

2.3.6 Halogen evidence and controlled analytical methods

Name: _____ Class: _____ Date: _____

Total: 45 marks

KEY WORDS electronegativity

Objective

Interpret halogen evidence and design controlled analytical comparisons. All questions and marking guidance are original; laboratory work uses the approved supervised method.

1 Key knowledge and worked examples

Electronegativity is attraction for the shared electron pair in a covalent bond. Oxidising power describes accepting electrons in a redox reaction. Both decrease down Cl, Br, I, but the attracted electrons are described in different contexts. Increasing radius and shielding weaken the relevant attraction despite increasing nuclear charge.

■ Worked interpretation

Bromine oxidises iodide: $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$. Aqueous iodine is brown; iodine dissolved in an inert non-polar solvent such as cyclohexane is purple. Chlorine is pale green in water and pale yellow-green in the stated inert organic solvent; bromine is orange in both phases in these test conditions. Identify the species and solvent before using colour. A colour change caused only by partitioning between solvents is not a redox equation.

In disproportionation, one element is both oxidised and reduced. Cold dilute alkali gives halide and halate(I); hot concentrated alkali can give halide and halate(V). Follow oxidation numbers as well as balancing every atom and charge.

For an analytical comparison, control the sample, reagent and observation conditions and use separate aliquots. Strong sodium flame contamination can mask another colour. In a titration, accurate transfer and burette reading matter separately from the indicator's endpoint signal. Written method reasoning is not a substitute for supervised practical performance.

2 Practice

2.1 Write balanced equations for sodium and magnesium reacting with chlorine. Explain the different chloride formulae and identify which reactant is oxidised in each reaction.[4]

2.2 Rank chlorine, bromine and iodine by electronegativity. Explain the trend despite increasing nuclear charge, then distinguish the electron attraction meant by electronegativity from that meant by oxidising power. [3]

2.3 State the characteristic aqueous and inert non-polar organic-solution colours of Cl_2 , Br_2 and I_2 . A small amount of bromine water is added separately to excess aqueous KI and aqueous KCl, then each mixture is shaken with cyclohexane under the stated supervised test conditions. Bromine is orange in cyclohexane; iodine is purple. Predict each organic-layer colour, write the reaction that occurs, and explain the result with KCl. Assume excess iodide consumes all added bromine. [7]

3 Exam-style questions

3.1 Predict balanced equations for Br_2 with cold dilute NaOH and I_2 with hot concentrated NaOH , by analogy with chlorine chemistry. Give the two halogen oxidation numbers in each pair of products. Name the chlorine-containing ion in bleach, and write the reversible chlorine–water equation. [6]

3.2 Concentrated sulfuric acid first forms HI from an iodide salt. Write three balanced redox equations using HI and H_2SO_4 that produce I_2 and, separately, SO_2 , S and H_2S . Give sulfur's change in oxidation number for all three and identify the species oxidised. Explain why concentrated H_2SO_4 is unsuitable for preparing pure HI . [6]

3.3 A 25.00 cm^3 aliquot of HCl is titrated with $0.1000\text{ mol dm}^{-3}\text{ NaOH}$. Concordant titres average 24.60 cm^3 . Calculate the HCl concentration and describe the complete accurate transfer-to-endpoint method: rinsing of pipette, burette and flask; filling/reading the burette; endpoint approach and colour using phenolphthalein; and repeat measurements. [7]

3.4 An approved supervised flame-test method is used to compare sodium, potassium, calcium and strontium salts. Describe how to avoid sample carry-over, state the four expected colours and one experimental condition to keep the same. Explain why a yellow contaminated flame is weak evidence for sodium in an unknown. Separately, describe the positive test for CO_2 released from a carbonate; a flame colour is not that gas test. [6]

3.5 Outline a controlled supervised comparison of thermal stability for Group 1 and Group 2 nitrates/carbonates. Explain how to control the amount and heating, what to measure instead of simply comparing elapsed bubble times, and how to identify CO_2 , O_2 and NO_2 among the possible gases. [6]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 reasoning. Alternative correct balanced ionic equations are acceptable when they retain the stated products and conditions.

