JEE MAIN · PAPER 1 · CHEMISTRY

20 Principles of Practical Chemistry

Formula & concept sheet

What the laboratory part of the syllabus asks: volumetric analysis ($KMnO_4$ against oxalic acid and Mohr's salt, standards and indicators), the systematic analysis of salts (anion tests, the cation groups and why the reagents are used, confirmatory tests, flame and borax-bead tests), tests for organic functional groups, standard preparations (Mohr's salt, alum, acetanilide, iodoform) and the small physical experiments. Each idea is explained first, then the tests tabulated with their colours.

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7 Last-minute checklist 7

READ ALONGSIDE NCERT · Chemistry Laboratory Manual

HOW TO USE THIS SHEET

1 **Skim**
Read the Key ideas, then

2 **Memorise**
Learn the formulas and

3 **Test**
Do the worked examples

4 **Revise**
Use the last-minute

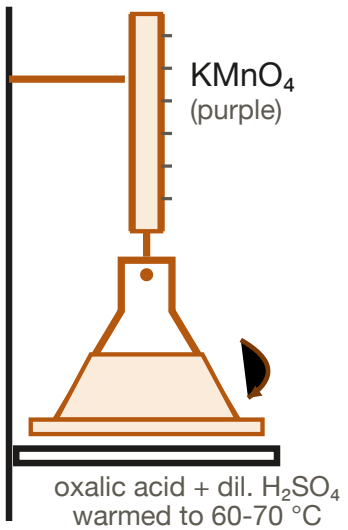
CHAPTER 20

Principles of Practical Chemistry

NCERT · Chemistry Laboratory Manual

Covers: volumetric analysis, primary standards, indicators · systematic analysis: anions and cations (groups 0 to VI), flame and borax-bead tests · functional-group tests · preparation of Mohr's salt, potash alum, acetanilide, p-nitroacetanilide, aniline yellow, iodoform · enthalpy of solution and neutralisation · colloids · chemical kinetics (iodine clock).

1 Volumetric analysis



end point: the first permanent pale pink; $KMnO_4$ acts as its own indicator

- A **titration** measures the volume of a solution of known concentration (**standard**) needed to react completely with a measured volume of the unknown. A **primary standard** is pure, stable, non-hygroscopic and of known formula: oxalic acid dihydrate, Mohr's salt, potassium hydrogen phthalate (KHP), Na_2CO_3, $K_2Cr_2O_7$. $NaOH$ (hygroscopic, absorbs CO_2) and $KMnO_4$ (slowly decomposes) are **secondary** standards and must be standardised.
- $KMnO_4$ is a **self-indicator** (the first permanent pale pink is the end point). It is acidified with dilute H_2SO_4 only: HCl is oxidised to Cl_2 and HNO_3 is itself an oxidant. Oxalic acid is titrated warm (60 to 70°C); Mohr's salt at room temperature.

EQUIVALENCE

$$N_1V_1 = N_2V_2, \quad M_1V_1n_1 = M_2V_2n_2$$

n-factors: $KMnO_4$ (acid) 5; oxalic acid, oxalate 2; Fe^{2+} (Mohr's salt) 1; $K_2Cr_2O_7$ (acid) 6; NaOH 1; H_2SO_4 2

REACTIONS BEHIND THE TITRATIONS

- Oxalate: $2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$, mole ratio $2:5$; the Mn^{2+} formed catalyses it (slow start, then fast).
- Mohr's salt: $MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$, mole ratio $1:5$.

MOLAR MASSES AND INDICATORS

ITEM	VALUE OR CHOICE
oxalic acid dihydrate $H_2C_2O_4 \cdot 2\,H_2O$	126 g mol^{-1} (primary standard)
Mohr's salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$	392 g mol^{-1}
$KMnO_4$; potash alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$	158; 948 g mol^{-1}
indicators	strong acid/strong base: either; weak acid/strong base: phenolphthalein (8.3 to 10, colourless to pink); strong acid/weak base: methyl orange (3.1 to 4.4, red to yellow); weak/weak: no sharp end point; KHP with NaOH: phenolphthalein

TRAP

Never acidify permanganate with HCl or HNO_3. Oxalic acid and Mohr's salt are primary standards; NaOH and $KMnO_4$ are not. Mohr's salt is preferred to ferrous sulphate because it is not oxidised in air (the double salt is stable) and is not efflorescent.

