Unit 8 · Chemical Equilibrium

STUDY NOTES

WHAT NEB'S GRADE 11 EXAM ASKS

- **CDC's grid (2077):** Physical Chemistry (Units 1–8 together): 28 of 75 marks
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: conditions that favor the backward reaction of $2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$, $\Delta H = -196$ kJ (high temperature, low pressure); short question: derive $K_p = K_c(RT)^{\Delta n}$ and give a reaction with $K_p > K_c$
- **MCQ (1 mark)**
  - what equilibrium means; which reaction is irreversible; what K doesn't depend on
  - conditions for most NH_3; $X_2 + 4Y_2 \rightleftharpoons 2XY_4$ ($\Delta H < 0$); ice $\rightleftharpoons$ water under pressure; $CaCO_3 \rightleftharpoons CaO + CO_2$
  - K_p–K_c relation; large K; unit of K_c for NH_3 ($L^2\,mol^{-2}$); lower pressure on $2SO_2 + O_2 \rightleftharpoons 2SO_3$ (shift left, K the same)
- **Short (5 marks, in parts)**
  - define with examples: reversible, irreversible, the five physical equilibria
  - reasons: soda fizzes, a solid's active mass is 1, equilibrium is dynamic, heat and exo/endothermic reactions
  - differences: reversible/irreversible, static/dynamic, physical/chemical, solid–vapor/liquid–vapor
  - state the law of mass action and derive K_c (or K_p); derive $K_p = K_c(RT)^{\Delta n}$; examples of $K_p > K_c$, $K_p = K_c$
  - write the reaction from a K expression; $K \gg 1$, $K \ll 1$; Le Chatelier with one example; pressure on melting ice; $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$ + heat
- **Long (8 marks)**: ice $\rightleftharpoons$ water as a physical equilibrium; rates against time (where equal, a disturbance); $N_2 + O_2 \rightleftharpoons 2NO$ (endothermic: K_c, K_p, temperature, pressure); $2SO_2 + O_2 \rightleftharpoons 2SO_3$ (inert gas, catalyst, pressure, K backward = 1/K); K_c, K_p for PCl_5, $CaCO_3$, NH_3 oxidation; propane burning

Key terms

Reversible reaction: products react to give back the reactants under the same conditions ($\rightleftharpoons$): $H_2 + I_2 \rightleftharpoons 2HI$.

Irreversible reaction: goes one way only, until a reactant is used up: $AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$.

Chemical equilibrium: forward rate = backward rate; concentrations constant.

Dynamic equilibrium: both reactions keep going (a book on a table is static).

Physical equilibrium: between two states or a solute and its solution (no new substance).

Active mass: molar concentration, [A] in mol/L; 1 for a pure solid or liquid.

Law of mass action: rate $\propto$ product of the reactants' molar concentrations, each to the power of its coefficient (exactly so for a one-step reaction).

Equilibrium constant K: k_f/k_b; fixed at a given temperature.

Partial pressure p: pressure of one gas in a mixture; $p = CRT$.

Δn: moles of gaseous products − moles of gaseous reactants.

Le Chatelier's principle: an equilibrium disturbed by a change of concentration, temperature or pressure shifts so as to undo the change in part.

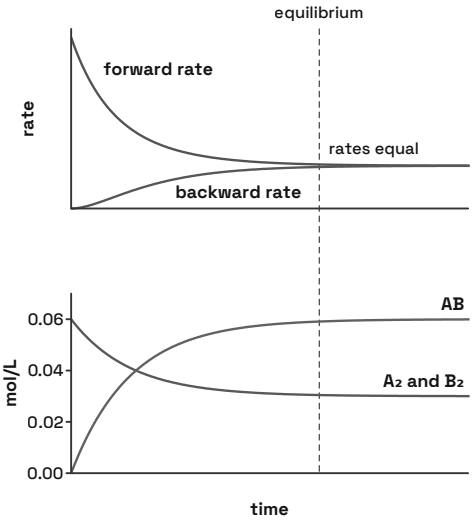
Exothermic / endothermic: gives out heat ($\Delta H < 0$) / takes it in ($\Delta H > 0$).

Inert gas: one that takes no part in the reaction (argon).

Formulas

$K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$	for aA + bB $\rightleftharpoons$ cC + dD **Use:** concentrations
$K_p = \dfrac{p_C^c\,p_D^d}{p_A^a\,p_B^b}$	gases only **Use:** pressures
$K_p = K_c(RT)^{\Delta n}$	R = 0.0821 L atm/(mol K) **Use:** relation
$K_{back} = \dfrac{1}{K}$	equation doubled: K^2 **Use:** reversed
unit of K_c: $(mol/L)^{\Delta n}$	Δn = 0: no unit **Use:** units

Equilibrium



$A_2 + B_2 \rightleftharpoons 2AB$ from A_2 and B_2 only: the forward rate falls and the backward rate rises until they are equal; then the concentrations stay constant.

