the S_N2 mechanism (single-step backside attack by the nucleophile).

13. Answer: **B** — As the non-polar Br_2 molecule approaches the electron-rich π bond of ethene, a dipole is induced in Br_2, making the nearer Br atom electron-deficient; it then behaves as an electrophile, accepting an electron pair from the π bond.

14. Answer: **B** — After the π bond attacks the δ^+ hydrogen of HBr, a positively charged carbon intermediate (carbocation) is formed; Br^- then attacks this carbocation to complete the addition.

15. Answer: **B** — A nucleophile ('nucleus-loving') is an electron pair donor: it has a lone pair (or π electrons) that it donates to form a new covalent bond with an electron-deficient (electrophilic) centre.

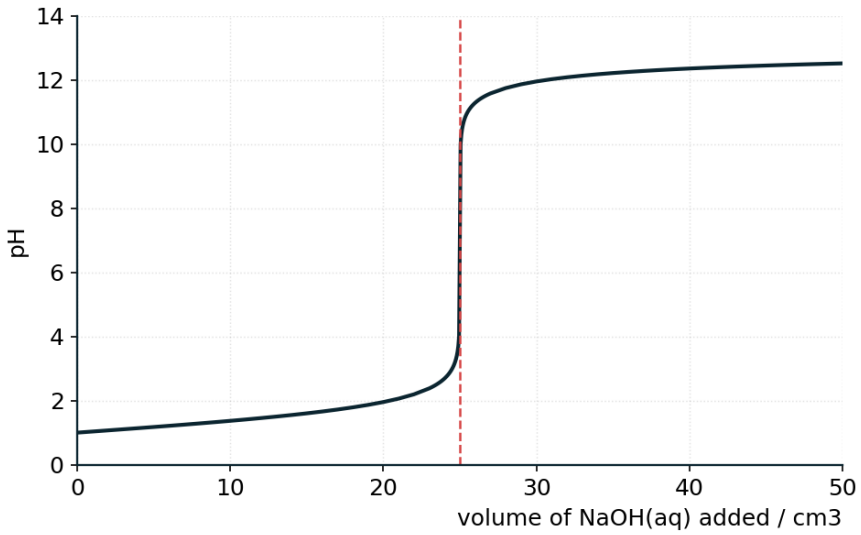
Section B — Structured Questions: Worked Solutions (65 marks)

Mark-scheme notation: M = method mark, A = accuracy mark (dependent on the preceding M mark), R = reasoning mark.

R3.1 Proton Transfer

Question 1 [7 marks]

25.0 cm^3 of hydrochloric acid, HCl(aq), of unknown concentration was titrated with 0.100 mol dm^{-3} sodium hydroxide, NaOH(aq). The graph shows how the pH of the mixture changed as NaOH(aq) was added.



Titration curve: HCl(aq) titrated with 0.100 mol dm^{-3} NaOH(aq) (computed from the reacting quantities).

(a) Using the graph, state the volume of NaOH(aq) added at the equivalence point, and explain how you identified it. **[2]**

The equivalence point is at **V = 25.0 cm^3**, identified by the almost-vertical (steep) portion of the curve, where the pH rises very sharply for only a tiny additional volume of NaOH(aq). **A1 A1**

(b) State the pH at the equivalence point for this titration, and explain why it has this value. **[2]**

The pH at the equivalence point is **7** (neutral). This is because HCl is a strong acid and NaOH is a strong base, so the salt formed, NaCl, is the salt of a strong acid and a strong base; neither Na^+ nor Cl^- hydrolyses in water, so the resulting solution is neutral. **A1 R1**

(c) Given that the NaOH(aq) has a concentration of 0.100 mol dm^{-3}, calculate the original concentration of the HCl(aq), which had an initial volume of 25.0 cm^3. **[3]**

At the equivalence point, n(NaOH) = n(HCl). n(NaOH) = 0.100·(25.0/1000) = 2.50×10^{-3} mol = n(HCl). [HCl] = n÷V = (2.50×10^{-3})÷(25.0/1000) = **0.100 mol dm^{-3}**. **M1 M1 A1**

Question 2 [6 marks]

Bronsted-Lowry theory describes acids and bases in terms of proton transfer.

