Unit 2 · Ionic Equilibrium

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: K_{sp} of chalk → its solubility in g/L; long (8): will $Zn(OH)_2$ precipitate from given concentrations (K_{sp}); a KOH solution of pH 8 diluted 1000 times: its pH
- **MCQ (1 mark)**
  - Arrhenius' limits; Brønsted–Lowry; conjugate acid of NH_3; HCl stronger than HF; not a Lewis acid; what a Lewis base needs
  - Ostwald's law; K_w and temperature; highest pK_a, highest pH; least soluble salt from K_{sp}
  - which pair is a buffer, what fixes its pH; phenolphthalein's titrations; acidic by hydrolysis; complex salt; pH of a hydrolyzed salt
- **Short (5 marks, in parts)**
  - define with examples: Brønsted and Lewis acid and base, conjugate acid; differences (conjugate acid/base, K_a/K_b, two hydrolyses, solubility/K_{sp}, acid/basic salt)
  - reasons: water amphoteric, PH_3 a Lewis base, pH of 10^{-7} M HCl not 7, Ostwald not for strong electrolytes, HCl before H_2S
  - NH_3 as Brønsted and Lewis base; 98% H_2SO_4 (1.84 g/mL): g/L, M, pH; derive Ostwald's law; pH of 0.01 M acetic acid
  - K_w with temperature; K_{sp} and solubility of AgCl, $Al_2(SO_4)_3$ ($108s^5$); common ion in H_2S; hydrolysis of CH_3COONa and three kinds of salt; indicators and their choice
- **Long (8 marks)**: acetate buffer (mechanism, uses in the body, pH by Henderson); K_{sp} table: solubility of $CaSO_4$ and $Fe(OH)_3$ in mol/L and g/L, $CaCO_3$ vs $BaSO_4$; reading titration curves (start pH, indicator, acid in the burette); amino acids as amphoteric

Key terms

Arrhenius acid / base: gives H^+ / OH^- in water.

Brønsted–Lowry acid / base: proton donor / proton acceptor.

Lewis acid / base: electron-pair acceptor (electrophile) / donor (nucleophile).

Conjugate pair: an acid and the base left when it loses one proton (HCl/Cl^-, NH_4^+/NH_3, H_3O^+/H_2O).

Amphoteric: acts as acid and base; **amphiprotic**: gives and takes protons (H_2O, HCO_3^-, HSO_4^-); ZnO is amphoteric, not amphiprotic.

Degree of ionization (α): fraction of dissolved molecules ionized, 0 to 1.

Ionic product of water (K_w): $[H^+][OH^-]$ in any aqueous solution at a given temperature.

Solubility product (K_{sp}): product of the ion concentrations in a **saturated** solution, each to the power of its coefficient.

Ionic product (K_{ip}, Q): the same product in **any** solution.

Molar solubility (s): mol/L that dissolves = (g/L) ÷ molar mass.

Common ion effect: a strong electrolyte with a shared ion suppresses a weak electrolyte's ionization (and a salt's solubility).

Buffer: resists a change of pH when a little acid or base is added; **buffer action**: its partners neutralize what is added.

Acid salt: has replaceable H ($NaHSO_4$, $NaHCO_3$); **basic salt**: has OH^- or O ($Mg(OH)Cl$, $CuCO_3{\cdot}Cu(OH)_2$).

Complex salt: has a complex ion, a metal ion with ligands ($[Cu(NH_3)_4]SO_4$).

Hydrolysis of a salt: its cation or anion reacts with water, making the solution acidic or basic; the reverse of neutralization.

