BP106T · B.PHARM THEORY

BP106T Pharmaceutical Inorganic and Analytical Chemistry

Unit III — Titrimetric Analysis

Pills & Python Notes

From-zero teaching standard: every technical term is defined before use.

Syllabus coverage: Unit III (14 hours).

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Foundation box for the whole unit. Titrimetry = measuring the **volume** of a solution of known strength (the **titrant**, in the burette) needed to completely react with a measured volume of the unknown (the **titrand** or analyte, in the flask). **Equivalence point** = the theoretical moment when reactants have combined in exact stoichiometric ratio. **Endpoint** = the experimental moment the indicator changes colour — we try to make it coincide with the equivalence point. The tiny difference is the **titration error**. **Standardisation** = finding the exact strength of a titrant using a **primary standard** (a substance pure, stable, and weighable with exact formula — e.g., anhydrous Na_2CO_3, KHP, $Na_2C_2O_4$, $K_2Cr_2O_7$, $CaCO_3$). A **secondary standard** (NaOH, $KMnO_4$, $Na_2S_2O_3$, HCl) is first prepared approximately, then standardised.

CHAPTER 8: ACID–BASE TITRATIONS AND INDICATORS

Unit III · ~3.5 hours

8.1 Introduction

Every antacid tablet, every bottle of dilute hydrochloric acid, and every ammonia solution in a pharmacy has a number on its label — its strength. How is that number measured? By **acid–base titration**: letting an acid and a base neutralise each other while watching an **indicator** change colour. It is the oldest, cheapest, and still most-used quantitative technique in pharmaceutical quality control, and the Indian Pharmacopoeia prescribes it for dozens of assays.

Learning objectives — after studying this chapter, you should be able to:

- define mole, molarity, normality, equivalent weight, titrant, titrand, endpoint, and equivalence point from scratch;
- explain the Ostwald and quinonoid theories of indicators;
- classify acid–base titrations and draw all four neutralisation curves;
- choose the correct indicator for each titration type;
- describe the preparation and standardisation of HCl and NaOH step by step;
- calculate normality from standardisation data and % purity from assay data;
- describe the assay of ammonium hydroxide.

8.2 Definition

Scientific definition: An acid–base titration is a volumetric analysis in which a solution of an acid (or base) of known concentration is added from a burette to a measured volume of a base (or acid) until neutralisation is complete, the completion being signalled by an indicator or a pH meter.

Simple explanation: You add a "measuring acid" drop by drop to an unknown base (or the reverse) until an indicator changes colour — the volume used tells you exactly how much acid or base was in the flask.

Indicator — scientific: a weak organic acid or base whose ionised and unionised forms have different colours, so its colour changes within a narrow pH range. **Indicator — simple:** a dye that changes colour to shout "stop — neutralisation is complete!"

8.3 Key Terminology

Term	Meaning	Simple explanation
Mole	6.022×10^{23} particles; mass of 1 mole = molar mass in grams	The chemist's "dozen" for counting molecules
Molarity (M)	Moles of solute per litre of **solution**	"How many molecular packets per litre"
Normality (N)	Gram-equivalents per litre of **solution**; N = M × n	"How many reactive packets per litre"
Equivalent weight	Molar mass ÷ n, where n = H^+ donated/accepted (acid–base), electrons exchanged (redox), or total ionic charge (precipitation)	The mass that does "one unit" of reaction
Primary standard	Ultra-pure, stable, weighable substance of exact composition	The "certified ruler" (Na_2CO_3, KHP, $Na_2C_2O_4$, $K_2Cr_2O_7$)
Secondary standard	Solution of approximate strength, fixed by standardisation	The "ruler you calibrate" (NaOH, HCl, $KMnO_4$, $Na_2S_2O_3$)
Meniscus	The curved liquid surface read at eye level in a burette	Read the bottom of the curve
Back titration	Excess reagent added, then the leftover titrated	Used when the analyte reacts slowly or is volatile

Why NaOH and HCl are secondary standards: NaOH pellets absorb water and CO_2 from air (forming Na_2CO_3), so a weighed amount is never pure NaOH. Concentrated HCl fumes and its strength drifts. Both must be **standardised**.

8.4 Detailed Explanation

8.4.1 Normality and equivalent weight — the calculation engine

Substance	n (acid–base)	Equivalent weight
HCl	1 (donates 1 H^+)	36.46/1 = 36.46
H_2SO_4	2	98.08/2 = 49.04
NaOH	1 (accepts 1 H^+)	40.00/1 = 40.00
Na_2CO_3	2	105.99/2 = 53.00
KHP (potassium hydrogen phthalate)	1	204.22/1 = 204.22
NH_3	1	17.03/1 = 17.03

Golden rule of titrimetry: at the equivalence point, **equivalents of titrant = equivalents of titrand**, i.e. $\mathbf{N_1V_1 = N_2V_2}$ (volumes in the same units).

Worked example 1 — standardisation of HCl. *25.0 mL of 0.100 N anhydrous sodium carbonate required 24.8 mL of dilute HCl (methyl orange indicator). Find the normality of HCl.*

- Reaction: $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
- $N_1V_1 = N_2V_2 \rightarrow 0.100 \times 25.0 = N_HCl \times 24.8$
- $N_HCl = 2.50 \div 24.8 =$ **0.1008 N** ✓ (every step: multiply first, then divide)

Worked example 2 — standardisation of NaOH. *0.510 g of dry KHP (eq. wt. 204.2) dissolved in water required 24.9 mL of NaOH (phenolphthalein). Find normality.*

- Equivalents of KHP = mass ÷ eq. wt. = 0.510 ÷ 204.2 = 0.0024975
- N_NaOH = equivalents ÷ volume in litres = 0.0024975 ÷ 0.0249 = **0.1003 N** ✓

8.4.2 Preparation and standardisation — step by step

0.1 N HCl: Dilute ~8.5 mL of concentrated HCl to 1 litre with water (approximate). **Standardise:** weigh accurately ~1.325 g of anhydrous Na_2CO_3 (previously dried — a primary standard), dissolve in water, add methyl orange, titrate with the HCl. Near the endpoint, boil briefly to expel CO_2, cool, and finish to the first permanent orange-pink. Calculate N by $N_1V_1 = N_2V_2$.

0.1 N NaOH: Dissolve ~4 g NaOH pellets in freshly boiled, cooled distilled water (boiling removes dissolved CO_2), make up to 1 litre, store protected from CO_2 (soda-lime guard tube). **Standardise:** weigh accurately ~0.5 g of dry KHP, dissolve, add phenolphthalein, titrate to the first permanent pale pink (persists ~30 seconds).

Exam Pearl: Na_2CO_3 is the primary standard for **acids**; KHP (or oxalic acid) is the primary standard for **bases**.

8.4.3 Theories of indicators

Ostwald theory: an indicator is itself a weak acid (HIn) or weak base. It ionises slightly: $HIn \rightleftharpoons H^+ + In^-$, where HIn has one colour and In^- another. In acidic solution (excess H^+), equilibrium shifts left → colour of HIn; in alkaline solution, H^+ is removed → shifts right → colour of In^-. The colour you see depends on the **ratio** $[In^-]/[HIn]$, which depends on pH. Each indicator changes colour over ~2 pH units centred on its pK_In.

Quinonoid theory: the colour change is caused by a **structural rearrangement** — the indicator molecule flips between a **benzenoid** form (one colour) and a **quinonoid** form (another colour). These are tautomers; pH decides which form dominates. Phenolphthalein: colourless benzenoid (acid) ⇌ pink quinonoid (alkaline).

Common indicators:

Indicator	pH range	Acid colour	Alkaline colour	Used for
Methyl orange	3.1–4.4	Red	Yellow	Strong acid vs weak base
Methyl red	4.2–6.3	Red	Yellow	Assay of ammonia (NH_4OH)
Phenolphthalein	8.3–10.0	Colourless	Pink	Weak acid vs strong base

8.4.4 Classification of acid–base titrations and neutralisation curves

Type	Equivalence pH	Curve shape	Correct indicator
Strong acid vs strong base (HCl vs NaOH)	7 (neutral salt)	Long steep rise, pH ~3→11	Methyl orange, methyl red, OR phenolphthalein
Weak acid vs strong base (CH_3COOH vs NaOH)	> 7 (salt hydrolyses basic: $CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$)	Steep portion ~pH 7→11	**Phenolphthalein only** (methyl orange changes before the steep part — wrong)
Strong acid vs weak base (HCl vs NH_4OH)	< 7 (NH_4^+ hydrolyses acidic)	Steep portion ~pH 3→7	**Methyl orange/methyl red only** (phenolphthalein changes after the steep part — wrong)
Weak acid vs weak base (CH_3COOH vs NH_4OH)	~7 but **no sharp steep portion**	Gradual curve, no vertical jump	**No indicator gives a sharp endpoint** — use potentiometric (pH meter) titration

Indicator selection rule: the indicator's colour-change range must lie **entirely within the steep (vertical) portion** of the curve.

> **Exam Pearl:** Weak–weak titrations have no steep jump, so no visual indicator works — this is a favourite one-mark question.

8.4.5 Theory of very weak acids and bases

Very weak acids (e.g., boric acid, phenols) and very weak bases give such a flat curve in water that no endpoint is visible. Two fixes: (1) convert them chemically — e.g., boric acid + glycerol forms a stronger complex acid, then titrate with NaOH; (2) move to a **non-aqueous solvent** (Chapter 9).

