

CUET · CHEMISTRY · CLASS XI · CODE 306

Equilibrium

CUET unit: Equilibrium

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Snapshot

- Establishes the idea that physical (phase) and chemical processes in a closed system reach a **dynamic** equilibrium where forward and reverse rates become equal and macroscopic properties stay constant.
- Develops the quantitative **Law of Chemical Equilibrium** (K_c , K_p), the relation $K_p = K_c (RT)^{\Delta n}$, and use of the reaction quotient Q to predict direction.
- Builds **Le Chatelier's principle** as the qualitative tool to predict how concentration, pressure/volume, temperature, catalyst and inert-gas changes shift equilibrium.
- Extends equilibrium ideas to ions in aqueous solution: Arrhenius/Brønsted-Lowry/Lewis acids and bases, K_a , K_b , K_w , pH, buffers, hydrolysis of salts and the solubility product K_{sp} .
- CUET routinely tests numerical K/Q comparisons, Le Chatelier shifts, buffer pH (Henderson-Hasselbalch), conjugate pair identification and K_{sp} /solubility relations.

Detailed Notes

2.1 Core concepts

- **Equilibrium is dynamic, not static.** For physical processes such as $H_2O(l) \rightleftharpoons H_2O(vap)$ the rate of evaporation equals the rate of condensation; double half-arrows denote both directions proceeding simultaneously (NCERT §6.1, p. 168-169).
- **Solid-liquid equilibrium** at the normal melting point: rate of melting = rate of freezing; mass of solid and liquid remain constant in a closed insulated vessel at the fixed T and P (NCERT §6.1.1, p. 169).
- **Liquid-vapour equilibrium** in a closed vessel produces a constant **equilibrium vapour pressure** at given T ; a liquid with higher vapour pressure is more volatile and has a lower boiling point (NCERT §6.1.2, p. 169-170).
- **Solid-vapour equilibrium** (sublimation): $I_2(s) \rightleftharpoons I_2(vap)$, camphor and NH_4Cl behave similarly — colour/mass becomes constant at equilibrium (NCERT §6.1.3, p. 170).
- **Dissolution equilibria** — saturated solution shows dynamic equilibrium between solid solute and dissolved solute (verified by radioactive-sugar tracer); for gases in

liquids, Henry's law gives $[\text{gas(aq)}]/[\text{gas(g)}] = \text{constant}$ at fixed T (NCERT §6.1.4, p. 171; Table 6.1).

- **General features of physical equilibria:** equilibrium requires a closed system, both opposing processes occur at equal rates, all measurable properties remain constant, and one parameter (vapour pressure, melting point, solubility, etc.) becomes characteristic at a given T (NCERT §6.1.5, p. 172).
- **Chemical equilibrium is dynamic too.** Demonstrated for Haber synthesis ($\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$) using D2 isotopic scrambling — equilibrium mixture continues to exchange H/D atoms, proving forward and reverse reactions do not stop (NCERT §6.2, p. 172-174).
- **Law of Chemical Equilibrium (Guldberg-Waage, 1864):** for $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, $K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$. Concentrations are equilibrium values; phases (s, l, g) are usually omitted in the K expression (NCERT §6.3, eq. 6.1 & 6.4, p. 175-176).
- **Reverse reaction and stoichiometric scaling:** $K_c(\text{reverse}) = 1/K_c$; multiplying the equation by n raises K to the n-th power (NCERT §6.3, Table 6.4, eq. 6.7-6.11, p. 176-177).
- **Homogeneous equilibria** have all species in one phase (e.g. gaseous $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, or aqueous esterification). For gas-phase reactions K_p uses partial pressures; the relation is $K_p = K_c (\text{RT})^{\Delta n}$, where $\Delta n = (\text{moles gaseous products}) - (\text{moles gaseous reactants})$; pressure must be expressed in bar (NCERT §6.4.1, eq. 6.13-6.15, p. 177-178).
- **Units of K:** K_c and K_p are dimensionless when standard states (1 mol L^{-1} for solutes, 1 bar for gases) are used; otherwise units arise only when numerator and denominator exponents differ (NCERT box, p. 180).
- **Heterogeneous equilibria** involve more than one phase. Concentrations of pure solids and pure liquids are constant and are absorbed into K; e.g. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ gives $K_p = p_{\text{CO}_2}$ (NCERT §6.5, eq. 6.16-6.18, p. 179-180).
- **Magnitude of K predicts extent:** $K_c > 10^3$ — products dominate (e.g. $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$, $K_c = 4.0 \times 10^{31}$); $K_c < 10^{-3}$ — reactants dominate (e.g. $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$, $K_c = 4.8 \times 10^{-31}$); $10^{-3} < K_c < 10^3$ — appreciable amounts of both (NCERT §6.6.1, p. 181-182).
- **Reaction quotient Q vs K:** if $Q_c < K_c$ the reaction proceeds in the forward direction; if $Q_c > K_c$ it proceeds in the reverse direction; if $Q_c = K_c$ the system is at equilibrium (NCERT §6.6.2, eq. 6.20, p. 182).
- **ICE table method** (Initial / Change / Equilibrium) is the standard route to compute equilibrium concentrations given K_c and initial values (NCERT §6.6.3, Problems 6.8-6.9, p. 183-184).
- **Thermodynamic link:** $\Delta G = \Delta G^\circ + RT \ln Q$; at equilibrium $\Delta G = 0$, so $\Delta G^\circ = -RT \ln K$. $K > 1$ when $\Delta G^\circ < 0$ (spontaneous forward); $K < 1$ when $\Delta G^\circ > 0$ (NCERT §6.7, eq. 6.21-6.23, p. 184).