Formulas

$K = \dfrac{C\alpha^2}{1-\alpha} \approx C\alpha^2$	$\alpha = \sqrt{K/C} = \sqrt{KV}$ **Use:** Ostwald, weak electrolyte, α under 5%
$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$	at 25 °C; larger when hotter **Use:** water
$pH + pOH = 14$	$[H^+] = 10^{-pH}$ **Use:** at 25 °C
$[H^+] = \sqrt{K_a C}$	$pH = \frac{1}{2}(pK_a - \log C)$ **Use:** weak acid
$[OH^-] = \sqrt{K_b C}$	then $pH = 14 - pOH$ **Use:** weak base
$K_a K_b = K_w$	$pK_a + pK_b = 14$ **Use:** a conjugate pair only
$K_{sp} = x^x y^y s^{x+y}$	AB: s^2; AB_2, A_2B: $4s^3$; A_3B_2: $108s^5$ **Use:** A_xB_y
$pH = pK_a + \log \dfrac{[salt]}{[acid]}$	$pH = pK_a$ when equal **Use:** acidic buffer
$pOH = pK_b + \log \dfrac{[salt]}{[base]}$	$pH = 14 - pOH$ **Use:** basic buffer
$K_h = K_w/K_b$, $h = \sqrt{K_h/C}$	$pH = 7 - \frac{1}{2}(pK_b + \log C)$ **Use:** strong acid + weak base salt
$K_h = K_w/K_a$	$pH = 7 + \frac{1}{2}(pK_a + \log C)$ **Use:** weak acid + strong base salt
$K_h = \dfrac{K_w}{K_a K_b}$	$pH = 7 + \frac{1}{2}(pK_a - pK_b)$, no C **Use:** weak acid + weak base salt

Acids and bases (2.1–2.5)

- **Arrhenius' limits**: only in water; H^+ really H_3O^+; NH_3 (no OH^-) a base, CO_2 (no H) an acid; can't explain amphoteric substances
- **Brønsted–Lowry** (1923): $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (water the acid); $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$ (water the base)
- conjugate base: one H^+ **removed**; conjugate acid: one H^+ **added**; two acids and two bases in every reaction
- mono-, di-, polyprotic (HCl; H_2SO_4, H_2CO_3; H_3PO_4 triprotic); only H that leaves counts
- amphoteric oxides: $Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$, $ZnO + 2\,NaOH + H_2O \longrightarrow Na_2[Zn(OH)_4]$
- **strong**: HCl, HBr, HI, HNO_3, H_2SO_4 (1st H), $HClO_4$; LiOH, NaOH, KOH, Ca/Sr/$Ba(OH)_2$
- **weak**: CH_3COOH, HCOOH, HF, HNO_2, H_2CO_3, HCN; NH_3, CH_3NH_2, $C_6H_5NH_2$; $Mg(OH)_2$, $Be(OH)_2$ not strong
- strength = fraction ionized, not concentration; **stronger acid, weaker conjugate base** (Cl^- very weak, CH_3COO^- stronger)
- **Lewis** (1923): $H_3N + BF_3 \longrightarrow H_3N{-}BF_3$ (coordinate bond, adduct); $Al^{3+} + 6\,H_2O \longrightarrow [Al(H_2O)_6]^{3+}$
- Lewis acids: metal cations (Cu^{2+}, Fe^{3+}, Al^{3+}), incomplete octet (BF_3, BCl_3, $AlCl_3$), CO_2, SO_2, carbocations; Lewis bases: NH_3, H_2O, OH^-, F^-, CN^-, PH_3 (lone pair)
- every Brønsted base is a Lewis base; Lewis' limits: protonic acids (HCl) don't take a pair themselves; no measure of strength

Ostwald's law, K_w, K_a, pH (2.6–2.10)