8.4.6 Assay of ammonium hydroxide (dilute ammonia solution)

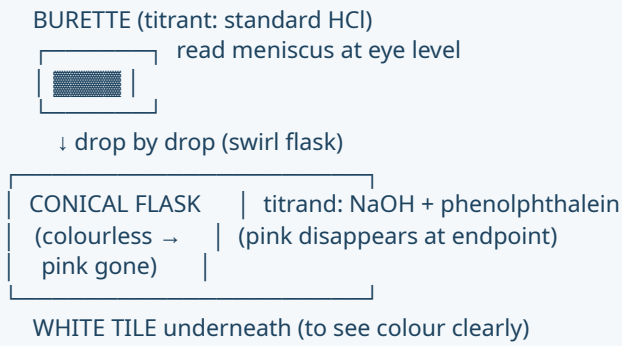
Principle: NH_4OH is a weak base assayed by direct titration with standard HCl using **methyl red** (strong acid vs weak base → endpoint below pH 7). **Reaction:** $NH_3 + HCl \rightarrow NH_4Cl$ (1:1; eq. wt. NH_3 = 17.03). **Equivalence:** 1 mL of 1 N HCl ≡ 17.03 mg of NH_3. **Worked example:** *10.0 mL of ammonium hydroxide sample required 5.90 mL of 1.0 N HCl. Calculate % w/v of NH_3.*

- Mass of NH_3 = N × V(L) × eq. wt. = 1.0 × 0.00590 × 17.03 = 0.100477 g (in 10 mL)
- Per 100 mL: 0.100477 × 10 = 1.00477 g → **1.00% w/v NH_3** ✓

8.5 Easy Analogy

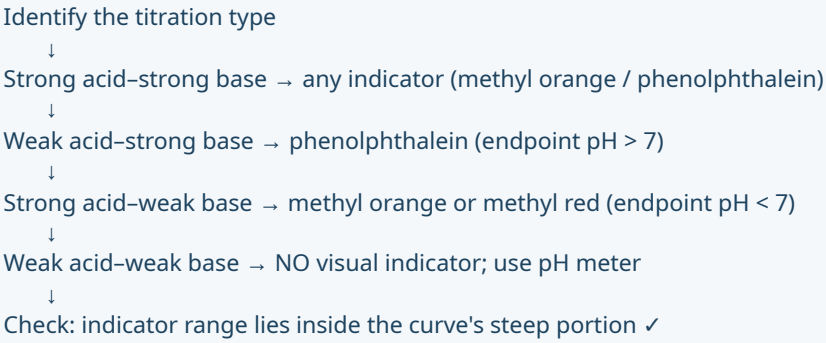
A titration is like **filling a bucket with a measuring jug**: the burette is the jug (known size), the flask is the bucket (unknown), and the indicator is a friend who shouts "full!" the moment water reaches the brim. The equivalence point is the brim; the endpoint is the shout — a good friend shouts exactly at the brim.

8.6 Diagram — Acid–Base Titration Assembly



AI Image Prompt: "Educational chemistry textbook diagram, white background, labelled titration apparatus: burette clamped on a stand dripping into a conical flask on a white tile, arrows showing titrant flow, labels for burette, titrant, titrand, indicator colour change, eye-level meniscus reading, clean pharmacy textbook style, minimal decoration."

8.7 Flowchart — Choosing an Indicator



8.8 Examples

- **Antacid assay:** $Mg(OH)_2$ tablets are assayed by back-titration with standard acid.
- **Aspirin assay:** a weak acid titrated with NaOH using phenolphthalein.
- **Ammonia solutions:** assayed with standard HCl, methyl red indicator.

8.9 Pharmacy Relevance

Acid–base titrimetry is the workhorse of QC labs: assay of acids, bases, salts, and many drugs (aspirin, ibuprofen — weak acids titrated with NaOH). It is cheap, fast, and needs no costly instrument — ideal for routine batch release.

India/IP context: The Indian Pharmacopoeia prescribes acid–base titrimetric assays for a large number of monographs (e.g., ammonium hydroxide, sodium hydroxide, boric acid preparations); procedures state the exact titrant, indicator, and equivalence factor "as per IP procedure."

8.10 Important Points to Remember

1. **Remember:** $N_1V_1 = N_2V_2$; N = M × n; equivalent weight = molar mass ÷ n.
2. **Exam Pearl:** Na_2CO_3 standardises acids; KHP standardises bases.
3. **Exam Pearl:** Ostwald = ionisation equilibrium ($HIn \rightleftharpoons H^+ + In^-$); Quinonoid = benzenoid ⇌ quinonoid structural change.
4. **Exam Pearl:** Indicator range must fall inside the steep portion of the curve.
5. Weak acid–strong base → phenolphthalein; strong acid–weak base → methyl orange/methyl red; weak–weak → no indicator (pH meter).
6. NaOH/HCl are secondary standards (NaOH absorbs $H_2O + CO_2$; HCl fumes).
7. 1 mL of 1 N HCl ≡ 17.03 mg NH_3 (ammonia assay).

8.11 Common Confusions & Common Mistakes

Do not confuse: Equivalence point ≠ endpoint (theoretical vs observed) · **Molarity ≠ normality** (M counts molecules; N counts reactive units) · **Acidimetric ≠ alkalimetric** (acidimetric = titrating with acid; alkalimetric = titrating with base). **Mistakes:** using methyl orange for acetic acid vs NaOH (changes too early); forgetting to convert mL to litres in N = equivalents/V(L); reading the burette from above instead of at eye level; in KHP standardisation, using molar mass (204.22) as equivalent weight is correct here only because n = 1.

8.12 Memory Tricks

- "**P**henolphthalein for **P**H above 7 (weak acid vs strong base); **M**ethyl **o**range for **M**ostly acidic endpoints (strong acid vs weak base)."
- "**O**stwald = i**O**nisation; **Q**uinonoid = **Q**uick structural flip."

8.13 Exam-Oriented Summary

Acid–base titration: standard acid/base from a burette neutralises the unknown; indicator signals the endpoint. $N_1V_1 = N_2V_2$. Indicators work by ionisation (Ostwald) or structural change (quinonoid). Four curve types decide the indicator: strong–strong (any), weak acid–strong base (phenolphthalein), strong acid–weak base (methyl orange), weak–weak (none — pH meter). HCl is standardised against Na_2CO_3; NaOH against KHP. Ammonia is assayed with standard HCl (methyl red); 1 mL 1 N HCl ≡ 17.03 mg NH_3.

One-Minute Revision: $N_1V_1 = N_2V_2$. Acids ↔ Na_2CO_3 standard; bases ↔ KHP standard. Phenolphthalein = alkaline endpoint; methyl orange = acidic endpoint; weak–weak = no indicator. Ostwald = ionisation; quinonoid = structure flip.

8.14 Questions

Very Short Answer: 1. Define normality. 2. State $N_1V_1 = N_2V_2$ and when it applies. 3. Name the primary standard for standardising HCl. 4. Why is NaOH a secondary standard? 5. State the Ostwald theory in one line.

Short Answer: 1. Explain the Ostwald and quinonoid theories of indicators. 2. Why can't methyl orange be used for titrating acetic acid with NaOH? 3. Describe the preparation and standardisation of 0.1 N HCl. 4. Draw and explain the neutralisation curve for a weak acid vs strong base.

Long Answer: 1. Classify acid–base titrations. Describe the four neutralisation curves and justify the choice of indicator for each. 2. Describe the preparation and standardisation of 0.1 N NaOH and 0.1 N HCl, with calculations.

MCQs

1. The primary standard used for standardising HCl is: (a) KHP (b) anhydrous Na_2CO_3 (c) oxalic acid (d) borax — **Ans: (b)**. Carbonate neutralises the acid; KHP is for bases.
2. Phenolphthalein is the correct indicator for: (a) HCl vs NH_4OH (b) CH_3COOH vs NaOH (c) CH_3COOH vs NH_4OH (d) all of these — **Ans: (b)**. Endpoint pH > 7 falls in its 8.3–10.0 range.
3. Equivalent weight of Na_2CO_3 (mol. wt. 105.99) is: (a) 105.99 (b) 53.00 (c) 35.33 (d) 26.50 — **Ans: (b)**. n = 2 (accepts 2 H^+).
4. In the quinonoid theory, colour change is due to: (a) ionisation (b) structural change benzenoid ⇌ quinonoid (c) precipitation (d) complex formation — **Ans: (b)**.
5. For a weak acid vs weak base titration: (a) use methyl orange (b) use phenolphthalein (c) no visual indicator gives a sharp endpoint (d) use starch — **Ans: (c)**. No steep pH jump exists.

Viva: Why is the NaOH solution prepared in freshly boiled distilled water? Why is CO_2 boiled off during Na_2CO_3 standardisation? What is the pH at the equivalence point of a strong acid–strong base titration?
Application-based: 1. *25.0 mL of 0.100 N Na_2CO_3 required 24.8 mL of HCl. Calculate the normality of HCl. (Ans: 0.1008 N — see worked example 1.)* 2. A QC chemist standardises NaOH and gets 0.0985 N instead of 0.1000 N. If she ignores this and uses 0.1000 N in an assay calculation, will the reported drug content be too high or too low? *(Ans: Too high — she thinks each mL carries more NaOH than it really does, so the calculated drug amount is inflated.)*

CHAPTER 9: NON-AQUEOUS TITRATIONS

Unit III · ~2.5 hours

9.1 Introduction

Some drugs are such **weak acids or weak bases** that water defeats them: in water they barely ionise, the titration curve is flat, and no indicator can find an endpoint. Examples include many alkaloidal drugs (very weak bases) and sulphonamides/barbiturates (very weak acids). The solution is to **change the solvent**: in a non-aqueous solvent, a weak base behaves like a strong one and gives a sharp endpoint. This technique assays a huge number of pharmacopoeial drugs.