(a) Define a Bronsted-Lowry acid and a Bronsted-Lowry base. **[2]**

A Bronsted-Lowry acid is a species that **donates a proton (H^+)**; a Bronsted-Lowry base is a species that **accepts a proton (H^+)**. **A1 A1**

(b) For the reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$, identify the two conjugate acid-base pairs. **[2]**

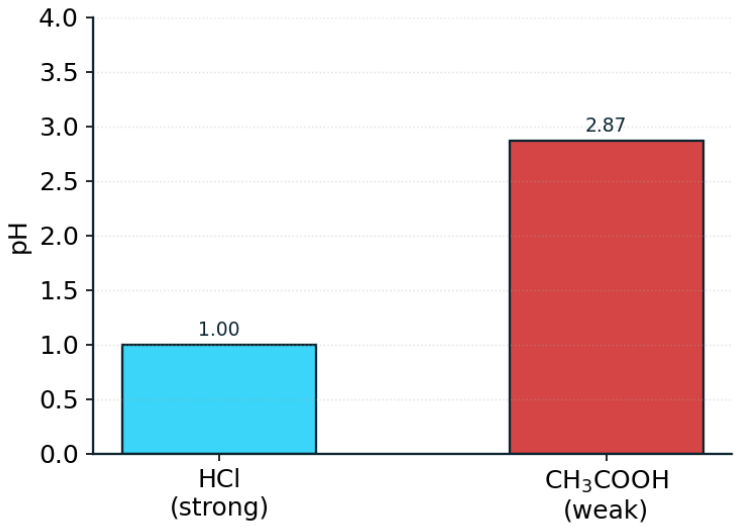
The two conjugate acid-base pairs are **NH_4^+ / NH_3** (NH_4^+ is the conjugate acid of the base NH_3) and **H_2O / OH^-** (H_2O is the conjugate acid of the base OH^-). **A1 A1**

(c) Explain why water can act as either an acid or a base, giving a suitable equation for each role. **[2]**

Water is **amphiprotic**: it can either donate a proton (acting as an acid) or accept a proton (acting as a base), depending on what it reacts with. As an acid: $H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$. As a base: $H_2O + HCl \rightarrow H_3O^+ + Cl^-$. **R1 A1**

Question 3 [7 marks]

The bar chart compares the pH of two 0.100 mol dm^{-3} acid solutions at 25°C.



pH of two 0.100 mol dm^{-3} acids (computed from the given K_a of ethanoic acid).

(a) Using the graph, identify which acid is the strong acid, and explain your reasoning. **[2]**

HCl is the strong acid, since it has the lower pH (pH ≈ 1.00) at the same concentration; a lower pH means a higher $[H^+]$, indicating (near-)complete dissociation. **A1 R1**

(b) Explain, in terms of the degree of dissociation, why the weak acid has a higher pH than the strong acid at the same concentration. **[2]**

The weak acid, CH_3COOH, only **partially dissociates** in water, so its equilibrium $[H^+]$ is much lower than the total acid concentration. The strong acid, HCl, **fully dissociates**, so its $[H^+]$ equals the full concentration of acid. The lower $[H^+]$ of the weak acid gives it a higher pH. **R1 R1**

(c) Calculate the $[H^+]$ corresponding to the pH of the weak acid, and hence show that only a small percentage of the acid molecules have dissociated. **[3]**

$[H^+] = 10^{-pH}$ = **1.34×10^{-3} mol dm^{-3}**. Percentage dissociated = $([H^+]\div[CH_3COOH]_{initial})\times100\%$ = $(1.34\times10^{-3}\div0.100)\times100\%$ = **1.34%**, confirming that only a small fraction of the weak acid molecules have dissociated. **M1 M1 A1**

R3.2 Electron Transfer

Question 4 [6 marks]

Oxidation and reduction can be defined and tracked using oxidation states.

