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PHYSICAL

CH 05

# Chemical Equilibrium — Kc, Kp & Le Chatelier

05

Equilibrium constants, Kp–Kc conversion, manipulating K, the reaction quotient, ICE-table numericals, degree of dissociation, Le Chatelier's principle and the van't Hoff equation — with every numerical type solved, an exam trap gallery, graded MCQs and a one-page revision sheet.

## WHAT YOU WILL BE ABLE TO DO

- Write Kc and Kp for any reaction, leaving out pure solids and liquids, and convert between them
- Manipulate K when an equation is reversed, multiplied or added
- Use Q to predict direction, and solve ICE-table and degree-of-dissociation numericals
- Apply Le Chatelier's principle to concentration, pressure, inert gas, temperature and catalysts
- Link K to ΔG° and use the van't Hoff equation for K at a new temperature

## INSIDE

A The big picture
B The equilibrium constant
C Kp and Kc
D Manipulating K
E Q and direction
F ICE tables
G Degree of dissociation
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I K, ΔG° and temperature
J Exam trap gallery

HOW TO USE THESE NOTES

| | | |
|---|---|---|
| **IN ONE LINE**<br>The core idea of a section | **KEY IDEA**<br>The concept to remember | **EXAM TRAP**<br>Where marks are usually lost |
| **SOLVED EXAMPLE**<br>Worked step by step | **CHECK YOURSELF**<br>Quick self-test | **MEMORY HOOK**<br>A line that sticks |

SECTION A

# The big picture

A

*Equilibrium is a balance of rates, not a stop.*

**IN ONE LINE**

At equilibrium the forward and backward rates are equal; K fixes the ratio of products to reactants at that point, changes only with temperature, and Le Chatelier tells you which way the system shifts when disturbed.

- **Dynamic:** both reactions continue at equal rates. Mixing $H_2$ + $I_2$ or starting from pure HI reaches the same equilibrium.
- **Closed system:** equilibrium needs a closed vessel ($CaCO_3$ in an open container decomposes completely as $CO_2$ escapes).
- **Physical equilibria** follow the same idea: ice ⇌ water at 273 K, liquid ⇌ vapour in a sealed bottle, a saturated solution.

**THINK OF IT LIKE THIS**

Picture an escalator going up and a crowd walking down it at the same speed. People are moving all the time, but the number on each floor stays the same. That is dynamic equilibrium — constant amounts, not zero activity.

SECTION B

# The equilibrium constant

B

*The law of mass action, written for any reaction.*

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

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

Concentrations at equilibrium, in mol $L^{-1}$, each raised to its stoichiometric coefficient

- **Leave out pure solids and pure liquids** — their concentration is constant. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_c = [CO_2]$ and $K_p = p(CO_2)$.
- **Water** is left out when it is the solvent, but included when it is a gas or one reactant among others in a non-aqueous mixture (e.g. esterification).
- **K depends only on temperature** — not on starting amounts, pressure, volume or a catalyst.

- **Size of K:** $K > 10^3$ → products dominate; $K < 10^{-3}$ → reactants dominate; in between, both are present in significant amounts.

**SOLVED EXAMPLE 01** — CALCULATING KC

For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium concentrations are $[H_2] = [I_2] = 0.10$ M and $[HI] = 0.70$ M. Find Kc.

SOLUTION

1. $K_c = [HI]^2 / ([H_2][I_2])$.
2. $= (0.70)^2 / (0.10 \times 0.10) = 0.49 / 0.010$.

ANSWER $K_c = 49$ (no units, since $\Delta n = 0$).

SECTION C

# Kp and Kc

C

*Partial pressures for gases, concentrations for solutions.*

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

$\Delta n$ = moles of gaseous products − moles of gaseous reactants; R = 0.0821 L atm $K^{-1}$ $mol^{-1}$ (or 0.0831 L bar $K^{-1}$ $mol^{-1}$)

| Δn | Relation | Example |
|---|---|---|
| 0 | Kp = Kc | $H_2 + I_2 \rightleftharpoons 2HI$; $N_2 + O_2 \rightleftharpoons 2NO$ |
| > 0 | Kp > Kc (when RT > 1) | $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ ($\Delta n = +1$) |
| < 0 | Kp < Kc (when RT > 1) | $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($\Delta n = -2$) |

KEY IDEA

**Match R to the pressure unit.** With pressures in atm use 0.0821; with bar use 0.0831. Using 8.314 here is the commonest error — that value belongs with SI pressure (Pa) and volume ($m^3$).