Learning objectives — after studying this chapter, you should be able to:

- explain why water fails for very weak acids/bases (levelling effect);
- classify solvents as aprotic, protophilic, protogenic, and amphiprotic with examples;
- describe acidimetric titrations (perchloric acid in glacial acetic acid) and alkalimetric titrations (alkoxides);
- describe preparation and standardisation of the acidic and basic titrants;
- estimate weakly acidic/basic substances and sodium benzoate with calculations.

9.2 Definition

Scientific definition: Non-aqueous titration is a titrimetric analysis carried out in a solvent other than water, used for the determination of very weak acids and very weak bases that cannot be titrated sharply in aqueous solution.

Simple explanation: When water makes a weak drug "too shy" to react fully, we swap water for a special solvent that makes the drug react boldly — then titrate normally.

9.3 Key Terminology

Term	Meaning	Simple explanation
Levelling effect	Water levels all strong acids to the strength of H_3O^+, and makes very weak acids/bases hard to distinguish	Water "flattens" acid–base strengths
Acidimetric titration	Titration **with** a standard acid (determines bases)	"Measuring with acid"
Alkalimetric titration	Titration **with** a standard base (determines acids)	"Measuring with base"
Glacial acetic acid	Pure (water-free) acetic acid, mp ~16.6 °C	The classic non-aqueous acidic solvent

9.4 Detailed Explanation

9.4.1 Why water fails — the levelling effect

Water is **amphiprotic** (can donate and accept H^+). It levels strong acids: HCl, HBr, $HClO_4$ all appear equally strong in water (all become H_3O^+). More importantly for pharmacy, very weak bases (many alkaloids, e.g., caffeine) accept H^+ so poorly from water that the titration curve has no steep jump. In **glacial acetic acid** (a protogenic solvent, poorer H^+ acceptor than water), the same weak base competes better for protons → behaves as a stronger base → sharp endpoint.

9.4.2 Types of solvents

Type	Behaviour toward protons	Examples	Use
Aprotic	Neither donates nor accepts H^+	Chloroform, benzene, acetone	Diluent to dissolve sample
Protophilic	**Accepts** protons (basic solvents)	Pyridine, dimethylformamide (DMF), butylamine	Enhance **acidity** of weak acids (alkalimetric titrations)
Protogenic	**Donates** protons (acidic solvents)	Glacial acetic acid, formic acid	Enhance **basicity** of weak bases (acidimetric titrations)
Amphiprotic	Both donates and accepts	Water, methanol, ethanol	Ordinary aqueous/organic work

Exam Pearl: Protophilic solvents are for titrating weak **acids**; protogenic solvents are for titrating weak **bases**. (The solvent does the opposite job of the titrand.)

9.4.3 Acidimetric titrations in non-aqueous solvents (for weak bases)

- **Titrant:** 0.1 M **perchloric acid ($HClO_4$) in glacial acetic acid**.
- **Preparation:** dilute 70% $HClO_4$ with glacial acetic acid, add acetic anhydride to remove water (water would level the effect).
- **Standardisation:** against **potassium hydrogen phthalate (KHP)** — a primary standard — using **crystal violet** indicator (violet → blue-green endpoint). Reaction: KHP + $HClO_4$ → phthalic acid + $KClO_4$.
- **Worked example:** *0.510 g of dry KHP (mol. wt. 204.22) required 24.9 mL of $HClO_4$ solution. Calculate molarity.* Moles KHP = 0.510 ÷ 204.22 = 0.0024975; M = 0.0024975 ÷ 0.0249 = **0.1003 M** ✓ (1:1 reaction, so M = N here).
- **Determines:** alkaloids and other weak bases (ephedrine, codeine salts), and salts of weak acids such as **sodium benzoate**.

9.4.4 Alkalimetric titrations in non-aqueous solvents (for weak acids)

- **Titrant:** 0.1 M **sodium methoxide (CH_3ONa)** (or lithium methoxide) in methanol–toluene or DMF.
- **Standardisation:** against **benzoic acid** (primary standard) using **thymol blue** indicator.
- **Determines:** very weak acids — barbiturates, sulphonamides, phenols.

9.4.5 Estimation of sodium benzoate

Principle: sodium benzoate is the salt of a weak acid; in glacial acetic acid it is titrated **acidimetrically** with standard $HClO_4$ (crystal violet indicator). **Reaction:** $C_6H_5COONa + HClO_4 \rightarrow C_6H_5COOH + NaClO_4$ (1:1). **Equivalence:** 1 mL of 0.1 M $HClO_4$ ≡ 14.41 mg of sodium benzoate (mol. wt. 144.11; 144.11 × 0.1 ÷ 1000 = 0.014411 g/mL). **Worked example:** *0.350 g of sodium benzoate sample required 24.1 mL of 0.1 M $HClO_4$. Calculate % purity.*

- Mass found = 24.1 × 14.41 mg = 347.28 mg = 0.34728 g
- % purity = (0.34728 ÷ 0.350) × 100 = **99.22%** ✓

9.5 Easy Analogy

Titrating a very weak base in water is like trying to hear a whisper in a noisy hall — water's own H^+ chatter drowns it out. A non-aqueous solvent is like moving to a **silent room**: suddenly the whisper (the weak base) is loud and clear, and you can pinpoint exactly when it stops.

9.6 Diagram — Non-Aqueous Titration Setup

Burette: 0.1 M HClO4 in glacial acetic acid
↓
Flask: weak base (e.g., ephedrine) dissolved in
glacial acetic acid + crystal violet
Colour change: VIOLET → BLUE-GREEN → GREEN (endpoint)
Note: keep water OUT — even traces level the endpoint

AI Image Prompt: "Educational chemistry textbook diagram, white background, non-aqueous titration: burette labelled '0.1 M HClO4 in glacial acetic acid' dripping into a conical flask labelled 'weak base + crystal violet', colour progression strip showing violet to blue-green to green, a crossed-out water droplet symbol meaning 'keep water out', clean pharmacy textbook style."

9.7 Flowchart — Choosing a Non-Aqueous Titration

Is the drug a very weak BASE? (alkaloid, amine salt)
→ YES: acidimetric — titrate with HClO4 in glacial acetic acid (protogenic solvent), crystal violet
Is the drug a very weak ACID? (barbiturate, sulphonamide, phenol)
→ YES: alkalimetric — titrate with sodium methoxide in DMF/toluene-methanol (protophilic solvent), thymol blue
Can it be done in water with a sharp endpoint?
→ YES: stay aqueous (Chapter 8) — non-aqueous is only for what water cannot do

9.8 Examples

- **Ephedrine hydrochloride, codeine phosphate** — weak bases assayed acidimetrically.
- **Phenobarbitone** — weak acid assayed alkalimetrically.
- **Sodium benzoate** (preservative) — assayed acidimetrically as above.

9.9 Pharmacy Relevance

A large fraction of IP drug monographs for alkaloids, antihistamines, and weak-acid drugs prescribe non-aqueous titration — it is the standard assay where water fails. Mastering it is essential for any QC chemist.

India/IP context: The Indian Pharmacopoeia gives non-aqueous titrimetric assays for many drug monographs, specifying the titrant (e.g., 0.1 M perchloric acid), indicator, and equivalence factor "as per IP procedure."

9.10 Important Points to Remember

1. **Remember:** Water's levelling effect hides very weak acids/bases — change the solvent.
2. **Exam Pearl:** Protogenic solvent (glacial acetic acid) → titrate weak **bases** with $HClO_4$; protophilic solvent (DMF, pyridine) → titrate weak **acids** with CH_3ONa.
3. **Exam Pearl:** $HClO_4$ is standardised against KHP (crystal violet); CH_3ONa against benzoic acid (thymol blue).
4. Solvent types: aprotic ($CHCl_3$), protophilic (pyridine), protogenic (glacial CH_3COOH), amphiprotic (water, alcohols).
5. 1 mL 0.1 M $HClO_4$ ≡ 14.41 mg sodium benzoate.
6. Keep water out — even traces ruin the sharpness.

9.11 Common Confusions & Common Mistakes

Do not confuse: Acidimetric vs alkalimetric (acidimetric uses an acid titrant for bases; alkalimetric uses a base titrant for acids) · **Protophilic vs protogenic** (protophilic *accepts* H^+, protogenic *donates* H^+). **Mistakes:** titrating a weak base with sodium methoxide (wrong pair — match solvent/titrant to the analyte's weakness); forgetting the 1:1 stoichiometry in the sodium benzoate calculation; using aqueous indicators' pH ranges in non-aqueous work (they don't apply).

9.12 Memory Tricks

- "**P**rotogenic = **P**rovides protons → for weak **B**ases; **P**rotophilic = **P**refers protons (accepts) → for weak **A**cids." (Solvent and analyte are opposites.)
- "**C**rystal **v**iolet for **c**lockwise acid work (a**c**idimetri**c**)."

9.13 Exam-Oriented Summary

Very weak acids/bases give no sharp endpoint in water (levelling effect) → titrate in non-aqueous solvents. Solvents: aprotic, protophilic (accept H^+), protogenic (donate H^+), amphiprotic. Weak bases: acidimetric titration with 0.1 M $HClO_4$ in glacial acetic acid (standardised vs KHP, crystal violet). Weak acids: alkalimetric titration with sodium methoxide (standardised vs benzoic acid, thymol blue). Sodium benzoate: $C_6H_5COONa + HClO_4 \rightarrow C_6H_5COOH + NaClO_4$; 1 mL 0.1 M $HClO_4 \equiv 14.41$ mg.

One-Minute Revision: Water levels weak analytes → go non-aqueous. Weak base → $HClO_4$/glacial acetic acid/crystal violet. Weak acid → CH_3ONa/DMF/thymol blue. Protogenic donates, protophilic accepts. Sodium benzoate: 14.41 mg per mL of 0.1 M $HClO_4$.