(a) Define oxidation and reduction in terms of electron transfer. **[2]**

Oxidation is the **loss of electrons** (an increase in oxidation state); reduction is the **gain of electrons** (a decrease in oxidation state). **A1 A1**

(b) Deduce the oxidation state of chromium in the dichromate ion, $Cr_2O_7^{2-}$. Show your working. **[2]**

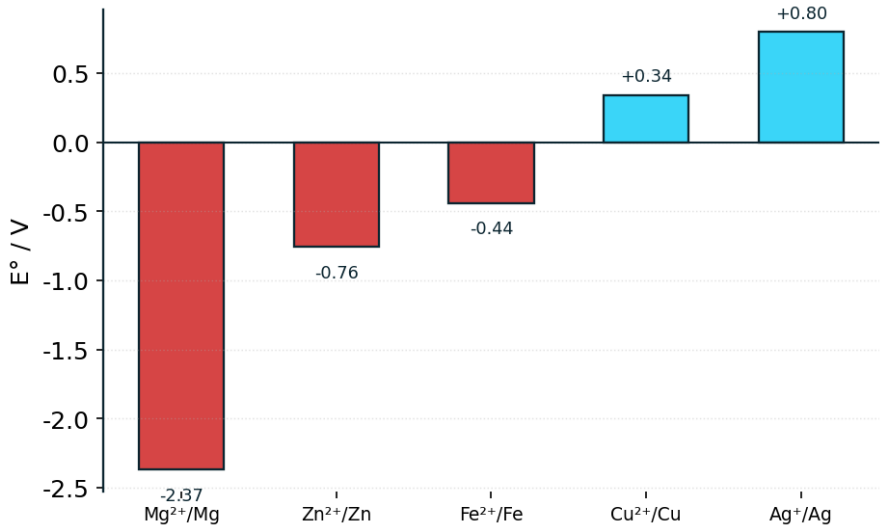
Let the oxidation state of Cr be x. Oxygen is −2, and there are 7 oxygens: 2x + 7(−2) = −2, so 2x = −2 + 14 = 12, giving x = **+6**. **M1 A1**

(c) For the reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, identify the species oxidized and the species reduced, and state the oxidation state change for each. **[2]**

Zn is oxidized (oxidation state changes from 0 to +2, losing 2 electrons). **Cu^{2+} is reduced** (oxidation state changes from +2 to 0, gaining 2 electrons). **A1 A1**

Question 5 [7 marks]

The graph shows standard electrode potentials, E°, for a series of half-reactions (data booklet values).



Standard electrode potentials, E° (data booklet values).

(a) Using the graph, identify the strongest reducing agent among the metals shown, and explain your reasoning. **[2]**

Mg is the strongest reducing agent, since Mg^{2+}/Mg has the most negative E° (−2.37 V); metals with a more negative E° lose electrons (are oxidized) more readily, making them stronger reducing agents. **A1 R1**

(b) Predict, with a reason, whether a reaction would occur if solid zinc were added to aqueous copper(II) sulfate. **[2]**

Yes, a reaction would occur. Zn^{2+}/Zn ($E° = -0.76$ V) has a more negative $E°$ than Cu^{2+}/Cu ($E° = +0.34$ V), so Zn is a stronger reducing agent than Cu and will reduce Cu^{2+} ions, displacing copper metal. **A1 R1**

(c) Calculate the standard cell potential, $E°_{cell}$, for a voltaic cell constructed from the Zn^{2+}/Zn and Cu^{2+}/Cu half-cells, and give the half-equation for the spontaneous cell reaction. **[3]**

$E°_{cell} = E°_{cathode} - E°_{anode} = E°(Cu^{2+}/Cu) - E°(Zn^{2+}/Zn) = (+0.34) - (-0.76) =$ **1.10 V**. Overall equation: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. **M1 A1 A1**

Question 6 [6 marks]

Redox reactions can be balanced by combining half-equations.