- derivation: $C(1-\alpha)$, $C\alpha$, $C\alpha$ at equilibrium → $K = C\alpha^2/(1-\alpha) \to \alpha \ll 1 \to \alpha = \sqrt{K/C}$
- $\alpha \propto 1/\sqrt{C} \propto \sqrt{V}$: diluting 100× raises α ~10×; ions meet less often (Le Chatelier)
- only weak electrolytes (a strong one has no molecule–ion equilibrium); fails when α is not small (shortcut gives $\alpha > 1$ when very dilute)
- 0.10 M acetic acid ($K_a = 1.75 \times 10^{-5}$): $\alpha = 1.3\%$, pH 2.88; 0.0010 M: α 12.4% (quadratic)
- water: $[H_2O] \approx 55.5$ M taken into K_w; self-ionization endothermic → K_w up with T: 1.14×10^{-15} (0 °C), 2.09×10^{-14} (35 °C), 5.47×10^{-14} (50 °C)
- hot pure water: pH below 7 yet **neutral** ($[H^+] = [OH^-]$); 60 °C: pH 6.51
- K_a, K_b depend only on T (α changes with dilution): fair comparison; lower pK_a = stronger acid
- pK_a: HCN 9.21, CH_3COOH 4.76, HCOOH 3.75, HF 3.20; pK_b: aniline 9.13, NH_3 4.75, CH_3NH_2 3.34; NH_4^+ pK_a 9.25
- 0.1 M HCl pH 1; 0.10 M NH_3 pH 11.13; pH 3 is 10× as acidic as pH 4
- 10^{-7} M HCl: water's H^+ counts, $[H^+] = 1.62 \times 10^{-7}$, **pH 6.79**; a diluted acid nears 7 from below, a diluted base (KOH of pH 8 diluted 1000×) from above, never passing it

Solubility product (2.11–2.13)

- solid's concentration constant → taken into K_{sp}; K_{sp} fixed at a temperature, so T is always given
- units: AgCl $mol^2\,L^{-2}$, MgF_2 $mol^3\,L^{-3}$, $Ca_3(PO_4)_2$ $mol^5\,L^{-5}$
- solubility in g/L = s × molar mass; $Mg(OH)_2$, $s = 1.71 \times 10^{-4}$: $K_{sp} = 4s^3 = 2.00 \times 10^{-11}$
- compare K_{sp} only for the same number of ions: Ag_2CrO_4 has smaller K_{sp} than AgCl yet is more soluble
- $K_{ip} < K_{sp}$ unsaturated; = saturated; > **precipitates**; mixing halves each concentration (50 + 50 mL)
- AgCl in 0.10 M NaCl: $s = 1.8 \times 10^{-9}$, ~7,000× less than in water (1.34×10^{-5}): wash precipitates with a common-ion solution
- $NH_4OH + NH_4Cl$: NH_4^+ common, less OH^-, pH falls; acetic acid + acetate (0.10 M each): α 1.3% → 0.0175%
- **group II** (Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Bi^{3+}, As, Sb, Sn): H_2S **after dil. HCl**; H^+ suppresses $H_2S \rightleftharpoons 2\,H^+ + S^{2-}$, low $[S^{2-}]$ exceeds only the small K_{sp} of group II sulphides (group IV stays in solution)
- **group IIIA** (Fe^{3+}, Al^{3+}, Cr^{3+}): **NH_4Cl, then NH_4OH**; NH_4^+ lowers $[OH^-]$, only the least soluble hydroxides fall (not Zn, Mn, Mg)

- **pure salt**: HCl gas into saturated brine; Cl^- raises $[Na^+][Cl^-]$ above K_{sp}, NaCl crystallizes
- **salting out soap**: NaCl's Na^+ brings out sodium stearate, $C_{17}H_{35}COONa$; glycerol stays below
- **baking soda (Solvay)**: $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 \downarrow + NH_4Cl$; high $[Na^+]$ in brine

Buffers and indicators (2.14–2.15)

- **acidic** buffer (pH < 7): weak acid + its salt with a strong base, CH_3COOH/CH_3COONa; acid added $CH_3COO^- + H^+ \longrightarrow CH_3COOH$; base added $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$
- **basic** buffer (pH > 7): weak base + its salt with a strong acid, NH_4OH/NH_4Cl; $NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O$, $NH_4^+ + OH^- \longrightarrow NH_4OH$
- examples: blood H_2CO_3/HCO_3^- (7.35–7.45, with lungs and kidneys), saliva phosphate, eye drops, soft drinks (citric acid/citrate), lotions
- pH set by the **ratio** (dilution hardly changes it); best within $pK_a \pm 1$; more concentrated = larger **buffer capacity**
- 10.0 g CH_3COONa in 200 mL of 1.00 M acid: 0.6095 M, pH = 4.757 + log 0.6095 = **4.54**; equal amounts: pH 4.76
- NH_4^+/NH_3 for pH 9.00: ratio = $[H^+]/K_a = 10^{-9}/5.6 \times 10^{-10} = 1.79$
- uses: enzymes and proteins, blood, fermentation, dyeing, tanning, electroplating, calibrating pH meters
- indicator: $HIn \rightleftharpoons H^+ + In^-$; color change over $\mathbf{pK_{In} \pm 1}$; it must change on the steep part of the curve
- methyl orange 3.1–4.4, methyl red 4.4–6.2, phenolphthalein 8.2–10