9.14 Questions

Very Short Answer: 1. Define non-aqueous titration. 2. What is the levelling effect of water? 3. Give one example each of protophilic and protogenic solvents. 4. Name the titrant and indicator for sodium benzoate assay. 5. Why must water be excluded?

Short Answer: 1. Classify non-aqueous solvents with examples. 2. Describe the preparation and standardisation of 0.1 M perchloric acid. 3. Explain the principle of estimation of sodium benzoate with the reaction.

Long Answer: 1. Why do very weak acids/bases fail in aqueous titration? Describe acidimetric and alkalimetric non-aqueous titrations with titrants, standardisation, indicators, and examples.

MCQs

1. For titrating a very weak base, the solvent of choice is: (a) pyridine (b) glacial acetic acid (c) water (d) benzene — **Ans: (b)**. Protogenic solvent enhances base strength.
2. Perchloric acid is standardised against: (a) Na_2CO_3 (b) KHP (c) benzoic acid (d) oxalic acid — **Ans: (b)**. KHP acts as the base here.
3. Sodium methoxide is standardised against: (a) KHP (b) benzoic acid (c) Na_2CO_3 (d) HCl — **Ans: (b)**. Benzoic acid is the primary standard for bases.
4. 1 mL of 0.1 M $HClO_4$ is equivalent to ___ of sodium benzoate: (a) 12.21 mg (b) 14.41 mg (c) 20.42 mg (d) 144.11 mg — **Ans: (b)**. 144.11 × 0.1/1000 g = 14.41 mg.
5. DMF is a ___ solvent: (a) aprotic (b) protophilic (c) protogenic (d) amphiprotic — **Ans: (b)**. It accepts protons.

Viva: Why is acetic anhydride added while preparing perchloric acid titrant? What colour change does crystal violet show at the endpoint? **Application-based:** 1. *0.350 g sodium benzoate required 24.1 mL of 0.1 M $HClO_4$. Calculate % purity. (Ans: 99.22% — see worked example.)* 2. A new antihistamine is a very weak base, insoluble in water. Which titration approach and solvent would you choose, and why? *(Ans: Non-aqueous acidimetric — 0.1 M $HClO_4$ in glacial acetic acid; water would give no sharp endpoint for a very weak base.)*

CHAPTER 10: PRECIPITATION TITRATIONS AND GRAVIMETRY

Unit III · ~3 hours

10.1 Introduction

Not every analysis is about acids and bases. Chloride in water, silver in a salt, sulphate in a drug — these are measured by **precipitation**: forming an insoluble solid and either measuring how much silver nitrate it took (titration) or **weighing** the solid itself (gravimetry). These are among the oldest quantitative methods, and they are still pharmacopoeial standards.

Learning objectives — after studying this chapter, you should be able to:

- state the principle and stepwise procedure of gravimetric analysis;
- define gravimetric factor and use it in calculations;
- explain Mohr's, Volhard's, modified Volhard's, and Fajans methods with conditions and indicators;
- estimate $BaSO_4$ gravimetrically with a worked calculation;
- choose the right argentometric method for a given halide.

10.2 Definition

Scientific definition: Precipitation titration is a volumetric analysis in which the titrant forms an insoluble precipitate with the analyte, the endpoint being detected by an indicator that responds to excess titrant. Gravimetric analysis is a quantitative method in which the analyte is converted into a pure, stable, weighable precipitate whose mass gives the analyte amount via the gravimetric factor.

Simple explanation: Titration version — "count the drops of silver nitrate until the colour changes." Gravimetric version — "make the solid, dry it, weigh it, calculate backwards."

10.3 Key Terminology

Term	Meaning	Simple explanation
Precipitate	Insoluble solid formed in the reaction	The "solid snow" that falls out
Argentometry	Precipitation titrations using $AgNO_3$	"Silver measuring" (argentum = silver)
Gravimetric factor (GF)	(Molar mass of sought × its coefficient) ÷ (molar mass of weighed form × its coefficient)	The "exchange rate" between weighed solid and analyte
Digestion	Letting the precipitate stand in hot mother liquor	Small crystals dissolve, big ones grow — purer, easier to filter
Coprecipitation	Impurities carried down with the precipitate	"Uninvited guests" in the solid — minimised by digestion and washing
Peptization	Precipitate breaking into colloidal particles during washing	Prevented by washing with a dilute electrolyte, not pure water

10.4 Detailed Explanation

10.4.1 Principle and steps of gravimetric analysis

Principle: convert the analyte quantitatively into a compound of **known, fixed composition** that is pure, insoluble, and stable to drying/weighing; from its mass, calculate the analyte using the gravimetric factor.

Steps:

1. **Sampling & weighing** — weigh the sample accurately.
2. **Dissolution** — dissolve in a suitable solvent (often dilute acid).
3. **Precipitation** — add the precipitating agent slowly, with stirring, to a **hot, dilute** solution (gives large, pure crystals); slight excess of reagent.
4. **Digestion** — keep hot for some time (Ostwald ripening: small crystals redissolve, large ones grow).
5. **Filtration** — filter through quantitative filter paper or a sintered crucible.
6. **Washing** — wash free of soluble impurities with a dilute electrolyte solution (prevents peptization).
7. **Drying/ignition** — heat to constant weight (e.g., $BaSO_4$ is ignited).
8. **Weighing & calculation** — mass of precipitate × GF = mass of analyte.

10.4.2 Gravimetric factor — with worked example

GF = (molar mass of substance sought) ÷ (molar mass of substance weighed), adjusted for stoichiometry.

Estimation of sulphate as $BaSO_4$: $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$ (weighed form, mol. wt. 233.39).

- GF for SO_4^{2-} = 96.06 ÷ 233.39 = 0.4116
- GF for Ba^{2+} = 137.33 ÷ 233.39 = 0.5884
- GF for S = 32.06 ÷ 233.39 = 0.1374

> **Worked example:** *0.500 g of a sample gave 0.412 g of $BaSO_4$ precipitate. Calculate % w/w of sulphate (SO_4^{2-}).*
>
> - Mass of SO_4^{2-} = 0.412 × 0.4116 = 0.16958 g
> - % = (0.16958 ÷ 0.500) × 100 = **33.92% w/w** ✓

10.4.3 Argentometric methods (titrations with $AgNO_3$)

Essential conditions for any precipitation titration: the precipitate must be **sparingly soluble**, form **rapidly**, be **pure**, and the endpoint must be detectable.

A. Mohr's method (direct titration)

- **Titrant:** standard $AgNO_3$; **analyte:** Cl^- or Br^- (neutral solution).
- **Indicator:** potassium chromate (K_2CrO_4).
- **How it works:** Ag^+ first precipitates white AgCl (less soluble). At the endpoint, the first excess Ag^+ forms **red silver chromate** (Ag_2CrO_4) — white → reddish tinge.
- **Conditions:** solution must be **neutral or slightly alkaline (pH ~6.5–9)**. In acid, chromate becomes dichromate (no red precipitate); in strong alkali, Ag^+ precipitates as Ag_2O/AgOH.
- **Not for:** I^- or SCN^- (they adsorb chromate, blur the endpoint).

B. Volhard's method (back titration)

- **Procedure:** add a **measured excess** of standard $AgNO_3$ to the halide (in **nitric acid medium**); filter may be skipped; back-titrate the leftover Ag^+ with standard **ammonium thiocyanate (NH_4SCN)**.
- **Indicator:** ferric alum — ferric ammonium sulphate; endpoint = first permanent **red colour** of $FeSCN^{2+}$.
- **Advantage:** works in **acidic** medium (unlike Mohr's) — ideal for samples that need acid dissolution. Used for Cl^-, Br^-, I^-.

C. Modified Volhard's method (for chloride)

- **Problem:** AgCl is **more soluble** than AgSCN, so during back-titration SCN^- attacks the AgCl precipitate: $AgCl + SCN^- \rightarrow AgSCN + Cl^-$ — the endpoint fades and extra thiocyanate is consumed (high results).
- **Fix: filter off the AgCl** before back-titration, or coat it with **nitrobenzene** (forms a protective layer stopping the reaction).

D. Fajans method (adsorption indicators)

- **Principle:** before the equivalence point, the colloidal AgCl particles adsorb excess **Cl^-** (negative surface) and repel the anionic dye. Just past the endpoint, particles adsorb excess **Ag^+** (positive surface) and attract the dye anion onto the surface → **colour change on the precipitate**.
- **Indicators:** fluorescein (Cl^-; yellow-green → pink on AgCl), dichlorofluorescein, eosin (Br^-, I^-, SCN^-).
- Dextrin is sometimes added to keep the precipitate colloidal (more surface = sharper change).

Method	Type	Indicator	Endpoint signal	Medium	For
Mohr's	Direct	K_2CrO_4	Red Ag_2CrO_4	Neutral/slightly alkaline	Cl^-, Br^-
Volhard's	Back titration	Ferric alum	Red $FeSCN^{2+}$	Acidic (HNO_3)	Cl^-, Br^-, I^-
Modified Volhard's	Back + filtration/nitrobenzene	Ferric alum	Red $FeSCN^{2+}$	Acidic	Cl^- (stops AgCl–SCN^- reaction)
Fajans	Direct	Fluorescein/eosin (adsorption)	Dye colour on precipitate	Near-neutral	Cl^-, Br^-, I^-, SCN^-

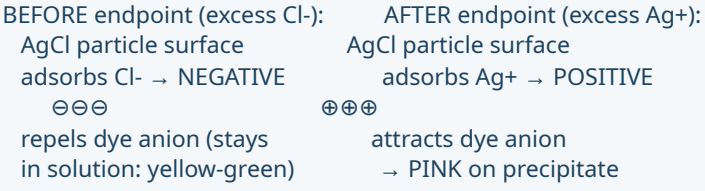
Worked example (Mohr's): *25.0 mL of a water sample required 12.4 mL of 0.02 N $AgNO_3$ (K_2CrO_4 indicator). Calculate chloride in mg/L.*

- 1 mL 0.02 N $AgNO_3$ ≡ 35.45 × 0.02 = 0.709 mg Cl^-
- Cl^- in 25 mL = 12.4 × 0.709 = 8.7916 mg
- Per litre: 8.7916 × (1000 ÷ 25) = **351.7 mg/L** ✓

10.5 Easy Analogy

Gravimetry is like **panning for gold**: you wash away everything soluble, keep the heavy solid, dry it, and weigh it — the weight of gold tells you how rich the soil was. Mohr's titration is like a **race with a photo finish**: silver ions "run" to chloride first (white precipitate), and the moment chloride is exhausted, they grab the chromate instead — the red flash is the finish-line photo.