(a) Construct the balanced half-equation for the reduction of MnO_4^- to Mn^{2+} in acidic solution. **[3]**

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (balanced for Mn, O, H, and charge: left = $-1+8-5 = +2$; right = $+2$). **M1 M1 A1**

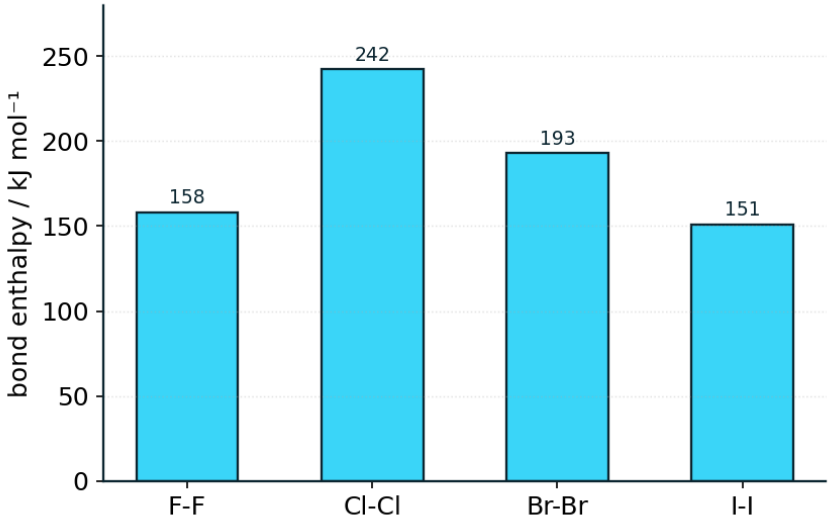
(b) Combine this with the half-equation $Fe^{2+} \rightarrow Fe^{3+} + e^-$ to construct the overall balanced ionic equation for the reaction between acidified MnO_4^- and Fe^{2+}. **[3]**

Multiply the Fe half-equation by 5 so the electrons cancel: $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$. Adding to the MnO_4^- half-equation and cancelling the $5e^-$: **$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$**. **M1 M1 A1**

R3.3 Radical Substitution

Question 7 [7 marks]

The graph shows the bond enthalpy of the X-X bond for four halogens (data booklet values).



X-X bond enthalpies for the halogens (data booklet values).

(a) Using the graph, identify which halogen molecule requires the least energy to undergo homolytic fission (bond breaking). **[2]**

I_2 requires the least energy to undergo homolytic fission, since it has the lowest X-X bond enthalpy ($151\ kJ\ mol^{-1}$) of the four halogens shown. **A1 A1**

(b) Write an equation for the initiation step of the reaction between methane and chlorine, and state the type of bond fission involved. **[2]**

$Cl_2 \rightarrow 2Cl\bullet$ (in the presence of UV or visible light). This is **homolytic fission** of the Cl-Cl bond: each Cl atom keeps one electron from the shared pair, producing two neutral chlorine free radicals. **A1 A1**

(c) Outline, with equations, the propagation steps that occur after initiation, and explain why this is described as a chain reaction. **[3]**

Propagation step 1: $Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$. Propagation step 2: $CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$. It is described as a **chain reaction** because each propagation step regenerates a radical ($Cl\bullet$) that can go on to react further, so the cycle of steps repeats many times from a single initiation event. **M1 M1 R1**

Question 8 [6 marks]

Free-radical substitution reactions eventually stop when radicals are removed from the system.

(a) Write equations for the three possible termination steps in the free-radical substitution of methane with chlorine. **[3]**

$Cl\bullet + Cl\bullet \rightarrow Cl_2$; **$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$**; **$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$** (any two radicals present in the mixture combine to form a stable molecule). **A1 A1 A1**