QUICK CHECK

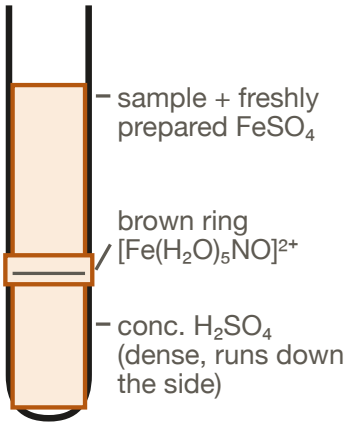
20 mL of 0.05 M $KMnO_4$ titrates 25 mL of oxalic acid solution. Its molarity, and the mass of oxalic acid dihydrate in 250 mL of this solution?

Answer: $M = \frac{5}{2} \times \frac{0.05 \times 20}{25} = 0.10$ M; $0.10 \times 0.25 \times 126 = 3.15$ g.

2 Salt analysis: anions

ANION TESTS

ANION	PRELIMINARY TEST (ACID)	CONFIRMATORY TEST
CO_3^{2-}	dil. H_2SO_4: brisk effervescence of CO_2, lime water turns milky	$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$
S^{2-}	dil. H_2SO_4: H_2S (rotten eggs), lead-acetate paper turns black	sodium nitroprusside: violet/purple (alkaline solution)
Cl^-	conc. H_2SO_4: HCl, white fumes with NH_3	$AgNO_3$: AgCl white, soluble in NH_4OH; chromyl chloride test: orange-red vapour (with $K_2Cr_2O_7$ + conc. H_2SO_4), yellow $PbCrO_4$ with lead acetate
Br^-	conc. H_2SO_4: red-brown Br_2 vapour	AgBr pale yellow, partly soluble in NH_4OH; layer test: orange-brown in CCl_4 with Cl_2 water
I^-	conc. H_2SO_4: violet I_2 vapour	AgI yellow, insoluble in NH_4OH; layer test: violet
NO_3^-	conc. H_2SO_4 + Cu turnings: brown NO_2	brown ring test
SO_4^{2-}	no gas with dilute or conc. acid	$BaCl_2$: $BaSO_4$ white, insoluble in conc. HCl; lead acetate: $PbSO_4$ white



brown ring test for nitrate: NO_3^- is reduced to NO by Fe^{2+} in conc. H_2SO_4 and forms the brown complex

BROWN RING TEST FOR NITRATE Add freshly prepared $FeSO_4$ to the solution, then run conc. H_2SO_4 down the side of the test tube: a brown ring forms at the junction. $NO_3^- + 3\,Fe^{2+} + 4\,H^+ \longrightarrow NO + 3\,Fe^{3+} + 2\,H_2O$; $[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$ (the brown ring). Bromides and iodides interfere (they give Br_2 and I_2 with conc. H_2SO_4) and must be removed first.

FACTS ON CONC. H_2SO_4 TESTS

- Heating a halide, nitrate or CaF_2 with conc. H_2SO_4: NaBr gives brown Br_2, $NaNO_3$ gives brown NO_2, KI gives violet I_2, NaCl gives colourless HCl, CaF_2 gives colourless HF (molar mass of CaF_2 is 78).
- Chloride with MnO_2 and conc. H_2SO_4 gives greenish-yellow Cl_2.

WHY IT WORKS

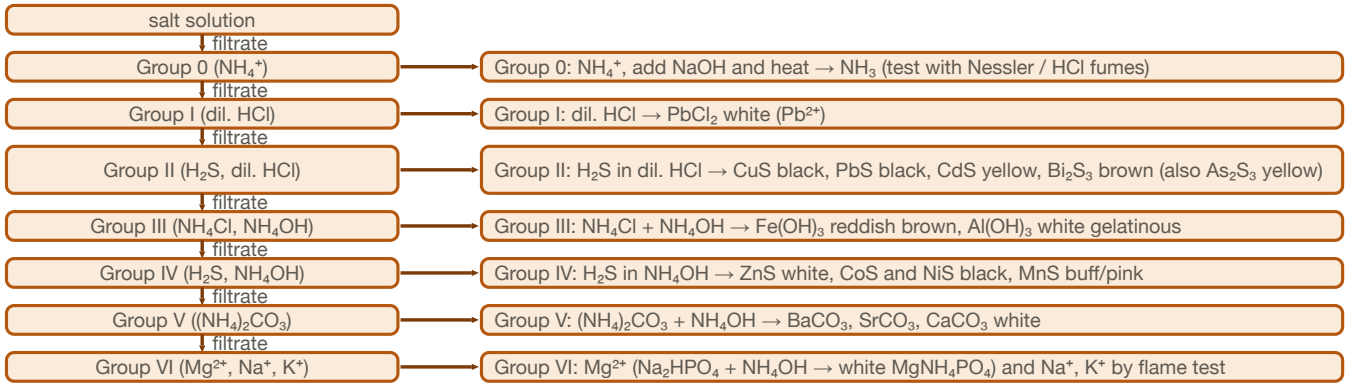
The acid test releases the gas of a volatile or unstable acid (CO_2, H_2S) with dilute acid, and a halogen halide or its oxidation product (Br_2, I_2, NO_2) with concentrated sulphuric acid, an oxidising acid. Sulphate does not volatilise, so it needs a precipitation test.