10.6 Diagram — Fajans Adsorption Mechanism



> **AI Image Prompt:** "Educational chemistry textbook diagram, white background, two panels showing silver chloride colloidal particles: left panel particles with negative signs repelling yellow-green fluorescein dye molecules in solution, right panel particles with positive signs attracting pink dye onto their surface, clear labels 'before endpoint' and 'after endpoint', pharmacy textbook style."

10.7 Flowchart — Choosing an Argentometric Method

> Halide to estimate?
> ↓
> Need acidic medium (sample dissolved in acid)? → Volhard's (back titration, ferric alum)
> ↓ no
> Chloride specifically, and worried about fading endpoint? → Modified Volhard's (filter AgCl or add nitrobenzene)
> ↓ no
> Neutral solution, Cl- or Br-? → Mohr's (K2CrO4, neutral pH)
> ↓
> Want a direct titration with sharp visual change? → Fajans (adsorption indicator)

10.8 Examples

- **Chloride in water/physiological saline** — Mohr's method.
- **Silver nitrate assay** — Volhard's (excess NaCl, back-titrate with SCN^-).
- **Sulphate drugs** — gravimetry as $BaSO_4$.

10.9 Pharmacy Relevance

Chloride estimation (saline infusions), silver assays, and sulphate determinations all rest on this chapter. Gravimetry, though slow, is an **absolute method** (no standard solution needed) — used to standardise other methods and as a referee technique.

India/IP context: The IP prescribes argentometric titrations (e.g., Mohr's for chlorides) and gravimetric procedures (e.g., sulphate as barium sulphate) in several monographs, with exact conditions "as per IP procedure."

10.10 Important Points to Remember

1. **Remember:** Gravimetry = precipitate → filter → wash → ignite → weigh → × GF.
2. **Exam Pearl:** GF = (molar mass sought × coeff.) ÷ (molar mass weighed × coeff.); GF(SO_4^{2-}/$BaSO_4$) = 0.4116.
3. **Exam Pearl:** Mohr's = $AgNO_3$ direct, K_2CrO_4, red Ag_2CrO_4 endpoint, neutral pH — for Cl^-, Br^-.
4. **Exam Pearl:** Volhard's = back titration, NH_4SCN, ferric alum (red $FeSCN^{2+}$), acidic medium.
5. **Exam Pearl:** Modified Volhard's fixes the AgCl + SCN^- reaction by filtration or nitrobenzene coating.
6. **Exam Pearl:** Fajans = adsorption indicators (fluorescein for Cl^-); colour change happens ON the precipitate surface.
7. Digestion grows large pure crystals; wash with dilute electrolyte to prevent peptization.

10.11 Common Confusions & Common Mistakes

Do not confuse: Mohr's vs Volhard's (direct/neutral vs back/acidic) · **Adsorption (Fajans) vs absorption** (dye sticks ON the surface, not inside) · **Gravimetric factor direction** (sought ÷ weighed — upside-down gives nonsense). **Mistakes:** running Mohr's in acidic solution (chromate → dichromate, no endpoint); forgetting the modified Volhard's step for chloride (fading endpoint, high results); using pure water to wash a gelatinous precipitate (peptization — use dilute electrolyte); weighing before constant weight is reached.

10.12 Memory Tricks

- "**M**ohr's = **M**easure directly, **M**ild pH; **V**olhard's = **V**ersatile (acid OK), back-titration **V**ictory."
- "**F**ajans = **F**luorescein **F**ixes onto the sur**f**ace."
- "GF = **S**ought over **W**eighed — **S**mall over **W**eight? No: **S**ought ÷ **W**eighed."

10.13 Exam-Oriented Summary

Precipitation methods: titrate with $AgNO_3$ (argentometry) or weigh the precipitate (gravimetry). Gravimetric steps: dissolve → precipitate (hot, dilute) → digest → filter → wash (electrolyte) → ignite → weigh → × GF. $BaSO_4$: GF(SO_4^{2-}) = 0.4116. Mohr's: direct, K_2CrO_4, red Ag_2CrO_4, neutral pH, for Cl^-/Br^-. Volhard's: back titration with SCN^-, ferric alum, acidic medium. Modified Volhard's: filter AgCl or nitrobenzene coat (AgCl more soluble than AgSCN). Fajans: adsorption indicators; dye changes colour on the precipitate surface after the endpoint.

One-Minute Revision: Gravimetry: precipitate, digest, filter, wash, ignite, weigh, × GF. Mohr = direct/neutral/chromate; Volhard = back/acidic/thiocyanate; modified = protect AgCl; Fajans = dye on surface. GF = sought ÷ weighed.

10.14 Questions

Very Short Answer: 1. Define gravimetric factor. 2. Name the indicator in Mohr's method. 3. Why is Volhard's done in acidic medium? 4. What is digestion? 5. Name one adsorption indicator.

Short Answer: 1. List and explain the steps of gravimetric analysis. 2. Explain the modified Volhard's method — what problem does it solve? 3. Explain the Fajans endpoint mechanism. 4. Why must Mohr's titration be done at neutral pH?

Long Answer: 1. Describe the principle and steps of gravimetric analysis. Estimate sulphate as $BaSO_4$ with a calculation. 2. Compare Mohr's, Volhard's, modified Volhard's, and Fajans methods (principle, indicator, conditions, applications).

MCQs

1. In Mohr's method, the endpoint is marked by: (a) white AgCl (b) red Ag_2CrO_4 (c) blue starch complex (d) pink phenolphthalein — **Ans: (b)**. Excess Ag^+ precipitates chromate.
2. Volhard's method is a: (a) direct titration (b) back titration (c) gravimetric method (d) redox titration — **Ans: (b)**. Excess $AgNO_3$ is back-titrated with SCN^-.
3. The nitrobenzene in modified Volhard's: (a) acts as indicator (b) coats AgCl preventing its reaction with SCN^- (c) oxidises chloride (d) buffers the pH — **Ans: (b)**.
4. Fajans indicators are called adsorption indicators because: (a) dye is absorbed inside the crystal (b) dye changes colour on the precipitate surface (c) dye forms a soluble complex (d) dye oxidises the halide — **Ans: (b)**.
5. GF for estimating SO_4^{2-} as $BaSO_4$ is: (a) 0.5884 (b) 0.4116 (c) 0.1374 (d) 2.430 — **Ans: (b)**. 96.06 ÷ 233.39.

Viva: Why is the precipitate digested hot? What happens if you wash AgCl with pure distilled water? Why can't Mohr's method be used for iodide? **Application-based:** 1. *0.500 g sample gave 0.412 g $BaSO_4$. Calculate % w/w sulphate. (Ans: 33.92% — see worked example.)* 2. A student runs Mohr's titration on an acidic sample without neutralising it and gets no sharp endpoint. Explain why, and how to fix it. *(Ans: In acid, chromate converts to dichromate, so red Ag_2CrO_4 never forms properly — neutralise to pH ~7 first.)*

CHAPTER 11: COMPLEXOMETRIC TITRATIONS

Unit III · ~2.5 hours

11.1 Introduction

Calcium in a calcium tablet, magnesium in an antacid, zinc in an eye drop — how are these metals measured? They form **complexes**: a metal ion gripped by a molecule with multiple "claws." The champion claw-molecule is **EDTA**, which grabs almost any metal ion in a strict 1:1 ratio. Add an indicator that changes colour the moment the metal is fully gripped, and you have complexometry — the standard pharmacopoeial method for metal assays.

Learning objectives — after studying this chapter, you should be able to:

- define complex, ligand, chelate, and coordination number from zero;
- explain why EDTA forms 1:1 complexes and why its disodium salt is used;
- classify complexometric titrations (direct, back, substitution, indirect);
- explain metal-ion indicators (Eriochrome Black T, murexide) and masking/demasking;
- describe preparation and standardisation of disodium EDTA;
- estimate $MgSO_4$ and calcium gluconate with calculations.

11.2 Definition

Scientific definition: Complexometric titration is a volumetric analysis in which the analyte metal ion is quantitatively converted into a soluble coordination complex (chelate) by a chelating titrant, the endpoint being signalled by a metal-ion indicator.

Simple explanation: The titrant (EDTA) "handcuffs" metal ions one-by-one; the indicator changes colour the moment the last free metal ion is handcuffed.

11.3 Key Terminology

Term	Meaning	Simple explanation
Complex	Metal ion bonded to surrounding molecules/ions	Metal "surrounded by helpers"
Ligand	The helper molecule/ion donating electron pairs	The "claw"
Chelate	Complex with a polydentate ligand forming ring structures	A "multi-claw hug" — very stable
Denticity	Number of donor atoms per ligand	EDTA is **hexadentate** (6 claws)
Coordination number	Total donor atoms around the metal	Usually 6 for EDTA complexes
Masking agent	Reagent that ties up an interfering ion so it can't react	"Blindfolding" the troublemaker
Demasking agent	Reagent that releases a masked ion when needed	"Removing the blindfold"

Why disodium EDTA, not EDTA acid? EDTA acid is poorly soluble in water; its **disodium salt ($Na_2H_2Y{\cdot}2H_2O$)** dissolves readily and is the standard titrant (usually 0.05 M).

