FREE NOTES · NCERT + JEE/NEET LEVEL

Equilibrium

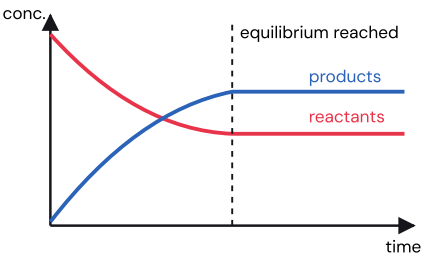
Physical and chemical equilibrium, law of mass action, Kc and Kp, reaction quotient, Le Chatelier's principle, acids and bases, ionisation of water, pH, weak acids and bases, common ion effect, hydrolysis of salts, buffers and solubility product.

01 Dynamic equilibrium
02 Equilibrium constants Kc, Kp & Q
03 Le Chatelier's principle
04 Acids & bases
05 Ionisation of water & pH
06 Weak acids & bases
07 Common ion effect, hydrolysis & buffers
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01 Dynamic equilibrium

In a closed system a reversible reaction reaches a state where **forward rate = backward rate**. Concentrations stay constant but reactions don't stop (dynamic).

- **Physical:** ice ⇌ water at 273 K; water ⇌ vapour (vapour pressure); solid ⇌ solution (saturated); gas in liquid (Henry's law).
- **Chemical:** $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $H_2 + I_2 \rightleftharpoons 2HI$.
- Can be approached from either side.



Concentrations become constant at equilibrium

02 Equilibrium constants Kc, Kp & Q

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = [C]^c[D]^d / [A]^a[B]^b$$

$K_p = K_c\,(RT)^{\Delta n}$ (Δn = gaseous moles of products − reactants; $R = 0.0831$ bar L/(mol K))

Pure solids and liquids are left out. K depends only on temperature.

- Reverse reaction: $K' = 1/K$. Multiply equation by n: $K' = K^n$. Add equations: multiply Ks.
- $K > 10^3$ ⇒ mostly products; $K < 10^{-3}$ ⇒ mostly reactants.
- **Reaction quotient Q** (same expression, any moment): $Q < K$ ⇒ goes forward; $Q > K$ ⇒ goes backward; $Q = K$ ⇒ at equilibrium.
- $\Delta G° = -RT \ln K$.

03 Le Chatelier's principle

If a system at equilibrium is disturbed, it shifts to undo the change.

Change	Shift
Add reactant / remove product	Forward
Increase pressure (decrease volume)	Towards fewer gaseous moles ($N_2 + 3H_2 \rightleftharpoons 2NH_3$ goes forward)
Increase temperature	Endothermic direction (K changes!)
Catalyst	No shift; equilibrium reached faster
Inert gas at constant volume	No effect
Inert gas at constant pressure	Towards more gaseous moles

Haber process (exothermic, $\Delta n = -2$): high pressure (~200 atm), moderate temperature (~700 K), Fe catalyst.

04 Acids & bases

Theory	Acid	Base
Arrhenius	Gives H^+ (H_3O^+) in water	Gives OH^- in water
Brønsted-Lowry	Proton donor	Proton acceptor
Lewis	Electron-pair acceptor (BF_3, $AlCl_3$, H^+)	Electron-pair donor (NH_3, OH^-)

Conjugate pairs differ by one H^+: HCl/Cl^-, NH_4^+/NH_3, H_2O/OH^-. A strong acid has a weak conjugate base. Water is amphoteric.

05 Ionisation of water & pH

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 298 \text{ K}$$

$$pH = -\log[H^+], \; pH + pOH = 14$$

Neutral pH 7 (at 298 K); acidic < 7; basic > 7. K_w rises with temperature, so neutral pH falls (but water stays neutral).

Also $pK_a + pK_b = 14$ for a conjugate pair; $K_a \times K_b = K_w$.

06 Weak acids & bases

$$HA \rightleftharpoons H^+ + A^-,\ K_a = c\alpha^2/(1-\alpha) \approx c\alpha^2$$

$$\alpha = \sqrt{(K_a/c)},\ [H^+] = c\alpha = \sqrt{(K_a c)}$$

$$pH = ½(pK_a - \log c)$$

Same for weak bases with K_b and $[OH^-]$ (Ostwald dilution law: α increases on dilution). Polyprotic acids: $K_{a1} >> K_{a2} >> K_{a3}$.

Acid strength factors: across a period, more electronegative A ⇒ stronger HA (CH_4 < NH_3 < H_2O < HF); down a group, bigger A ⇒ weaker H–A bond ⇒ stronger acid (HF < HCl < HBr < HI).

07 Common ion effect, hydrolysis & buffers

- **Common ion effect:** adding an ion already present suppresses ionisation (CH_3COONa reduces dissociation of CH_3COOH).