- **Le Chatelier's principle:** a system at equilibrium responds to a stress by shifting in the direction that counteracts the stress (NCERT §6.8, p. 185).
- **Concentration change:** adding a reactant or removing a product drives the reaction forward; removing a reactant or adding a product drives it backward (NCERT §6.8.1, p. 185-186).
- **Pressure/volume change (gaseous):** compression shifts the equilibrium to the side with fewer moles of gas (e.g. $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ shifts forward); reactions with $\Delta n(\text{gas}) = 0$ are unaffected. Pure solids and liquids are ignored (NCERT §6.8.2, p. 186-187).
- **Inert gas:** at constant volume, addition of inert gas does not alter partial pressures or molar concentrations and equilibrium is undisturbed; at constant pressure it would change the situation (NCERT §6.8.3, p. 187).
- **Temperature change** actually changes K . K decreases with rise in T for an exothermic reaction and increases for an endothermic reaction. Low T favours NH_3 formation but practically a catalyst is used (NCERT §6.8.4, p. 187).
- **Catalyst** lowers activation energy of forward and reverse steps equally; it speeds attainment of equilibrium but does **not** change the equilibrium composition or K (NCERT §6.8.5, p. 188).
- **Electrolytes:** strong electrolytes (NaCl , HCl , NaOH) ionize completely; weak electrolytes (CH_3COOH , NH_4OH) ionize partially with an ionic equilibrium between molecules and ions (NCERT §6.9, p. 188-189).
- **Acid-base concepts:** Arrhenius — acid gives $\text{H}^+(\text{aq})$, base gives $\text{OH}^-(\text{aq})$; Brønsted-Lowry — acid is a proton donor, base a proton acceptor, every acid has a conjugate base differing by one H^+ ; Lewis — acid is an electron-pair acceptor, base is an electron-pair donor (NCERT §6.10.1-6.10.3, p. 190-192).
- **Strong vs weak acids:** strong acids (HClO_4 , HCl , HBr , HI , HNO_3 , H_2SO_4) ionize almost completely and have very weak conjugate bases; weak acids (CH_3COOH , HF , HNO_2) have very strong conjugate bases (NCERT §6.11, p. 192-193).
- **Ionic product of water:** $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$; **$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M}^2$ at 298 K**, so in pure water $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$ (NCERT §6.11.1, eq. 6.27-6.28, p. 193).
- **pH = $-\log[\text{H}^+]$** ; $\text{pH} < 7$ acidic, $\text{pH} = 7$ neutral, $\text{pH} > 7$ basic at 298 K; $\text{pH} + \text{pOH} = \text{p}K_w = 14$. A change of one pH unit corresponds to a tenfold change in $[\text{H}^+]$ (NCERT §6.11.2, eq. 6.29, p. 193-194).
- **K_a and K_b** measure the ionization of weak acids/bases: $K_a = \frac{c \alpha^2}{(1 - \alpha)}$ and $K_b = \frac{c \alpha^2}{(1 - \alpha)}$. Larger K_a/K_b means stronger acid/base. $\text{p}K_a = -\log K_a$, $\text{p}K_b = -\log K_b$ (NCERT §6.11.3-6.11.4, eq. 6.30-6.34, p. 195-198).
- **Conjugate pair relation:** $K_a \times K_b = K_w$, so $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14$ at 298 K (NCERT §6.11.5, eq. 6.36, p. 198-199).

