Unit 1 · Volumetric Analysis

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Physical Chemistry (Units 1–5 together): 22 of 75 marks; 4 MCQs, 2 short and 1 long question
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: equivalent weight of H_3PO_3 in $2NaOH + H_3PO_3 \rightarrow Na_2HPO_3 + 2H_2O$ (M/2); short: Na_2CO_3 standard against H_2SO_4: how the end point is seen, is Na_2CO_3 a primary standard and why, g of H_2SO_4 still needed after 2.16 g Na_2CO_3 meets 400 mL of N/10 acid
- **MCQ (1 mark)**
  - principle of gravimetric analysis; ppb; a primary standard and its properties; law of equivalence
  - E of Fe in Fe_3O_4, of $K_2Cr_2O_7$ (M/6), of an acid from a titration
  - molarity from mass; volume from M; mass in a volume; what stays the same on dilution
  - $KMnO_4$'s role with oxalic acid (oxidizing agent, self-indicator)
- **Short (5 marks, in parts)**
  - differences: molarity/normality/molality, ppm/ppb, moles/gram equivalents, primary/secondary, acid–base/redox titration
  - volumetric vs gravimetric, uses, a limit; $BaCl_2$ by weighing $BaSO_4$
  - E of H_3PO_4, $FeSO_4$, $K_2Cr_2O_7$ in given reactions; % w/w to % w/v (68% HNO_3, sp. gr. 1.4)
  - law of equivalence with a sum; Mohr's salt as primary standard; mg/dL to % w/v, g/L, ppm, M
  - dilution (12 M to 0.100 M HCl, precautions); argentometric titration; $KMnO_4$ and oxalic acid
- **Long (8 marks)**: 0.5 N H_2SO_4 from 98% acid (density 1.84); molarity and normality of 2% NaCl; NaOH–oxalic acid titration; mixtures of acids; standardizing $KMnO_4$; $KMnO_4$ and Fe^{2+}; numerical sets (purity, washing soda, water of crystallization, mole fraction)

Key terms

Qualitative analysis: what is present; **quantitative**: how much; **analyte**: the substance being measured.

Gravimetric analysis: amount found by measuring a **mass** (often a precipitate filtered, dried, weighed).

Volumetric analysis: concentration found by measuring the **volume** of a solution that reacts with the analyte.

Equivalent weight (element): mass that combines with or displaces **1.008 g H, 8 g O or 35.5 g Cl**; in grams, the gram equivalent weight.

n-factor (valence factor): H^+ given (acid, **basicity**), OH^- given (base, **acidity**), total + charge (salt), electrons gained or lost (redox), **in that reaction**.

Normal solution (1 N): 1 gram equivalent of solute per liter of solution; **molar (1 M)**: 1 mole per liter.

Primary standard: pure, stable, non-hygroscopic, soluble; weighed straight into a standard solution.

Secondary standard: impure or changing (hygroscopic, deliquescent, efflorescent, decomposes); its solution is standardized.

Law of equivalence: substances react and form in equal numbers of gram equivalents.

Titrant: standard solution in the burette; **titrand (analyte)**: in the flask.

Equivalence point: titrant exactly enough to react; **end point**: indicator changes; difference = **titration error**.

Alkalimetry: acid found with standard base; **acidimetry**: base found with standard acid.

Self-indicator: $KMnO_4$, its own color shows the end point.

Iodometric: iodine set free is titrated with thiosulphate; **iodimetric**: standard iodine itself.

Formulas

$E = \frac{A}{v}$	A atomic weight, v valency **Use:** element
$E = \frac{M}{n}$	M molar mass, n n-factor **Use:** compound, radical
$\mathrm{N} = \mathrm{M} \times n$	0.1 M H_2SO_4 = 0.2 N **Use:** normality from molarity
$N_1V_1 = N_2V_2$	or $M_1n_1V_1 = M_2n_2V_2$ **Use:** titration
$M_1V_1 = M_2V_2$	moles unchanged **Use:** dilution (a reaction only if 1 : 1)

- element by experiment: E = mass of element ÷ mass of H × 1.008 (or ÷ O × 8, ÷ Cl × 35.5)
- gram equivalents = mass ÷ E = N × V(mL) ÷ 1000
- molarity = mass × 1000 ÷ (M × V mL) = (g/L) ÷ M; mol/L of **solution**
- molality = mass × 1000 ÷ (M × g of **solvent**); mol/kg
- normality = mass × 1000 ÷ (E × V mL) = % w/v × 10 ÷ E
- mole fraction of A = $n_A/(n_A + n_B)$; no unit; all add to 1
- % w/v = % w/w × sp. gr.; g/L = % w/v × 10
- ppm = mass ratio × 10^6, ppb × 10^9; in water 1 ppm = 1 mg/L, 1 ppb = 1 µg/L

Analysis (1.1)

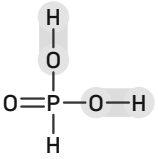
- quantitative: physical (density, refractive index) or chemical (precipitation, neutralization, oxidation)

