

IB Chemistry – Reactivity 3: Mechanisms of Change

IB Chemistry SL & HL (2023 syllabus) · Total marks: 43 · Answers on the last page

This worksheet covers Reactivity 3: proton transfer reactions (acids and bases), electron transfer reactions (redox), and electron sharing reactions (organic mechanisms). Questions marked HL extend beyond the SL syllabus. A calculator is allowed; use $K_w = 1.0 \times 10^{-14}$ at 298 K.

Section A – Proton Transfer Reactions

- For the reaction $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$:
 - Identify the Brnsted–Lowry acid on the left-hand side.
 - Identify the two conjugate acid–base pairs. [3]
- Calculate the pH of $0.010 \text{ mol dm}^{-3}$ hydrochloric acid, a strong acid.
 - Calculate the pH of $0.0025 \text{ mol dm}^{-3}$ sodium hydroxide, a strong base. [4]
- A weak acid HA has $K_a = 1.8 \times 10^{-5}$ and an initial concentration of 0.10 mol dm^{-3} . Using the approximation $[\text{H}^+] \approx \sqrt{K_a c}$, calculate the pH of the solution. [3]
- (HL) A buffer solution is prepared containing 0.20 mol dm^{-3} ethanoic acid ($K_a = 1.8 \times 10^{-5}$) and 0.10 mol dm^{-3} sodium ethanoate.
 - State the two components needed to make an acidic buffer.
 - Use the Henderson–Hasselbalch equation, $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$, to calculate the pH of this buffer. [4]

Section B – Electron Transfer Reactions

- For the reaction $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$:
 - State the change in oxidation number of manganese and of iron.
 - Identify the oxidising agent and the reducing agent. [4]
- Write the two half-equations for the reaction between acidified potassium manganate(VII) and iron(II) ions, and combine them to give the overall balanced ionic equation. [4]
- (HL) An electrochemical cell is set up using a zinc half-cell ($E^\ominus = -0.76 \text{ V}$) connected to a copper half-cell ($E^\ominus = +0.34 \text{ V}$) via a salt bridge.
 - State which electrode is the cathode (positive electrode).
 - Calculate the standard cell potential, $E_{\text{cell}}^\ominus$.
 - State whether the cell reaction is spontaneous, giving a reason. [4]
- Explain, in terms of electron transfer, what happens to a species during oxidation and during reduction. Use the mnemonic OIL RIG in your answer. [2]

Section C – Electron Sharing Reactions: Organic Mechanisms (HL emphasis)

- (HL) Bromoethane reacts with hydroxide ions in an $\text{S}_{\text{N}}2$ mechanism to form ethanol. Describe the mechanism, including the role of the nucleophile, the direction of attack, and the shape of the transition state. [4]

10. (HL) 2-bromo-2-methylpropane (a tertiary haloalkane) reacts with water predominantly by an S_N1 mechanism, whereas bromoethane (a primary haloalkane) reacts by S_N2 .
Explain why the tertiary haloalkane favours S_N1 while the primary haloalkane favours S_N2 . [3]
11. Propene reacts with hydrogen bromide by electrophilic addition to form predominantly 2-bromopropane rather than 1-bromopropane.
(a) Outline the mechanism, stating which carbon the electrophile (H^+) adds to first.
(b) Explain, in terms of carbocation stability, why 2-bromopropane is the major product (Markovnikov's rule). [4]
12. Methane reacts with chlorine in the presence of ultraviolet light by a free-radical substitution mechanism.
(a) Write an equation for the initiation step.
(b) Write equations for the two propagation steps.
(c) State the type of bond breaking that occurs in the initiation step. [4]

Answers

Check your working against these. If an answer does not match, try the question again before looking for the method.

- HNO_2 is the acid (proton donor).
 - $\text{HNO}_2/\text{NO}_2^-$ and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.
- $[\text{H}^+] = 0.010$, so $\text{pH} = -\log(0.010) = 2.00$
 - $[\text{OH}^-] = 0.0025$, $\text{pOH} = -\log(0.0025) = 2.60$, so $\text{pH} = 14.00 - 2.60 = 11.40$
- $[\text{H}^+] = \sqrt{(1.8 \times 10^{-5})(0.10)} = \sqrt{1.8 \times 10^{-6}} \approx 1.34 \times 10^{-3} \text{ mol dm}^{-3}$
 $\text{pH} = -\log(1.34 \times 10^{-3}) \approx 2.87$
- A weak acid and its conjugate base (usually as a soluble salt), present in comparable concentrations.
 - $\text{p}K_a = -\log(1.8 \times 10^{-5}) \approx 4.74$; $\text{pH} = 4.74 + \log\left(\frac{0.10}{0.20}\right) = 4.74 - 0.30 \approx 4.44$
- Manganese: $+7 \rightarrow +2$ (reduced by 5). Iron: $+2 \rightarrow +3$ (oxidised by 1, per Fe atom).
 - Oxidising agent: MnO_4^- (it is reduced). Reducing agent: Fe^{2+} (it is oxidised).
- Reduction: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 Oxidation: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ (
times 5 to balance electrons)
 Overall: $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$
- Copper is the cathode (higher, less negative $E^\ominus$, so Cu^{2+} is reduced).
 - $E_{\text{cell}}^\ominus = E_{\text{cathode}}^\ominus - E_{\text{anode}}^\ominus = 0.34 - (-0.76) = 1.10 \text{ V}$
 - Spontaneous, because $E_{\text{cell}}^\ominus$ is positive.
- Oxidation Is Loss of electrons (the species loses electrons and its oxidation number increases);
 Reduction Is Gain of electrons (the species gains electrons and its oxidation number decreases).
- The hydroxide ion (nucleophile, with a lone pair) attacks the carbon bonded to bromine from the side opposite to the leaving group (backside attack), as the C–Br bond breaks heterolytically and bromide (Br^-) leaves. The reaction proceeds in a single step through a five-coordinate transition state, and the carbon centre undergoes inversion of configuration.
- In $\text{S}_{\text{N}}1$, the rate-determining step is formation of a carbocation; tertiary carbocations are stabilised by the electron-donating (hyperconjugation/inductive) effect of three alkyl groups, so tertiary haloalkanes readily form a stable intermediate. Steric hindrance from the bulky alkyl groups also makes backside attack (needed for $\text{S}_{\text{N}}2$) very difficult. Primary haloalkanes have an unhindered carbon and a very unstable primary carbocation, so they instead react in a single concerted step ($\text{S}_{\text{N}}2$).
- The π electrons of the $\text{C}=\text{C}$ double bond act as the nucleophile and attack H^+ from HBr ; H^+ adds to the terminal carbon (C1), forming a carbocation on the central carbon (C2), and Br^- then bonds to this carbocation.
 - The secondary carbocation formed at C2 is more stable than the primary carbocation that would form at C1, because alkyl groups on either side donate electron density (inductive/hyperconjugation effect) and stabilise the positive charge; the more stable intermediate is formed faster, so 2-bromopropane is the major product.
- $\text{Cl}_2 \rightarrow 2\text{Cl}^\bullet$ (initiated by UV light)
 - $\text{Cl}^\bullet + \text{CH}_4 \rightarrow \text{CH}_3^\bullet + \text{HCl}$ and $\text{CH}_3^\bullet + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^\bullet$

(c) Homolytic fission (the Cl–Cl bond breaks so that each chlorine atom keeps one electron, forming two radicals).

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