- **Polyprotic acids** ionize stepwise; $K_{a1} > K_{a2} > K_{a3}$ because removing a proton from a negative ion is progressively harder (NCERT §6.11.6, Table 6.8, p. 199-200).
- **Acid strength factors:** in same group, larger A weakens H-A bond, so $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ in acidity; in same row, increasing electronegativity of A increases acidity ($\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$) (NCERT §6.11.7, p. 200).
- **Common ion effect:** addition of an ion already present in the equilibrium shifts it according to Le Chatelier, suppressing dissociation (e.g. adding acetate ion to acetic acid lowers $[\text{H}^+]$) (NCERT §6.11.8, p. 200-201).
- **Salt hydrolysis:** salts of strong acid + strong base (NaCl) are neutral ($\text{pH} \approx 7$); salts of weak acid + strong base (CH_3COONa) hydrolyse to give alkaline solution ($\text{pH} > 7$); salts of strong acid + weak base (NH_4Cl) give acidic solution ($\text{pH} < 7$); salts of weak acid + weak base have $\text{pH} = 7 + \frac{1}{2}(\text{p}K_a - \text{p}K_b)$ (NCERT §6.11.9, eq. 6.38, p. 201-202).
- **Buffer solutions** resist pH change. Acidic buffer (weak acid + its salt): Henderson-Hasselbalch — $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{Salt}]}{[\text{Acid}]}\right)$. Basic buffer (weak base + salt of its conjugate acid): $\text{pOH} = \text{p}K_b + \log\left(\frac{[\text{Salt}]}{[\text{Base}]}\right)$. When $[\text{Salt}] = [\text{Acid}]$, $\text{pH} = \text{p}K_a$ (NCERT §6.12, eq. 6.39-6.42, p. 202-204).
- **Solubility product K_{sp}** for sparingly soluble salt M_xX_y : $K_{sp} = [\text{M}^{p+}]^x [\text{X}^{q-}]^y = x^x \cdot y^y \cdot S^{(x+y)}$. For BaSO_4 , $K_{sp} = S^2$; for $\text{Ni}(\text{OH})_2$, $K_{sp} = 4S^3$; for A_2X_3 , $K_{sp} = 108 S^5$ (NCERT §6.13.1, eq. 6.43-6.45, p. 204-205).
- **Common ion effect on solubility:** addition of an ion common to the salt suppresses dissolution; e.g. solubility of $\text{Ni}(\text{OH})_2$ in 0.10 M NaOH falls to $S = K_{sp}/(0.10)^2$ (NCERT §6.13.2, Problem 6.28, p. 206).

2.2 Definitions to memorise

Term	Definition	Page
Dynamic equilibrium	State in which forward and reverse rates are equal so net composition is constant though both processes continue	168-169
Equilibrium vapour pressure	Constant pressure exerted by vapour over its liquid in a closed vessel at fixed T	170
Henry's law	Mass of a gas dissolved in a given mass of solvent at any T is proportional to the pressure of the gas above the solvent	171
Law of mass action / Equilibrium constant K_c	$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$ at equilibrium for $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$	175-176
K_p - K_c relation	$K_p = K_c (\text{RT})^{\Delta n}$, $\Delta n = \sum n(\text{gaseous products}) - \sum n(\text{gaseous reactants})$, pressure in bar	178
Homogeneous equilibrium	All reactants and products in the same phase	177

Term	Definition	Page
Heterogeneous equilibrium	More than one phase present; pure solids/liquids do not appear in K	179-180
Reaction quotient Q_c	Same algebraic expression as K_c but with arbitrary (non-equilibrium) concentrations	182
Le Chatelier's principle	A system at equilibrium responds to any stress so as to reduce the stress	185
Arrhenius acid / base	Substance that produces $H^+(aq)$ / $OH^-(aq)$ in water	190
Brønsted-Lowry acid / base	Proton donor / proton acceptor; pair differing by one H^+ is a conjugate acid-base pair	190-191
Lewis acid / base	Electron-pair acceptor / electron-pair donor	192
Ionic product of water K_w	$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} M^2$ at 298 K	193
pH	$pH = -\log[H^+]$; $pH + pOH = 14$ at 298 K	193-194
K_a , K_b	Ionization constants of weak acid/base; $K_a \times K_b = K_w$ for a conjugate pair	195, 198
Common ion effect	Shift of an ionic equilibrium when a substance providing an ion already present is added	200-201
Salt hydrolysis	Reaction of cation/anion of a salt with water to yield acidic, basic, or neutral solution	201-202
Buffer solution	Solution that resists pH change on dilution or on addition of small amounts of acid/base; Henderson-Hasselbalch: $pH = pK_a + \log\left(\frac{[Salt]}{[Acid]}\right)$	202-203
Solubility product K_{sp}	Equilibrium constant for the dissolution of a sparingly soluble salt; $K_{sp} = [M^{p+}]^x[X^{q-}]^y$	204

2.3 Diagrams / processes to remember

- **Fig. 6.1, p. 170** — Manometer experiment measuring equilibrium vapour pressure of water at constant T.
- **Fig. 6.2, p. 172** — Concentration vs time plot showing decrease of reactants and rise of products till equilibrium is reached.
- **Fig. 6.3, p. 173** — Student activity with two measuring cylinders and tubes of different diameters demonstrating dynamic equilibrium.
- **Fig. 6.4, p. 174** — Composition vs time plot for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (Haber process).
- **Fig. 6.5, p. 174** — $H_2 + I_2 \rightleftharpoons 2HI$: equilibrium reached from either direction yielding the same composition.
- **Fig. 6.6, p. 182** — Dependence of extent of reaction on K_c (regions: reactants only, both, products only).