2.1 $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$; $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$. Na^+ requires one Cl^- , while Mg^{2+} requires two Cl^- for neutrality. Both metals are oxidised from 0 to +1/+2; chlorine is reduced from 0 to -1.

2.2 $\text{Cl} > \text{Br} > \text{I}$. Greater radius and shielding down the group weaken attraction despite greater nuclear charge. Electronegativity concerns the shared bonding pair; oxidising power concerns accepting electrons in redox, so the two descriptions must not be conflated.

2.3 Cl_2 : pale green aqueous, pale yellow-green organic; Br_2 : orange/brown aqueous, orange organic; I_2 : brown aqueous, purple/violet organic. KI gives a purple organic layer containing I_2 ; KCl retains orange Br_2 . $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$. Bromine is a weaker oxidising agent than chlorine and does not oxidise Cl^- under these conditions. Colour interpretation explicitly uses cyclohexane rather than the brown aqueous-iodine colour.

3.1 $\text{Br}_2 + 2\text{NaOH} \rightarrow \text{NaBr} + \text{NaBrO} + \text{H}_2\text{O}$; $3\text{I}_2 + 6\text{NaOH} \rightarrow 5\text{NaI} + \text{NaIO}_3 + 3\text{H}_2\text{O}$. Bromine products contain Br -1 and +1; iodine products contain I -1 and +5. Bleach contains chlorate(I)/hypochlorite, ClO^- . $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$. These are disproportionation reactions: some halogen is reduced and some oxidised.

3.2 $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$; $6\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 3\text{I}_2 + \text{S} + 4\text{H}_2\text{O}$; $8\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$. Sulfur changes +6 $\rightarrow$ +4, 0 and -2 respectively. Iodide/HI is oxidised from I -1 to I_2 0. The oxidising acid consumes the desired HI and introduces iodine/reduced-sulfur products, preventing pure HI preparation by this route.

3.3 $n(\text{NaOH}) = 0.1000 \times 0.02460 = 0.002460 \text{ mol}$; $\text{HCl}:\text{NaOH} = 1:1$; $c(\text{HCl}) = 0.002460/0.02500 = 0.09840 \text{ mol dm}^{-3}$. Rinse the pipette with HCl, burette with NaOH, and flask with deionised water; transfer the aliquot with the pipette using a filler. Fill the burette jet, remove the funnel and read initial/final menisci at eye level. Add indicator and swirl; approach the endpoint dropwise over a white tile, rinsing flask walls with deionised water if needed. Phenolphthalein changes from colourless to the first persistent pale pink as slight alkali excess is reached. Obtain a rough titre, then repeat accurately to concordance and average the accepted concordant titres, rather than including the rough run.

3.4 Clean the test wire according to the approved method, using hydrochloric acid and heating until no colour remains, and avoid carrying material from one salt to the next. Sodium is yellow; potassium lilac. Calcium is brick-red; strontium crimson-red. Keep the wire, sample-loading method and flame region/conditions matched. Sodium contamination gives a strong yellow signal that may mask another salt, so a contaminated yellow flame alone does not establish sample identity. Bubble the evolved CO_2 through limewater: it turns milky from CaCO_3 ; this is distinct from a flame test.

3.5 Use comparable measured molar amounts and similar particle size/apparatus; keep the heating rate and other apparatus conditions matched. Record sample temperature at an agreed detectable onset/extent of decomposition, rather than interpreting bubble time alone as a decomposition temperature. CO_2 turns limewater milky; O_2 relights a glowing splint; NO_2 is a brown gas with acidic behaviour on damp indicator. These

are observations in an approved ventilated supervised setup, not instructions to smell or handle decomposition gases independently. The detected onset depends on apparatus and sensitivity; compare it consistently rather than claiming a universal sharp decomposition temperature.