11.4 Detailed Explanation

11.4.1 The EDTA reaction

EDTA (as H_2Y^{2-}) reacts with metal ions in a **1:1 molar ratio regardless of the metal's charge**: $M^{n+} + H_2Y^{2-} \rightarrow MY^{(n-4)} + 2H^+$. Because H^+ is released, the reaction is pH-dependent — a **buffer** holds the pH (usually pH ~10, NH_4Cl/NH_4OH) so the reaction goes to completion. **Use molarity, not normality**, for EDTA calculations (1:1 stoichiometry).

11.4.2 Classification of complexometric titrations

1. **Direct titration:** EDTA added straight to the metal ion (e.g., Mg^{2+}, Zn^{2+}) — indicator EBT.
2. **Back titration:** excess EDTA added, leftover back-titrated with standard Zn^{2+}/Mg^{2+} — for metals that react slowly or precipitate at pH 10 (e.g., Al^{3+}).
3. **Substitution (displacement) titration:** for metals whose EDTA complex is weak or that lack a good indicator — displace an equivalent amount of another metal (e.g., Mg^{2+}) from its EDTA complex and titrate that.
4. **Indirect (alkalimetric) titration:** the H^+ released in complex formation is titrated with standard base — for metals like… (principle level).

11.4.3 Metal-ion indicators

An indicator that is **itself a chelating agent**, forming a coloured complex with the metal — but a **weaker** complex than EDTA forms, so EDTA snatches the metal away at the endpoint.

- **Eriochrome Black T (EBT):** wine-**red** with metal ions → **blue** when free. Works at pH ~10 (ammonia buffer). The classic general indicator.
- **Murexide:** for Ca^{2+} (at high pH ~12, where Mg^{2+} precipitates as hydroxide and doesn't interfere), Ni^{2+}, Cu^{2+}.
- **Xylenol orange:** for Bi^{3+}, Pb^{2+}, Zn^{2+} in acidic medium.

11.4.4 Masking and demasking agents

When two metals are present and only one is wanted:

- **Masking:** add a reagent that locks the interferent into an unreactive complex. Examples: **potassium cyanide** masks Cu^{2+}, Co^{2+}, Ni^{2+} (as stable cyano complexes); **sodium fluoride** masks Al^{3+} and Fe^{3+}; **triethanolamine** masks Fe^{3+}, Al^{3+}, Mn^{2+}.
- **Demasking:** release the masked ion when its turn comes — e.g., **formaldehyde** (or chloral hydrate) destroys the Zn–cyanide complex, freeing Zn^{2+} for titration.
- **Safety note:** cyanide masking is a textbook/classical method; modern labs prefer safer alternatives — know the principle for exams.

11.4.5 Preparation and standardisation of disodium EDTA

Preparation: dissolve ~18.61 g of disodium EDTA dihydrate (mol. wt. 372.24; 372.24 × 0.05 = 18.612 g) in water, make up to 1 litre → ~0.05 M. It is not a primary standard (variable water content). **Standardisation:** against a primary standard — **calcium carbonate** (dried; dissolved in dilute HCl) or standard **zinc sulphate** — using EBT indicator at pH 10. Reaction is 1:1, so M_EDTA = (moles of standard) ÷ (volume in litres).

11.4.6 Estimation of magnesium sulphate

Principle: direct titration of Mg^{2+} with standard EDTA at pH 10 (ammonia buffer), EBT indicator (wine red → blue). **Equivalence:** 1 mL of 0.05 M EDTA ≡ 6.02 mg of anhydrous $MgSO_4$ (mol. wt. 120.37; 120.37 × 0.05 ÷ 1000 = 0.0060185 g/mL). **Worked example:** *0.300 g of $MgSO_4$ sample required 49.5 mL of 0.05 M EDTA. Calculate % purity.*

- Mass found = 49.5 × 6.0185 mg = 297.92 mg = 0.29792 g
- % = (0.29792 ÷ 0.300) × 100 = **99.31%** ✓

11.4.7 Estimation of calcium gluconate

Principle: direct titration of Ca^{2+} with standard EDTA; **murexide** indicator (or EBT) at appropriate pH. **Equivalence:** 1 mL of 0.05 M EDTA ≡ 22.42 mg of calcium gluconate monohydrate (mol. wt. 448.39; 448.39 × 0.05 ÷ 1000 = 0.0224195 g/mL). **Worked example:** *0.550 g of calcium gluconate required 24.4 mL of 0.05 M EDTA. Calculate % purity.*

- Mass found = 24.4 × 22.4195 mg = 547.04 mg = 0.54704 g
- % = (0.54704 ÷ 0.550) × 100 = **99.46%** ✓

11.5 Easy Analogy

EDTA is a **six-armed octopus** that hugs each metal ion exactly once — always one octopus per ion, no exceptions. The indicator (EBT) is a weaker friend holding the metal's hand (red); the octopus is stronger, so it pulls the metal away — and the friend, left alone, turns blue. That's the endpoint.

11.6 Diagram — EDTA Chelate of a Metal Ion

```
        OOC—CH2
          \     / CH2—COO-
           N——M——N       M = metal ion (e.g., Ca2+, Mg2+)
          /     \       gripped at 6 points (hexadentate)
      -OOC—CH2    CH2—COO-
(EDTA wraps the metal like a claw — 1:1 complex, very stable)
```

AI Image Prompt: "Educational chemistry textbook diagram, white background, EDTA molecule shown as a claw-like hexadentate ligand wrapping around a central metal ion sphere labelled M2+, six coordination bonds drawn as lines, label '1:1 chelate — very stable', clean pharmacy textbook style, minimal decoration."

11.7 Flowchart — Planning an EDTA Titration

```
Which metal? (Ca2+, Mg2+, Zn2+...)
    ↓
Any interfering metals? → YES: add masking agent (KCN / fluoride / triethanolamine)
    ↓ no / masked
Set pH with buffer (usually pH 10, NH3/NH4Cl)
    ↓
Add metal-ion indicator (EBT / murexide)
    ↓
Titrate with standard EDTA → colour change (red → blue) = endpoint
    ↓
Calculate using MOLARITY (1:1): moles EDTA = moles metal
```

11.8 Examples

- **Calcium tablets / calcium gluconate injection** — EDTA titration.
- **Magnesium in antacids** — EDTA titration.
- **Water hardness** (Ca^{2+} + Mg^{2+}) — the classic EDTA application with EBT.

11.9 Pharmacy Relevance

Metal assays (calcium, magnesium, zinc, bismuth) in drugs and raw materials are done complexometrically — fast, sharp, and specific with masking. Water hardness testing (purified water for manufacturing) also uses EDTA.

India/IP context: The IP prescribes complexometric (EDTA) assays for calcium and magnesium salts and related preparations, giving the molarity of EDTA, indicator, and equivalence factor "as per IP procedure."

11.10 Important Points to Remember

1. **Remember:** EDTA is hexadentate; complexes are always **1:1** — calculate with **molarity**.
2. **Exam Pearl:** Use disodium EDTA (soluble); the acid form is poorly soluble.
3. **Exam Pearl:** EBT: wine red → blue at pH 10; murexide for Ca^{2+}.
4. **Exam Pearl:** Masking (KCN, fluoride, triethanolamine) hides interferents; demasking (formaldehyde) releases them.
5. Four types: direct, back, substitution, indirect.
6. 1 mL 0.05 M EDTA ≡ 6.02 mg $MgSO_4$ (anhydrous); ≡ 22.42 mg calcium gluconate.
7. pH control by buffer is essential (H^+ is released in the reaction).

11.11 Common Confusions & Common Mistakes

Do not confuse: Chelate vs complex (every chelate is a complex, but a complex with a monodentate ligand like NH_3 is not a chelate) · **Masking vs demasking** (hide vs release). **Mistakes:** using normality for EDTA calculations (use molarity — 1:1); titrating without buffer (pH falls as H^+ is released, reaction stalls); adding EBT at the wrong pH (colour change fails); forgetting that back titration is for slow/blocked reactions.

11.12 Memory Tricks

- "**E**DTA = **E**ight? No — h**E**xa (6) dentate, **1:1** always."
- "**EBT** turns from **R**ed to **B**lue — '**E**ndpoint **B**lue **T**ime'."

11.13 Exam-Oriented Summary

EDTA (hexadentate) forms 1:1 chelates with metal ions; disodium salt is the titrant (0.05 M, standardised vs $CaCO_3$/Zn^{2+}). Types: direct, back, substitution, indirect. Indicators: EBT (red → blue, pH 10), murexide (Ca^{2+}). Masking agents (cyanide, fluoride, triethanolamine) hide interferents; demasking (formaldehyde) frees them. $MgSO_4$: 1 mL 0.05 M EDTA ≡ 6.02 mg; calcium gluconate: ≡ 22.42 mg. Always buffer the pH; calculate with molarity.

One-Minute Revision: EDTA = hexadentate, 1:1, use molarity. Disodium salt (soluble). EBT red → blue at pH 10. Mask = hide, demask = release. Direct/back/substitution/indirect. $MgSO_4$: 6.02 mg/mL; calcium gluconate: 22.42 mg/mL (0.05 M EDTA).

11.14 Questions

Very Short Answer: 1. Define chelate. 2. Why is disodium EDTA used instead of EDTA acid? 3. What is the stoichiometry of EDTA–metal complexes? 4. Name one masking and one demasking agent. 5. Why is a buffer needed in EDTA titrations?