QUICK CHECK

Which anion gives violet vapour with conc. H_2SO_4 and a yellow, NH_4OH-insoluble silver salt?

Answer: Iodide: violet I_2 vapour; AgI is yellow and insoluble in NH_4OH.

3 Salt analysis: cations



each group reagent precipitates a set of cations; the filtrate goes to the next group

WHY THE GROUP REAGENTS WORK

STEP	REASON
Group II: H_2S in dilute HCl	group II sulphides (PbS, CuS, CdS, Bi_2S_3, As_2S_3) have very low K_{sp}; H^+ from HCl (common ion) suppresses H_2S ionisation, so the small $[S^{2-}]$ is just enough for group II only
Group IV: H_2S in NH_4OH	base removes H^+, raising $[S^{2-}]$ enough for the higher-K_{sp} sulphides (ZnS, NiS, CoS, MnS)
Group III: NH_4Cl then NH_4OH	NH_4^+ (common ion) suppresses NH_4OH ionisation, so $[OH^-]$ is low and only the very insoluble hydroxides ($Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$) precipitate, not Zn, Ni, Mn, Mg; conc. HNO_3 is boiled first to oxidise Fe^{2+} to Fe^{3+}
Group V: $(NH_4)_2CO_3$	carbonates of Ba, Sr, Ca are insoluble; NH_4Cl keeps Mg^{2+} in solution
rule behind all of it	a salt precipitates when the ionic product $Q > K_{sp}$

CONFIRMATORY TESTS FOR CATIONS

CATION	TEST AND OBSERVATION
NH_4^+	warm with NaOH: NH_3 (white fumes with HCl); Nessler's reagent ($K_2[HgI_4]$, alkaline): brown precipitate
Pb^{2+}	$PbCl_2$ white, dissolves in hot water; KI: yellow PbI_2 (golden spangles on cooling); K_2CrO_4: yellow $PbCrO_4$
Cu^{2+}	excess NH_4OH: deep blue $[Cu(NH_3)_4]^{2+}$; $K_4[Fe(CN)_6]$ in acetic acid: chocolate-brown $Cu_2[Fe(CN)_6]$
Fe^{3+}	$K_4[Fe(CN)_6]$: Prussian blue $Fe_4[Fe(CN)_6]_3$; KSCN: blood-red $[Fe(SCN)(H_2O)_5]^{2+}$
Al^{3+}	$Al(OH)_3$ white, gelatinous, dissolves in NaOH (amphoteric); blue litmus + NH_4OH gives a blue "lake"
Zn^{2+}	ZnS white; dissolves in NaOH (zincate); $K_4[Fe(CN)_6]$: white/bluish-white precipitate
Ni^{2+}	dimethylglyoxime + NH_4OH: bright red (rosy) $Ni(dmg)_2$
Ba^{2+}	K_2CrO_4 in acetic acid: yellow $BaCrO_4$; flame apple green
Ca^{2+}	$(NH_4)_2C_2O_4$: white CaC_2O_4; flame brick red
Mg^{2+}	Na_2HPO_4 + NH_4OH: white crystalline $Mg(NH_4)PO_4$

FLAME AND BORAX-BEAD TESTS

TEST	OBSERVATION
flame colours	Na golden yellow; K lilac (violet, through blue glass); Ca brick red; Sr crimson; Ba apple green; Cu blue-green; Zn, Co, Fe: no characteristic flame
borax bead (oxidising flame)	Cu blue (cold); Fe yellow-brown; Cr green; Co deep blue; Mn violet (amethyst); Ni violet (hot) / reddish-brown (cold). $Na_2B_4O_7 \longrightarrow 2\,NaBO_2 + B_2O_3$, then $B_2O_3 + MO \longrightarrow M(BO_2)_2$ (metaborate)
coloured sulphides	As_2S_3, CdS, SnS_2 yellow; Sb_2S_3 orange; MnS buff or pink; ZnS white; PbS, CuS, NiS, CoS, HgS black

TRAP

Pb^{2+} appears in both group I and group II ($PbCl_2$ is fairly soluble). $K_4[Fe(CN)_6]$ gives characteristic precipitates with Cu^{2+} (brown), Fe^{3+} (blue) and Zn^{2+} (white): three. $AgBr$ is only partly soluble in NH_4OH. Nessler's reagent detects NH_3/NH_4^+ only; dmg detects Ni^{2+} only.