Characteristics

- only in a **closed system**
- **dynamic**: rates equal, both going on
- concentrations, color, pressure, density constant
- reached **from either side** ($H_2 + I_2$, or HI alone)
- a **catalyst** only gets there sooner
- equal **rates**, not equal amounts

Physical equilibria (closed vessel)

Kind	Equation	Equal rates of
solid–liquid	$H_2O(s) \rightleftharpoons H_2O(l)$, 0 °C	melting, freezing
liquid–vapor	$H_2O(l) \rightleftharpoons H_2O(g)$, any T	evaporation, condensation
solid–vapor	$I_2(s) \rightleftharpoons I_2(g)$; camphor	sublimation, deposition
solid–solution	sugar(s) ⇌ sugar(aq), saturated	dissolving, crystallizing
gas–solution	$CO_2(g) \rightleftharpoons CO_2(aq)$, soda	dissolving, escaping

- soda fizzes on opening: pressure falls, CO_2 less soluble, escapes
- lime kiln is open: CO_2 carried away, so $CaCO_3 \rightarrow CaO$ goes to completion

The equilibrium constant

Deriving K_c (aA + bB ⇌ cC + dD)

1. $r_f = k_f[A]^a[B]^b$, $r_b = k_b[C]^c[D]^d$
2. at equilibrium $r_f = r_b$
3. $k_f/k_b = K_c$ = products over reactants as above

Deriving $K_p = K_c(RT)^{\Delta n}$

1. $pV = nRT$, so $p = (n/V)RT = CRT$
2. put $p_A = [A]RT$ etc. into K_p
3. $K_p = K_c\,(RT)^{(c+d)-(a+b)} = K_c(RT)^{\Delta n}$

Δn	Relation	Example
0	$K_p = K_c$	$H_2 + I_2 \rightleftharpoons 2HI$
+	$K_p > K_c$	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (+1)
−	$K_p < K_c$	$2SO_2 + O_2 \rightleftharpoons 2SO_3$ (−1); $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (−2)

- solids and pure liquids left out: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$: $K_c = [CO_2]$, $K_p = p_{CO_2}$, $\Delta n = +1$
- $2CO_2 \rightleftharpoons 2CO + O_2$: $K_p = p_{CO}^2\, p_{O_2}/p_{CO_2}^2$, $\Delta n = +1$
- $2HI \rightleftharpoons H_2 + I_2$ at 425 °C: K = 1/54 = 0.019

What K tells you

- depends only on **temperature** (for a given equation); not on starting amounts, pressure or a catalyst
- **K ≫ 1** (10^3 or more): mostly products, lies to the right; **K ≪ 1**: mostly reactants ($N_2 + O_2 \rightleftharpoons 2NO$, 4×10^{-31} at 25 °C)
- says **how far, not how fast**: $2H_2 + O_2$, K ~10^{80}, yet no reaction without a spark

Le Chatelier's principle

Change	Shifts	K
add reactant / remove product	right	same
add product / remove reactant	left	same
raise T	endothermic way	changes
lower T	exothermic way	changes
raise P	fewer gas moles (none if Δn = 0)	same
lower P	more gas moles	same
catalyst	no shift, sooner	same
inert gas, constant V	no shift	same
inert gas, constant P	more gas moles	same

- exothermic: K falls as T rises; endothermic: K rises
- ice ⇌ water: water has the smaller volume, so pressure melts ice; endothermic, so heat melts it too
- water ⇌ vapor: pressure favors the liquid (boils higher in a pressure cooker)

Haber's process: $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$, $\Delta H = -92$ kJ

- low T, high P (4 volumes → 2), high $[N_2]$, $[H_2]$, NH_3 removed
- low T is too slow, so a compromise: about 450 °C, about 200 atm, iron catalyst

Nitric oxide: $N_2 + O_2 \rightleftharpoons 2\,NO$, $\Delta H = +181$ kJ

- high T favors NO (car engines, lightning); pressure has no effect (Δn = 0)

Contact process: $2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$, $\Delta H = -198$ kJ

- more SO_3: low T, high P, more O_2; backward: high T, low P

Ostwald step: $4\,NH_3 + 5\,O_2 \rightleftharpoons 4\,NO + 6\,H_2O$ + heat

- low T, low P (9 moles → 10), more NH_3 or O_2

COMMON MISTAKES

✗ irreversible reactions are faster
✓ reversible says how far, not how fast.

✗ liquid–vapor equilibrium only at the boiling point
✓ at any temperature, in a closed vessel.

✗ larger K, faster reaction
✓ larger K, more product.

✗ rate law powers = coefficients always
✓ only for a one-step reaction.

✗ $N_2 + O_2 \rightarrow 2NO$, $\Delta H = +4.32$ kcal
✓ +181 kJ (+43.2 kcal).

✗ $4NH_3 + 5O_2 \rightleftharpoons 4NO_2 + 6H_2O$
✓ 4NO (it balances).

✗ K changes on adding H_2
✓ only temperature changes K.

✗ $H_2 + Cl_2 \rightleftharpoons 2HCl$ as a reversible example
✓ K ~10^{33}: it goes one way.