Short Answer: 1. Explain the action of Eriochrome Black T as a metal-ion indicator. 2. Classify complexometric titrations with one example each. 3. Describe the preparation and standardisation of 0.05 M disodium EDTA. 4. Explain masking and demasking with examples.

Long Answer: 1. Describe the principle of complexometric titrations. Discuss metal-ion indicators, masking/demasking, and the four titration types. 2. Describe the estimation of magnesium sulphate and calcium gluconate by EDTA titration with calculations.

MCQs

1. EDTA forms complexes with metal ions in the ratio: (a) 1:2 (b) 2:1 (c) 1:1 (d) 1:3 — **Ans: (c)**. Hexadentate ligand saturates the metal in one molecule.
2. Eriochrome Black T at the endpoint changes from: (a) blue to red (b) red to blue (c) colourless to pink (d) yellow to green — **Ans: (b)**. Metal–EBT (red) → free EBT (blue).
3. Which masks Cu^{2+}, Co^{2+}, Ni^{2+} in EDTA titrations? (a) Fluoride (b) Cyanide (c) Formaldehyde (d) Ammonia — **Ans: (b)**. Stable cyano complexes; formaldehyde is a demasker.
4. 1 mL of 0.05 M EDTA ≡ ___ of anhydrous $MgSO_4$: (a) 12.04 mg (b) 6.02 mg (c) 3.01 mg (d) 22.42 mg — **Ans: (b)**. 120.37 × 0.05/1000 g.
5. Back titration in complexometry is preferred when: (a) the metal reacts too quickly (b) the metal reacts slowly or precipitates at the working pH (c) no indicator exists at all (d) EDTA is unavailable — **Ans: (b)**.

Viva: Why must EDTA calculations use molarity rather than normality? What pH is used for EBT titrations and why? Name the indicator for calcium at high pH. **Application-based:** 1. *0.300 g $MgSO_4$ required 49.5 mL of 0.05 M EDTA. Calculate % purity. (Ans: 99.31% — see worked example.)* 2. You must estimate Zn^{2+} in a sample also containing Cu^{2+}. Design the approach. *(Ans: Mask Cu^{2+} with KCN, titrate Zn^{2+} directly with EDTA/EBT at pH 10; or demask Zn with formaldehyde after masking both, then titrate.)*

CHAPTER 12: REDOX TITRATIONS

Unit III · ~2.5 hours

12.1 Introduction

Bleaching powder, hydrogen peroxide, vitamin C tablets, iron tonics — their strengths are measured by **electron transfer**. One substance gives electrons (oxidised), another takes them (reduced), and we count the exchange with a standard oxidant or reductant. These are redox titrations: dramatic colour changes (purple permanganate going colourless, blue starch appearing) and some of the most beautiful chemistry in the QC lab.

Learning objectives — after studying this chapter, you should be able to:

- define oxidation and reduction from zero (electron and oxidation-number views);
- assign oxidation numbers and balance simple redox equations;
- explain permanganometry, cerimetry, iodimetry, iodometry, and potassium iodate titrations with indicators and conditions;
- describe preparation and standardisation of $KMnO_4$, iodine, and sodium thiosulphate;
- perform redox assay calculations step by step.

12.2 Definition

Scientific definition: A redox titration is a volumetric analysis based on oxidation–reduction reactions, in which a standard oxidising or reducing agent is titrated against the analyte, the endpoint being detected by the reagent's own colour, a specific indicator, or a redox indicator.

Simple explanation: Count electrons the way acid–base titration counts H^+ — add a standard "electron taker" (or "electron giver") until the colour tells you the exchange is complete.

12.3 Key Terminology

Term	Meaning	Simple explanation
Oxidation	**Loss** of electrons (or gain of O / loss of H)	"OIL" — Oxidation Is Loss
Reduction	**Gain** of electrons (or loss of O / gain of H)	"RIG" — Reduction Is Gain
Oxidising agent	Takes electrons; itself gets reduced	The "electron thief" ($KMnO_4$, $K_2Cr_2O_7$, I_2)
Reducing agent	Gives electrons; itself gets oxidised	The "electron donor" ($Na_2S_2O_3$, Fe^{2+}, ascorbic acid)
Oxidation number	The charge an atom *appears* to have in a compound	Bookkeeping for electrons
Self-indicator	Titrant whose own colour marks the endpoint	$KMnO_4$ — first permanent pink
Redox indicator	Changes colour with the solution's oxidation state	Ferroin, diphenylamine

Oxidation-number rules (from zero): free element = 0; monatomic ion = its charge; oxygen usually −2; hydrogen usually +1; alkali metals +1, alkaline earths +2; the sum equals the molecule/ion's charge. Example: in $KMnO_4$, K = +1, O_4 = −8, so Mn = +7; in Mn^{2+}, Mn = +2 → Mn gains 5 electrons (reduced).

12.4 Detailed Explanation

12.4.1 The five redox titration families

A. Permanganometry ($KMnO_4$)

- **Reaction (acidic medium):** $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (Mn: +7 → +2; **5 electrons** → eq. wt. = 158.03 ÷ 5 = 31.61).
- **Indicator:** none needed — **self-indicator**; first permanent pale pink = endpoint.
- **Conditions:** strongly acidic with **H_2SO_4** (never HCl — permanganate oxidises Cl^- to Cl_2; never HNO_3 — it is itself an oxidant).
- **Not a primary standard:** $KMnO_4$ always contains MnO_2 impurities → prepare approximately, **standardise against sodium oxalate** (primary standard) in warm acidic solution (Mn^{2+} formed autocatalyses the reaction — slow at first, then fast).
- **Uses:** Fe^{2+}, oxalates, H_2O_2 estimations.
- > **Worked example:** *25.0 mL of 0.100 N sodium oxalate required 24.7 mL of $KMnO_4$. Calculate normality.* N = (0.100 × 25.0) ÷ 24.7 = 2.50 ÷ 24.7 = **0.1012 N** ✓

B. Cerimetry (ceric sulphate, $Ce(SO_4)_2$)

- **Reaction:** $Ce^{4+} + e^- \rightarrow Ce^{3+}$ (**1 electron** → eq. wt. = molar mass).
- **Indicator: ferroin** (red → pale blue) or potentiometric.
- **Advantages over permanganate:** stable solutions (can be a primary-standard-like reagent), works in **HCl medium**, single-electron change gives simple stoichiometry.
- **Uses:** Fe^{2+}, arsenites, oxalates.

C. Iodimetry (direct titration WITH iodine)

- **Titrant:** standard **iodine solution** (I_2 dissolved with KI as KI_3 — iodine alone is poorly soluble and volatile).
- **Analyte:** a **reducing agent** (e.g., ascorbic acid/vitamin C, sodium thiosulphate, sulphites).
- **Reaction:** $I_2 + 2e^- \rightarrow 2I^-$ (eq. wt. I_2 = 253.8 ÷ 2 = 126.9).
- **Indicator: starch** — deep blue complex with iodine; endpoint = disappearance of blue.
- **Standardisation:** against **arsenic trioxide** (primary standard) or against standard thiosulphate.

D. Iodometry (indirect — liberate iodine, then titrate it)

- **Principle:** the **oxidising** analyte (e.g., Cu^{2+}, $K_2Cr_2O_7$, peroxides) oxidises KI in acid, **liberating I_2**; the liberated iodine is titrated with standard **sodium thiosulphate**.
- **Reactions:** $2Cu^{2+} + 4I^- \rightarrow 2CuI\downarrow + I_2$; then $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ (tetrathionate).
- **Titrant:** standard **$Na_2S_2O_3$** — not a primary standard (effloresces, attacked by CO_2/bacteria) → standardised against **$K_2Cr_2O_7$** (primary standard): $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$.
- **Indicator:** starch — add **near the endpoint** (pale straw colour), not at the start (starch–iodine complex adsorbs and won't fully release).
- > **Worked example (copper):** *25.0 mL of a copper sulphate sample, treated with KI, required 18.6 mL of 0.100 N $Na_2S_2O_3$. Calculate mg of Cu per 100 mL.* (1 mL 0.1 N thio ≡ 6.354 mg Cu; eq. wt. Cu = 63.54.)
- Cu in 25 mL = 18.6 × 6.354 = 118.18 mg
- Per 100 mL: 118.18 × 4 = **472.7 mg** ✓

E. Potassium iodate titrations (KIO_3 — Andrews method)

- **Principle:** in **strong HCl**, iodate titrations proceed with formation of iodine monochloride (ICl); the endpoint is the **disappearance of iodine colour** (in chloroform layer or solution).
- **Uses:** As(III), Sb(III), iodide estimations. KIO_3 is obtainable pure enough to be a near-primary standard.

Method	Titrant	Indicator	Key condition	Determines
Permanganometry	$KMnO_4$	Self (pink)	H_2SO_4 medium, not HCl	Fe^{2+}, oxalate, H_2O_2
Cerimetry	$Ce(SO_4)_2$	Ferroin	Works even in HCl	Fe^{2+}, As(III)
Iodimetry	I_2 (standard)	Starch	Analyte is a reductant	Ascorbic acid, sulphites
Iodometry	$Na_2S_2O_3$ (standard)	Starch (add late)	Analyte liberates I_2 from KI	Cu^{2+}, $Cr_2O_7^{2-}$, peroxides
Iodate (Andrews)	KIO_3	Iodine colour disappearance	Strong HCl	As(III), Sb(III)

12.4.2 Redox indicators and starch — how they work

- **Self:** $KMnO_4$'s own purple colour.
- **Specific:** starch forms a deep-blue complex specifically with iodine.
- **True redox indicators** (ferroin, diphenylamine, N-phenylanthranilic acid): exist in oxidised/reduced forms of different colours; change colour when the solution's potential crosses their transition potential — the redox analogue of pH indicators.