Titration (0.1 M)	Start	Jump	At equivalence	Indicator
strong acid + strong base	1	4.3–9.7	7	any of the three
strong acid + weak base	1	3.7–6.9	5.3 (NH_4Cl)	methyl red, methyl orange
weak acid + strong base	2.9	~7–10	8.7 (acetate)	phenolphthalein
weak acid + weak base		none sharp		none suitable

- half-way to equivalence: [salt] = [acid], $\mathbf{pH = pK_a}$ (how pK_a is measured; 4.76 for acetic acid)
- acid in the burette instead: the curve runs the other way, high pH to low

Salts and hydrolysis (2.16–2.17)

- **simple** salt: full neutralization (NaCl, $CuSO_4$, CH_3COONa, CH_3COONH_4); its solution may be acidic, basic or neutral
- $H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$ (acid salt); $H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O$ (normal)
- "acidic salt" two meanings: solution acidic ($CuSO_4$, NH_4Cl) or has replaceable H ($NaHSO_4$); $NaHCO_3$ an acid salt, solution basic (~8.3)
- **complex**: $CuSO_4 + NH_4OH \rightarrow$ pale blue $Cu(OH)_2\downarrow$; excess $NH_3 \rightarrow$ deep blue $\mathbf{[Cu(NH_3)_4]SO_4}$ (NH_3 Lewis bases $\rightarrow Cu^{2+}$)
- only ions of **weak** acids or bases hydrolyze (Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-} don't)

Salt of	Example	Hydrolysis	Solution
strong acid + strong base	NaCl, KNO_3, Na_2SO_4	none, ions hydrated	neutral, pH 7
strong acid + weak base	NH_4Cl, $CuSO_4$, $FeCl_3$, $Al_2(SO_4)_3$	cationic	acidic
weak acid + strong base	CH_3COONa, Na_2CO_3, KCN	anionic	basic
weak acid + weak base	CH_3COONH_4	both	by K_a vs K_b

- cationic: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$; 0.10 M NH_4Cl pH 5.13, h = 7.5×10^{-5}
- anionic: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$; 0.10 M CH_3COONa pH 8.88 (8.73 at 0.05 M: phenolphthalein)
- alum (*fitkiri*): $Al^{3+} + 3\,H_2O \rightleftharpoons Al(OH)_3 + 3\,H^+$, the jelly settles mud; soap solution slightly basic

COMMON MISTAKES

✗ $\alpha = KV$
✓ $\alpha = \sqrt{KV} = \sqrt{K/C}$.

✗ $pK_a + pK_b = 14$ for any acid and base
✓ only a conjugate pair, at 25 °C.

✗ 10^{-8} M HCl has pH 8
✓ slightly below 7 (water's own H^+).

✗ K_{sp} of $Mg(OH)_2 = 4s^2$
✓ $s(2s)^2 = 4s^3$.

✗ smaller K_{sp}, always less soluble
✓ only for the same number of ions.

✗ basic buffer: weak base + salt of a weak acid
✓ salt of a **strong** acid (NH_4Cl).

✗ $pK_b = pH - \log([salt]/[base])$
✓ $pOH = pK_b + \log([salt]/[base])$.

✗ "K_b of NH_4^+"
✓ NH_4^+ is an acid: $K_a = K_w/K_b$.

✗ Solvay: Na_2CO_3 precipitates
✓ $NaHCO_3$ precipitates, heated to Na_2CO_3.

✗ every alkaline earth hydroxide strong
✓ not $Mg(OH)_2$, $Be(OH)_2$.

✗ bromothymol blue for HCl + NH_3
✓ methyl red (jump 3.7–6.9).