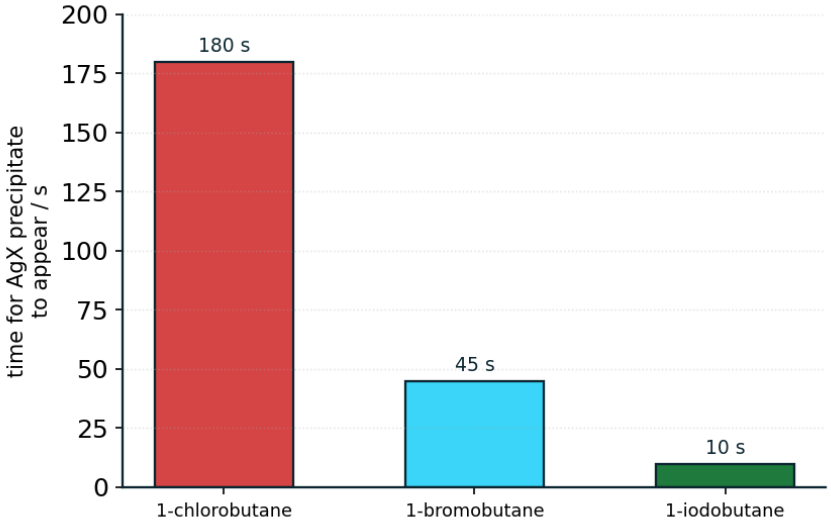
(b) Explain why the free-radical substitution of methane commonly produces a mixture of products, including CH_2Cl_2, $CHCl_3$ and CCl_4, even when methane is in excess. **[3]**

Chlorine radicals collide **randomly** with whatever molecules are present, including molecules of CH_3Cl that have already formed, not only with unreacted CH_4. Further substitution of the remaining C-H bonds in CH_3Cl (and then CH_2Cl_2, and then $CHCl_3$) can occur at any stage, so a **statistical mixture** of mono-, di-, tri-, and tetra-substituted products is obtained. **R1 R1 A1**

R3.4 Electron Pair Sharing

Question 9 [7 marks]

The bar chart shows the time taken for a precipitate to form when equal volumes of three halogenoalkanes are each treated with excess ethanolic silver nitrate solution (given data).



Time for AgX precipitate to appear with ethanolic $AgNO_3$ (given data).

(a) Using the graph, identify which halogenoalkane reacts fastest, and state the trend in reactivity shown going down group 17. **[2]**

1-iodobutane reacts fastest (shortest time for a precipitate, 10 s). The trend shown is that reactivity **increases down group 17**: 1-iodobutane > 1-bromobutane > 1-chlorobutane. **A1 A1**

(b) Explain, in terms of bond enthalpy, why this trend in reactivity is observed. **[3]**

Bond enthalpy of the C-X bond **decreases down group 17** (C-I is weaker than C-Br, which is weaker than C-Cl), because atomic radius increases down the group, so the shared electron pair is further from the nuclei and the bond is weaker. A **weaker C-X bond breaks more easily**, so the halogenoalkane with the weakest C-X bond (1-iodobutane) undergoes nucleophilic substitution fastest. **R1 R1 A1**

(c) State the type of mechanism occurring in this reaction, and identify the nucleophile involved. **[2]**

The mechanism is **nucleophilic substitution** (of the halogen by water/the solvent, followed by precipitation of AgX). The nucleophile is **H_2O** (water), which uses a lone pair on oxygen to attack the δ^+ carbon bonded to the halogen. **A1 A1**

Question 10 [6 marks]

Halogenoalkanes and alkenes undergo characteristic addition and substitution reactions.

(a) For the reaction between bromoethane and aqueous NaOH, write the overall equation, name the mechanism, and briefly describe it. **[3]**

$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$. The mechanism is **$S_N2$** (bimolecular nucleophilic substitution): the nucleophile OH^- attacks the δ^+ carbon from the side directly opposite the leaving group (Br^-) in a single step, resulting in **inversion of configuration** at that carbon as Br^- leaves. **A1 A1 A1**

(b) For the reaction between ethene and HBr, write the equation, and state the type of intermediate formed. **[3]**

$CH_2=CH_2 + HBr \rightarrow CH_3CH_2Br$. This is an **electrophilic addition** reaction: the π bond attacks the δ^+ H of HBr, forming a **carbocation intermediate** ($CH_3CH_2^+$); Br^- then attacks the carbocation to complete the addition. **A1 A1 A1**