QUICK CHECK

Why is NH_4Cl added before NH_4OH in group III, and why is HCl present for group II?

Answer: Common-ion effect: NH_4^+ lowers $[OH^-]$ so only the least soluble hydroxides precipitate; H^+ lowers $[S^{2-}]$ so only the group II sulphides precipitate.

4 Tests for organic functional groups

FUNCTIONAL-GROUP TESTS

GROUP	TEST AND OBSERVATION
unsaturation	Br_2/CCl_4 decolourised; cold dilute alkaline $KMnO_4$ (Baeyer) decolourised, brown MnO_2
alcohol	Na metal gives H_2; ceric ammonium nitrate: red; Lucas reagent ($ZnCl_2$/HCl): 3° turbid at once, 2° in about 5 min, 1° none at room temperature
phenol	neutral $FeCl_3$: violet/purple; Br_2 water: white precipitate (2,4,6-tribromophenol); Liebermann nitroso test
aldehyde	2,4-DNP orange/yellow precipitate (also ketones); Tollens': silver mirror; Fehling's/Benedict's: red Cu_2O (aliphatic aldehydes only; benzaldehyde negative); Schiff's: pink
ketone	2,4-DNP positive; Tollens' and Fehling's negative; methyl ketones give the iodoform test
carboxylic acid	$NaHCO_3$: brisk effervescence of CO_2; with ethanol and conc. H_2SO_4 a fruity ester smell
primary amine	carbylamine ($CHCl_3$ + KOH): foul isocyanide; aromatic 1°: diazotise at 273 to 278 K, then β-naphthol: orange-red dye; Hinsberg separates 1°, 2°, 3°
nitro compound	reduce to the amine with Sn/HCl, then diazotise and couple
elements (N, S, X, P)	Lassaigne's sodium fusion extract (see the Purification sheet)

5 Preparations and small experiments

STANDARD PREPARATIONS

PREPARATION	METHOD AND THE REASON FOR THE KEY REAGENT
Mohr's salt	equimolar $FeSO_4 \cdot 7\,H_2O$ and $(NH_4)_2SO_4$ in water with **dilute** H_2SO_4 (prevents hydrolysis and oxidation of Fe^{2+}); crystallise, do not overheat
potash alum	K_2SO_4 + $Al_2(SO_4)_3$ in water with dilute H_2SO_4 (prevents hydrolysis of $Al_2(SO_4)_3$); crystallise
acetanilide	$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$ (glacial acetic acid; zinc dust prevents oxidation of aniline)
p-nitroacetanilide	acetanilide + conc. HNO_3 + conc. H_2SO_4 below 283 K; $-NHCOCH_3$ is o/p-directing and moderates the ring; para is major
aniline yellow	diazotise aniline ($NaNO_2/HCl$, 273 to 278 K) and couple with aniline: *p*-aminoazobenzene
iodoform	$CH_3COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3 + CH_3COONa + 3\,NaI + 3\,H_2O$ (or ethanol, or KI + $NaOCl$); yellow crystals, antiseptic smell

PHYSICAL EXPERIMENTS

EXPERIMENT	FACTS
enthalpy of neutralisation	$q = (mc + C_{cal})\Delta T$, $\Delta H = -q/n$; strong acid + strong base ≈ -57.1 kJ mol^{-1} ($H^+ + OH^- \longrightarrow H_2O$), less for weak acid or base (part of the heat ionises it)
enthalpy of solution of $CuSO_4$	anhydrous $CuSO_4$ dissolves exothermically, $CuSO_4 \cdot 5\,H_2O$ endothermically; the difference is the enthalpy of hydration
lyophilic sols	starch, gum, gelatin, egg albumin: warm with water; reversible and stable
lyophobic sols	$Fe(OH)_3$: $FeCl_3 + 3\,H_2O \longrightarrow Fe(OH)_3 + 3\,HCl$ in boiling water (hydrolysis); As_2S_3: $As_2O_3 + 3\,H_2S \longrightarrow As_2S_3 + 3\,H_2O$ (double decomposition)
kinetics (iodine clock)	$H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow I_2 + 2\,H_2O$; a fixed amount of thiosulphate and starch ($I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_4O_6^{2-}$): the time for the blue colour to appear gives the rate