- gravimetric, volumetric, instrumental
- gravimetric: flour 5.00 g → 4.40 g dried: 0.60 g water, 12%
- $NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3$: 143.5 g AgCl holds 35.5 g Cl
- $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\,HCl$, excess acid to precipitate all Ba
- glassware: burette and measuring cylinder (any volume); pipette and volumetric flask (one volume, very accurate); beaker ±5%
- 1 L = 1 dm^3; 1 mL = 1 cm^3
- the reaction: known, fast, complete, clear end
- uses: water hardness and arsenic, medicines, food acidity, nitrate and phosphate in rivers

Equivalent weights (1.2, 1.3)

- why: compare substances without formulas; three standards H, O, Cl (1.008 g H ≡ 8 g O ≡ 35.5 g Cl)
- $E = A/v$: 1 atom takes v H atoms, so A g takes $v \times 1.008$ g H
- Mg 24/2 = 12; Fe 56/2 = 28 (Fe^{2+}), 56/3 = 18.7 (Fe^{3+}); Fe in Fe_3O_4 168/64 × 8 = 21

Acid	M	Basicity	E
HCl, HNO_3	36.5, 63	1	36.5, 63
CH_3COOH	60	1	60
H_2SO_4	98	2	49
$H_2C_2O_4{\cdot}2H_2O$	126	2	63
H_3PO_3	82	2	41
H_3PO_4 (to Na_3PO_4)	98	3	32.7



replaceable H
phosphorous acid: basicity 2

H_3PO_3: one H on P can't leave, so basicity 2.

- only H that leaves as H^+ counts: CH_3COOH basicity 1
- $H_3PO_4 \rightarrow NaH_2PO_4$ (98), Na_2HPO_4 (49), Na_3PO_4 (32.7): the reaction decides
- base: $Mg(OH)_2$ 58/2 = 29; NaOH, KOH, NH_4OH monoacidic
- salt: NaCl 58.5; $MgCl_2$ 95/2 = 47.5; Na_2CO_3 106/2 = 53; $Al_2(SO_4)_3$ 342/6 = 57
- radical: CO_3^{2-} 60/2 = 30; PO_4^{3-} 95/3 = 31.7

Oxidizing and reducing agents: M ÷ electrons per formula unit (total change of oxidation number)

$KMnO_4$ in	Half-equation	n	E
acid	$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$	5	31.6
neutral, weak alkali	$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-$	3	52.7
strong alkali	$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	1	158

- purple → colorless Mn^{2+} (acid), brown MnO_2 (neutral), green MnO_4^{2-} (strong alkali)
- $K_2Cr_2O_7$ (Cr +6 → +3, 2 Cr): 294/6 = 49
- $H_2C_2O_4$ (C +3 → +4): 90/2 = 45; crystals 126/2 = 63
- $FeSO_4$ ($Fe^{2+} \rightarrow Fe^{3+}$): 152; Mohr's salt 392
- $Na_2S_2O_3$: $2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2\,e^-$, n = 1: 158 (crystals $\cdot 5H_2O$ 248)

Concentration (1.4)

- dilution lowers concentration, not the amount
- % w/w: 98.3% H_2SO_4 = 98.3 g in 100 g; for a solid, percentage purity
- % w/v: normal saline 0.9% = 9 g/L NaCl
- % v/v: 175 mL ethanol + 75 mL water ≈ 243 mL (contraction) → always **make up to the mark**
- molar names: M, M/2 semimolar, M/10 decimolar, M/100 centimolar (NaOH 40, 20, 4, 0.4 g/L)
- normal names: N, N/2 seminormal, N/10 decinormal (Na_2CO_3 53, 26.5, 5.3 g/L)
- molality for heating and cooling (boiling, freezing points)
- **formality (F)**: formula units before dissociation per liter; 58.5 g NaCl in 1 L = 1 F (2 mol of ions); same number as molarity
- Nepal's lead limit 0.01 mg/L = 0.01 ppm = 10 ppb
- **don't change with temperature**: molality, mole fraction, % w/w; **change**: molarity, normality, % w/v, % v/v (volume expands)

Standard substances (1.5)

Primary standard must be

1. highly pure
2. stable (air, CO_2, moisture)
3. non-hygroscopic
4. readily soluble
5. helpful: large E (weighing error small), quick complete reaction

Primary

- Na_2CO_3 (E 53)
- oxalic acid, $H_2C_2O_4{\cdot}2H_2O$
- sodium oxalate (67)
- $K_2Cr_2O_7$ (49)
- Mohr's salt (392)
- borax (190.6)
- $KBrO_3$
- sulphamic acid

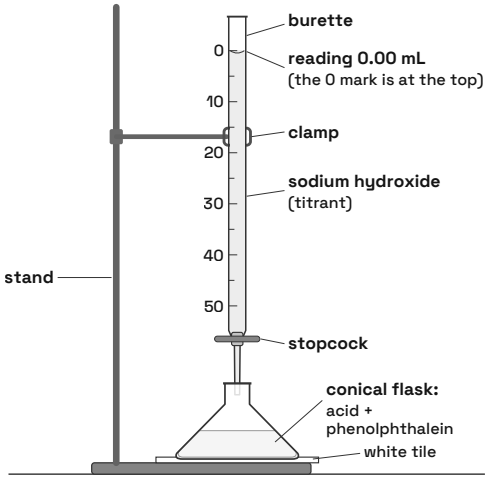
Secondary (and why)