Salt of	Solution	pH
Strong acid + strong base (NaCl)	No hydrolysis	7
Weak acid + strong base (CH_3COONa)	Basic	$7 + ½(pK_a + \log c)$
Strong acid + weak base (NH_4Cl)	Acidic	$7 - ½(pK_b + \log c)$
Weak acid + weak base (CH_3COONH_4)	Depends	$7 + ½(pK_a - pK_b)$

BUFFER SOLUTIONS

Resist change in pH. Acidic buffer: weak acid + its salt (CH_3COOH + CH_3COONa). Basic buffer: weak base + its salt (NH_4OH + NH_4Cl). **Henderson equation:** pH = pK_a + log([salt]/[acid]); pOH = pK_b + log([salt]/[base]). Blood is buffered at pH ~7.4.

08 Solubility product (K_{sp})

$$A_xB_y(s) \rightleftharpoons xA^{y+} + yB^{x-},\ K_{sp} = [A]^x[B]^y$$

$$K_{sp} = x^x\, y^y\, S^{x+y}\ \ (S = \text{molar solubility})$$

AB: $K_{sp} = S^2$. AB_2: $4S^3$. A_2B_3: $108S^5$.

- Ionic product > K_{sp} ⇒ **precipitation**; < K_{sp} ⇒ more dissolves.
- Common ion lowers solubility (AgCl less soluble in NaCl solution). Used to purify NaCl by passing HCl gas.

09 JEE Extra + Tricks

JEE LEVEL

- $K_p = K_c(RT)^{\Delta n}$; reverse reaction $K' = 1/K$; reaction × n ⇒ K^n; adding reactions ⇒ multiply K.
- Degree of dissociation from vapour density: $\alpha = (D - d)/((n - 1)d)$.
- pH of salt: weak acid + strong base $pH = 7 + \frac{1}{2}(pK_a + \log C)$; strong acid + weak base $pH = 7 - \frac{1}{2}(pK_b + \log C)$; weak–weak $pH = 7 + \frac{1}{2}(pK_a - pK_b)$.
- Buffer (Henderson): $pH = pK_a + \log([salt]/[acid])$; maximum buffer capacity when $pH = pK_a$.
- Solubility product: AB_2 ⇒ $K_{sp} = 4s^3$; A_2B_3 ⇒ $108s^5$; precipitation when ionic product > K_{sp}.
- Very dilute strong acid (10^{-8} M HCl): add water's H^+ ⇒ pH ≈ 6.98, not 8.

10 Solved numericals

Q1. pH of 0.001 M HCl?

$[H^+] = 10^{-3}$ ⇒ **pH = 3**.

Q2. pH of 0.1 M acetic acid ($K_a = 1.8 \times 10^{-5}$)?

$[H^+] = \sqrt{(1.8 \times 10^{-6})} = 1.34 \times 10^{-3}$ ⇒ **pH ≈ 2.87**.

Q3. K_{sp} of AgCl = 1.8×10^{-10}. Solubility?

$S = \sqrt{K_{sp}}$ = **1.34×10^{-5} mol/L**.

Q4. For $N_2 + 3H_2 \rightleftharpoons 2NH_3$, relation between K_p and K_c?

$\Delta n = -2$ ⇒ $K_p = K_c(RT)^{-2}$.

Q5. Buffer of 0.1 M CH_3COOH + 0.1 M CH_3COONa (pK_a 4.74). pH?

$pH = 4.74 + \log 1$ = **4.74**.

11 Mistakes & practice

- Putting solids or pure liquids in K expressions.
- Saying a catalyst changes K or shifts equilibrium.
- Thinking pressure changes K (only T does).
- Using pH = -log c for a weak acid.

1. Effect of increasing T on an exothermic equilibrium?
2. Lewis acid in $AlCl_3 + Cl^- \rightarrow AlCl_4^-$?
3. Nature of aqueous NH_4Cl?
4. K_{sp} of $Ca_3(PO_4)_2$ in terms of S?
5. Conjugate base of HSO_4^-?

ANSWERS

1) Shifts backward, K decreases · 2) $AlCl_3$ · 3) Acidic · 4) $108S^5$ · 5) SO_4^{2-}

12 Quick revision: 5 minutes before the exam

CHEMICAL EQUILIBRIUM

- $K_p = K_c(RT)^{\Delta n}$.
- $Q < K \Rightarrow$ forward.
- Only T changes K.

LE CHATELIER

- ↑p ⇒ fewer gas moles.
- ↑T ⇒ endothermic side.
- Catalyst: no shift.

IONIC

- pH + pOH = 14; $K_w = 10^{-14}$.
- Weak: $[H^+] = \sqrt{(K_a c)}$.
- Buffer: $pH = pK_a + \log(\text{salt/acid})$.

K_{SP}

- AB: S^2, AB_2: $4S^3$.
- $IP > K_{sp} \Rightarrow$ ppt.
- Common ion ↓ solubility.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.