12.5 Easy Analogy

A redox titration is a **tug-of-war over electrons**: the oxidant pulls, the reductant holds. The indicator is the referee's flag — starch waves blue while iodine still holds the rope and drops it the moment iodine is gone; permanganate doesn't even need a referee, because its own purple jersey is visible until the last molecule is used up.

12.6 Diagram — Iodometric Titration (Copper Estimation)

```
Flask: Cu2+ sample + KI (excess) + H2SO4
      → brown I2 liberated, white CuI precipitate
    ↓ titrate with standard Na2S2O3 from burette
Brown fades → pale STRAW → add starch → BLUE
    ↓ continue dropwise
Blue DISAPPEARS → colourless/white CuI = endpoint
(starch added LATE — early addition traps iodine)
```

AI Image Prompt: "Educational chemistry textbook diagram, white background, sequential illustration of iodometric titration: four conical flasks showing colour progression from brown iodine solution to pale straw to deep blue after starch addition to colourless endpoint, burette labelled 'standard Na2S2O3' above, clear labels and arrows, pharmacy textbook style, minimal decoration."

12.7 Flowchart — Choosing a Redox Method

```
Is the analyte a REDUCING agent (Fe2+, ascorbic acid, oxalate)?
  → YES: titrate directly — KMnO4 (self-indicator, H2SO4) or Ce(SO4)2 (ferroin) or I2 (starch) = iodimetry
Is the analyte an OXIDISING agent (Cu2+, Cr2O7 2-, peroxides)?
  → YES: iodometry — liberate I2 from KI, titrate with standard Na2S2O3, starch near endpoint
Is it As(III)/Sb(III) in strong HCl?
  → YES: KIO3 titration (Andrews)
```

12.8 Examples

- **Iron tonics (Fe^{2+})** — permanganometry or cerimetry.
- **Vitamin C tablets** — iodimetry with standard iodine, starch indicator.
- **Copper sulphate** — iodometry.
- **Hydrogen peroxide** — permanganometry.

12.9 Pharmacy Relevance

Redox titrimetry assays iron preparations, ascorbic acid, peroxides, and many raw materials. Iodine–thiosulphate is one of the most-used systems in pharmaceutical QC because the starch endpoint is unmistakable.

India/IP context: The IP prescribes redox titrimetric assays (permanganometric, iodometric, cerimetric) for numerous monographs — iron salts, ascorbic acid, hydrogen peroxide, and others — with titrant, indicator, and equivalence factors "as per IP procedure."

12.10 Important Points to Remember

1. **Remember:** OIL RIG — Oxidation Is Loss, Reduction Is Gain (of electrons).
2. **Exam Pearl:** $KMnO_4$ is self-indicating; use H_2SO_4 medium — never HCl (oxidised to Cl_2).
3. **Exam Pearl:** $KMnO_4$ eq. wt. = M/5 (acidic); Ce^{4+} eq. wt. = M/1; I_2 eq. wt. = M/2.
4. **Exam Pearl:** Iodimetry = titrate WITH standard I_2 (analyte is reductant); Iodometry = liberate I_2 from KI, titrate with thio (analyte is oxidant).
5. **Exam Pearl:** Add starch NEAR the endpoint in iodometry, not at the start.
6. **Exam Pearl:** $Na_2S_2O_3$ standardised vs $K_2Cr_2O_7$ (primary standard); $KMnO_4$ vs sodium oxalate; I_2 vs As_2O_3.
7. Cerimetry works in HCl medium and is more stable than permanganate.

12.11 Common Confusions & Common Mistakes

Do not confuse: Iodimetry vs iodometry (direct I_2 titration vs liberate-then-titrate — the single most confused pair in this unit) · **Oxidising agent vs oxidised substance** (the agent gets reduced). **Mistakes:** acidifying permanganate titrations with HCl (Cl_2 evolved, wrong results); adding starch at the start of iodometry (irreversible adsorption, overshoot endpoint); using $KMnO_4$ molarity as normality (divide by 5 in acid); standardising thiosulphate against iodine instead of dichromate as the primary reference.

12.12 Memory Tricks

- "**OIL RIG**" — Oxidation Is Loss, Reduction Is Gain.
- "**I**od**i**metry = **I**odine **i**n the burette (direct); iod**o**metry = **o**ut comes iodine from KI (indirect)."
- "**S**tarch **S**hould wait — add at the **S**traw stage."

12.13 Exam-Oriented Summary

Redox titrations count electrons. Permanganometry: $KMnO_4$, self-indicator (pink), H_2SO_4 medium (never HCl), standardised vs sodium oxalate, eq. wt. M/5. Cerimetry: $Ce^{4+} \rightarrow Ce^{3+}$, ferroin, stable, HCl-tolerant. Iodimetry: direct titration with standard I_2 (analyte = reductant), starch. Iodometry: oxidising analyte liberates I_2 from KI; titrate with standard $Na_2S_2O_3$ (standardised vs $K_2Cr_2O_7$); starch added near endpoint. KIO_3 (Andrews): strong HCl, ICl endpoint, for As(III)/Sb(III). 1 mL 0.1 N thio ≡ 6.354 mg Cu.

One-Minute Revision: OIL RIG. $KMnO_4$: self-indicator, H_2SO_4 only, M/5, vs oxalate. Iodimetry = I_2 in burette; iodometry = I_2 liberated, thio titrant, starch late. Thio vs $K_2Cr_2O_7$. Cerimetry: 1 e^-, ferroin, HCl OK.

12.14 Questions

Very Short Answer: 1. Define oxidation and reduction (electron view). 2. Why is $KMnO_4$ called self-indicating? 3. Why is HCl not used to acidify permanganate titrations? 4. Distinguish iodimetry from iodometry in one line each. 5. Name the indicator in iodometric titrations.

Short Answer: 1. Explain why $KMnO_4$ must be standardised and describe its standardisation. 2. Describe the iodometric estimation of copper with reactions. 3. Compare permanganometry and cerimetry. 4. Why is starch added near the endpoint in iodometry?

Long Answer: 1. Define redox titrations. Describe permanganometry, cerimetry, iodimetry, iodometry, and potassium iodate titrations with reactions, indicators, conditions, and standardisation. 2. Explain oxidation numbers with rules and use them to find the equivalent weight of $KMnO_4$ in acidic medium.

MCQs

1. In acidic medium, the equivalent weight of $KMnO_4$ (mol. wt. 158.03) is: (a) 158.03 (b) 79.02 (c) 52.68 (d) 31.61 — **Ans: (d)**. 5 electrons gained (Mn +7 → +2).
2. Iodometry differs from iodimetry in that: (a) iodine is in the burette (b) iodine is liberated from KI by the analyte and then titrated (c) no indicator is used (d) it is done in non-aqueous medium — **Ans: (b)**.
3. Sodium thiosulphate is standardised against: (a) Na_2CO_3 (b) $K_2Cr_2O_7$ (c) KHP (d) $CaCO_3$ — **Ans: (b)**. Dichromate is the primary standard; liberated I_2 is titrated.
4. Starch indicator is added near the endpoint because: (a) it reacts with copper (b) early addition causes irreversible adsorption of iodine (c) it is unstable in acid (d) it reduces iodine — **Ans: (b)**.
5. Cerimetry has an advantage over permanganometry in that: (a) it needs no indicator (b) it can be used in HCl medium and is more stable (c) it involves 5 electrons (d) it is self-indicating — **Ans: (b)**.

Viva: What is autocatalysis in the permanganate–oxalate titration? Why is iodine dissolved in KI solution rather than water alone? What is the Andrews method? **Application-based:** 1. *25.0 mL of 0.100 N sodium oxalate required 24.7 mL of $KMnO_4$. Calculate the normality of $KMnO_4$. (Ans: 0.1012 N — see worked example.)* 2. A student acidifies a permanganate titration of Fe^{2+} with HCl instead of H_2SO_4 and reports high iron content. Explain the error. *(Ans: $KMnO_4$ oxidises Cl^- to Cl_2, consuming extra permanganate — the titre is falsely high, so the calculated iron is inflated.)*

UNIT III INFOGRAPHIC CONCEPT — "THE TITRATION FAMILY TREE"

Layout: a tree diagram. Trunk: "TITRIMETRY — measure volumes, count equivalents ($N_1V_1 = N_2V_2$)". Five main branches, each with leaves:

- **Acid–Base** (Ch 8): leaves — indicators (Ostwald/quinonoid), 4 curves, HCl/NaOH standardisation, NH_4OH assay
- **Non-Aqueous** (Ch 9): leaves — 4 solvent types, $HClO_4$/crystal violet, CH_3ONa/thymol blue, sodium benzoate assay
- **Precipitation & Gravimetry** (Ch 10): leaves — Mohr/Volhard/modified Volhard/Fajans, $BaSO_4$ gravimetry, GF = 0.4116
- **Complexometric** (Ch 11): leaves — EDTA 1:1 hexadentate, EBT/murexide, masking/demasking, $MgSO_4$ & calcium gluconate assays
- **Redox** (Ch 12): leaves — $KMnO_4$/Ce^{4+}/I_2/thio/KIO_3, starch, OIL RIG

Roots of the tree: "Primary standards: Na_2CO_3, KHP, $Na_2C_2O_4$, $K_2Cr_2O_7$, $CaCO_3$, benzoic acid". **Banner:** "Right titrant + right indicator + right conditions = right result."

UNIT III REFERENCES (combined)

- Vogel AI. *Vogel's Textbook of Quantitative Chemical Analysis.* (Standard reference for titrimetric methods.)
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- Mendham J, Denney RC, Barnes JD, Thomas MJK. *Vogel's Quantitative Chemical Analysis.* 6th ed. (Gravimetry, titrimetry.)