- **Fig. 6.7, p. 182** — Direction-of-reaction diagram comparing Q_c with K_c .
- **Fig. 6.8, p. 185** — Effect of adding H_2 on the concentrations in $H_2 + I_2 \rightleftharpoons 2HI$.
- **Fig. 6.9, p. 187** — Brown NO_2 / colourless N_2O_4 temperature-effect experiment at 273 K, room T, and 363 K.
- **Fig. 6.10, p. 189** — Dissolution of $NaCl$ in water and hydration of Na^+ and Cl^- .
- **Fig. 6.11, p. 194** — Multi-strip pH paper.
- **Table 6.1, p. 171** — Features of physical equilibria.
- **Table 6.4, p. 176** — Relations between K for the original reaction and its multiples/reverse.
- **Table 6.5, p. 195** — pH values of common substances ($NaOH \approx 13$, blood 7.4, gastric juice 1.2, etc.).
- **Tables 6.6 / 6.7 / 6.8, p. 195, 197, 200** — K_a of weak acids, K_b of weak bases, K_a of polyprotic acids.
- **Table 6.9, p. 205** — K_{sp} values for common sparingly soluble salts.

2.4 Common confusions / NTA trap points

- Equilibrium is **dynamic**, not static — beware of distractors saying "reactions stop".
- For $K_p = K_c(RT)^{\Delta n}$, Δn must use **gaseous** species only, and pressure is in **bar** (since standard state is 1 bar) — distractors often use atm or include solids.
- **Catalyst** changes the rate to reach equilibrium, not the value of K or the equilibrium composition.
- Addition of an **inert gas at constant volume** leaves the equilibrium unaffected (partial pressures unchanged). At constant pressure it would matter.
- For pressure changes on a heterogeneous gaseous equilibrium, count moles of gas **only** — solids/liquids do not contribute.
- The conjugate base of a strong acid is a **very weak** base (and vice versa) — students often invert this.
- The Henderson-Hasselbalch ratio uses $[Salt]/[Acid]$ for an **acidic** buffer; for a basic buffer use $[Salt]/[Base]$ with pK_b (or work via pOH).
- For the salt of strong acid + weak base, the solution is **acidic** ($pH < 7$); for weak acid + strong base it is **basic** — NTA flips these in distractors.
- Solubility S and K_{sp} are **not** numerically equal except for 1:1 salts; for MX_2 , $K_{sp} = 4S^3$, for M_2X_3 it is $108 S^5$.

Practice MCQs

Q1. Which of the following statements about the equilibrium in the closed-vessel reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ demonstrated by Haber using D_2 is correct?

- A. At equilibrium the forward and reverse reactions both stop.
- B. The composition of equilibrium mixture starting from H_2/N_2 is different from that starting with NH_3 .
- C. Isotopic scrambling (formation of NH_3 , NH_2D , NHD_2 , ND_3) shows the reactions continue in both directions at equilibrium.
- D. Equilibrium can be approached only from the reactant side.

Q2. For the equilibrium $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$ at 1069 K, $K_c = 3.75 \times 10^{-6}$. The value of K_p at the same temperature is closest to ($R = 0.0831 \text{ bar L mol}^{-1} \text{ K}^{-1}$):

- A. 3.75×10^{-6}
- B. 0.033
- C. 3.3×10^{-3}
- D. 333

Q3. For the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, the equilibrium constant expression is:

- A. $K_p = p_{\text{CO}_2} \cdot p_{\text{CaO}} / p_{\text{CaCO}_3}$
- B. $K_p = p_{\text{CO}_2}$
- C. $K_c = [\text{CaO}][\text{CO}_2]/[\text{CaCO}_3]$
- D. $K_c = [\text{CaCO}_3]/([\text{CaO}][\text{CO}_2])$

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PYQ Alignment

Equilibrium is one of the densest scoring units in CUET-UG Chemistry and typically contributes 8-12 MCQs per year across Class XI and the related Class XII ionic-equilibrium spillover. Past papers consistently mix (i) one-step K calculations and K_p - K_c conversions, (ii) Q vs K direction prediction, (iii) Le Chatelier conceptuels (pressure, temperature, inert gas, catalyst), (iv) conjugate acid-base identification and Lewis vs Brønsted classification, (v) pH/pOH of strong and weak acids and bases, (vi) Henderson-Hasselbalch buffer pH , and (vii) K_{sp} -solubility numericals including the common-ion effect.