CALORIMETRY

$$\Delta T = \frac{n\,|\Delta H|}{m\,c}$$

50 mL 1 M HCl + 50 mL 1 M NaOH: $n = 0.05$, $q = 2855$ J,

$$\Delta T = \frac{2855}{100 \times 4.18} = 6.8 \text{ K}$$

KEY IDEA

When a question asks "why is X added", the answer is nearly always one of: common-ion suppression (NH_4Cl, HCl), preventing hydrolysis (dilute H_2SO_4 in Mohr's salt and alum), or preventing oxidation (Zn dust, H_2SO_4).

6 Worked examples

TITRATION

1.26 g of impure oxalic acid dihydrate in 100 mL; 10 mL needs 20 mL of 0.02 M $KMnO_4$. Purity?

$20 \times 0.02 = 0.4$ mmol $MnO_4^- \rightarrow 1.0$ mmol oxalate in 10 mL, 10 mmol in 100 mL $= 1.26$ g: 100% pure

MOHR'S SALT

Mass of Mohr's salt for 250 mL of 0.05 M, and the volume of 0.02 M $KMnO_4$ needed by 25 mL of it.

$392 \times 0.05 \times 0.25 = 4.9$ g; $25 \times 0.05 = 1.25$ mmol Fe^{2+} needs 0.25 mmol MnO_4^-: $\dfrac{0.25}{0.02} = 12.5$ mL

IDENTIFY THE SALT

A salt with dilute acid gives a colourless gas turning lime water milky; its solution gives a white precipitate with $BaCl_2$ soluble in HCl, and with NH_4OH a white precipitate that dissolves in excess NaOH. Identify.

anion CO_3^{2-} ($BaCO_3$ dissolves in HCl); cation Al^{3+} or Zn^{2+} (amphoteric hydroxide): e.g. zinc carbonate (aluminium carbonate does not exist in water)

COUNT IONS

How many of Cu^{2+}, Fe^{3+}, Zn^{2+}, Ba^{2+}, Ni^{2+} give a characteristic precipitate with $K_4[Fe(CN)_6]$?

Cu^{2+} (brown), Fe^{3+} (blue), Zn^{2+} (white): 3

GAS TEST

A salt heated with NaOH gives a gas that forms white fumes with HCl and a brown precipitate with Nessler's reagent. Cation?

NH_4^+ (the gas is NH_3)

CHOICE OF INDICATOR

Indicator for CH_3COOH + NaOH, and for $HCl + NH_4OH$?

phenolphthalein (equivalence point above 7); methyl orange (below 7)

7 Last-minute checklist

BEFORE YOU ANSWER

Gas or precipitate? Colour? Dilute or concentrated acid? Which group reagent separated it? For a titration: which n-factor and which acid medium?

- Titration: $N_1V_1 = N_2V_2$; $KMnO_4$ (5), oxalate (2), Fe^{2+} (1); acidify with dilute H_2SO_4 only; self-indicator; primary standards: oxalic acid, Mohr's salt, KHP, Na_2CO_3.
- Anions: CO_3^{2-} (CO_2), S^{2-} (H_2S, nitroprusside violet), Cl^- (HCl, AgCl white, chromyl chloride), Br^- (brown Br_2, AgBr pale yellow), I^- (violet, AgI yellow), NO_3^- (brown ring), SO_4^{2-} ($BaSO_4$).
- Cations: 0 NH_4^+ (NaOH, Nessler), I Pb^{2+} (HCl), II Cu^{2+}/Pb^{2+} (H_2S/HCl), III Al^{3+}/Fe^{3+} ($NH_4Cl + NH_4OH$), IV Zn^{2+}/Ni^{2+} (H_2S/NH_4OH), V Ba^{2+}/Ca^{2+} (carbonate), VI Mg^{2+}; dmg for Ni, $KSCN$ for Fe.
- Organic: Lucas (3° fast), $FeCl_3$ violet (phenol), Tollens' and Schiff's (aldehyde), Fehling's (aliphatic aldehyde only), 2,4-DNP (carbonyl), iodoform (methyl ketone), $NaHCO_3$ (acid), carbylamine (1° amine).
- "Why added": common ion (NH_4Cl, HCl), prevent hydrolysis or oxidation (dilute H_2SO_4, Zn); neutralisation ≈ -57 kJ mol^{-1}.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**