- NaOH: deliquescent, takes up CO_2
- HCl: a gas, solution changes
- H_2SO_4: hygroscopic
- $KMnO_4$: decomposed by light, organic matter
- I_2: sublimes
- $Na_2S_2O_3$
- sodium dichromate hygroscopic; potassium dichromate a primary standard
- Mohr's salt: a **double salt**, $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ (ions of both salts in water); pure, stable in air ($FeSO_4$ alone oxidizes), E 392

Equivalence and dilution (1.6)

- titrant's gram equivalents = analyte's, whatever the coefficients
- two ways: $N_1V_1 = N_2V_2$, or moles from the balanced equation; they agree
- trap: $M_1V_1 = M_2V_2$ for a reaction only if 1 : 1
- dilution: $M_1V_1 = M_2V_2$ and $N_1V_1 = N_2V_2$; 200 mL of 0.5 N + 300 mL water → 0.2 N
- **acid into water**, slowly, stirring; never water into acid (spatters)

Titration (1.7)



Titration: burette (titrant), conical flask on a white tile (analyte + indicator).

Doing it well

- rinse the burette with titrant, the pipette with analyte (flask may be wet)
- no air bubble in the tip
- read the bottom of the meniscus at eye level, to 0.05 mL ($KMnO_4$: the top)
- rough run first, then drop by drop; two within 0.10 mL

Errors

1. apparatus or method (dirty burette, bubble)
2. temperature changes
3. meniscus read wrongly
4. weighing or dilution mistakes
5. indicator changing away from the equivalence point

kept small by calibrated glassware, a suitable indicator, repeats

Acid–base: $H^+ + OH^- \longrightarrow H_2O$

- methyl orange 3.1–4.4, methyl red 4.4–6.2, litmus ~4.5–8.3, phenolphthalein ~8.2–10
- strong acid + strong base: any; weak acid (CH_3COOH) + NaOH: phenolphthalein; HCl + NH_3: methyl orange or methyl red
- HCl + NaOH: equivalence pH 7, phenolphthalein end point ~pH 9, a fraction of a drop later
- $Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$: **methyl orange**, yellow → orange-red (CO_2 makes the end acidic, ~pH 4); phenolphthalein fades at the half-way $NaHCO_3$ (~pH 8.3)

Redox: oxidizing + reducing agent; redox indicator or a colored titrant

- **permanganometry**: $KMnO_4$ titrant, self-indicator; end point the **first permanent pale pink**; in dil. H_2SO_4, oxalic acid warmed to ~60 °C

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2C_2O_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O$$

$$MnO_4^- + 8\,H^+ + 5\,Fe^{2+} \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

- **not HCl**: Cl^- oxidized to Cl_2 (too much $KMnO_4$ used); not HNO_3 (itself an oxidizer)
- **dichromatometry**: $K_2Cr_2O_7$, a primary standard; orange → green; diphenylamine sulphonate (violet)

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,Fe^{2+} \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$$

- **iodometry** (iodine in Ayo noon, 50 ppm, as KIO_3): starch, blue-black → colorless

$$KIO_3 + 5\,KI + 3\,H_2SO_4 \longrightarrow 3\,K_2SO_4 + 3\,H_2O + 3\,I_2$$

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow 2\,NaI + Na_2S_4O_6$$

- I_2 the oxidizing agent (0 → −1); thiosulphate the reducing agent (S +2 → +2.5)
- **precipitation (argentometric)** titration: $AgNO_3$ titrant, $Ag^+ + Cl^- \longrightarrow AgCl\downarrow$ (NaCl/NaBr mixtures)

COMMON MISTAKES

✗ $KMnO_4$ goes pink to colorless
✓ purple, decolorized; end point the first permanent pale pink.

✗ $KMnO_4$ titration in HCl
✓ dilute H_2SO_4: permanganate oxidizes Cl^-.

✗ $MnO_4^- + 8H^+ + C_2O_4^{2-} \rightarrow Mn^{2+} + 4H_2O + CO_2$
✓ $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$.

✗ E of $Na_2S_2O_3$ = 126
✓ 158 (126 is Na_2SO_3; crystals 248).

✗ n is the base's basicity, the salt's basicity
✓ acid basicity, base acidity, salt total charge.

✗ N = % w/v × 10 × E
✓ N = % w/v × 10 ÷ E.

✗ 15 ppb lead = 15 mg/L
✓ 15 µg/L.

✗ 70% v/v ethanol: add 75 mL water to 175 mL
✓ make up to 250 mL in a flask.

✗ indicator ranges 3–5, 8–10
✓ methyl orange 3.1–4.4, phenolphthalein 8.2–10.

✗ sodium dichromate as primary standard
✓ hygroscopic; use $K_2Cr_2O_7$.