**SOLVED EXAMPLE 02** — KP FROM KC

For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K_c = 6.0 \times 10^{-2}$ at 500 K. Find Kp (atm).

SOLUTION

1. $\Delta n = 2 - 4 = -2$.
2. $RT = 0.0821 \times 500 = 41.05$; $(RT)^2 = 1685$.
3. $K_p = K_c / (RT)^2 = 6.0 \times 10^{-2} / 1685$.

ANSWER $K_p \approx 3.6 \times 10^{-5}$ $atm^{-2}$.

SECTION D

# Manipulating K

D

*What happens to K when you change the equation.*

| Change to the equation | New constant | Example |
|---|---|---|
| Reverse it | 1/K | $2HI \rightleftharpoons H_2 + I_2$: K = 1/49 |
| Multiply by n | $K^n$ | $2H_2 + 2I_2 \rightleftharpoons 4HI$: K = $49^2$ = 2401 |
| Divide by n (e.g. halve) | $K^{1/n}$ (the nth root) | $\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$: K = √49 = 7 |
| Add two equations | $K_1 \times K_2$ | Overall K is the product |

**SOLVED EXAMPLE 03** — REVERSING AND HALVING

For $N_2 + 3H_2 \rightleftharpoons 2NH_3$ the constant is K. Write the constant for $NH_3 \rightleftharpoons \frac{1}{2}N_2 + 3/2\ H_2$.

SOLUTION

1. Reverse the equation → 1/K.
2. Halve it → square root.

ANSWER K′ = 1/√K.

CHECK YOURSELF

C1 Write Kp for $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$.

C2 If K = 4 for $A \rightleftharpoons 2B$, what is K for $2B \rightleftharpoons A$?

*Answers at the end of the chapter.*

SECTION E

# Q and the direction of change

E

*Compare the present mixture with equilibrium.*

The **reaction quotient Q** has the same form as K but uses the concentrations right now, not at equilibrium.

| Comparison | What the system does |
|---|---|
| Q < K | Too few products: reaction goes **forward** |
| Q = K | At equilibrium: no net change |
| Q > K | Too many products: reaction goes **backward** |

**SOLVED EXAMPLE 04** — WHICH WAY?

For $H_2 + I_2 \rightleftharpoons 2HI$, K = 49. A mixture has [HI] = 0.50 M and $[H_2] = [I_2]$ = 0.10 M. Which way does it move?

SOLUTION

1. $Q = (0.50)^2 / (0.10 \times 0.10) = 0.25 / 0.010 = 25$.
2. Q (25) < K (49).

ANSWER The reaction moves forward, forming more HI.

SECTION F

# ICE tables

F

*Initial, Change, Equilibrium — the method for every "find the amounts" numerical.*

1. Write the balanced equation.
2. **I:** initial amounts (mol $L^{-1}$, or moles if $\Delta n = 0$).
3. **C:** changes in terms of x, in the ratio of the coefficients (reactants −, products +).
4. **E:** initial + change. Substitute into K and solve for x.

**SOLVED EXAMPLE 05** — SOLVING AN ICE TABLE

1.0 mol each of $H_2$ and $I_2$ are heated in a 1 L flask. Kc = 64. Find the equilibrium concentrations.

SOLUTION

1. I: $H_2$ 1.0, $I_2$ 1.0, HI 0. C: −x, −x, +2x. E: 1 − x, 1 − x, 2x.
2. $Kc = (2x)^2 / (1 - x)^2 = 64 \rightarrow$ take square roots: $2x / (1 - x) = 8$.
3. $2x = 8 - 8x \rightarrow 10x = 8 \rightarrow x = 0.8$.

ANSWER $[HI] = 1.6$ M; $[H_2] = [I_2] = 0.2$ M.

KEY IDEA

**Perfect squares save time.** When both sides are squares (as above), take the square root instead of solving a quadratic. When K is very small, assume x is negligible beside the initial amount — then check that x is under about 5% of it.

SECTION G

# Degree of dissociation

G

*How much of one substance falls apart.*

For a dissociation, α is the fraction of one mole that dissociates. For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ starting with 1 mol: at equilibrium $PCl_5 = 1 - \alpha$, $PCl_3 = \alpha$, $Cl_2 = \alpha$, total $= 1 + \alpha$.

$$K_p = \alpha^2 P / (1 - \alpha^2)$$

P = total pressure at equilibrium. If α is small: $\alpha \approx \sqrt{(K_p / P)}$

$$\alpha = (D - d) / [(n - 1) d]$$

Vapour density method: D = vapour density before dissociation, d = observed (mixture) vapour density, n = moles of products from one mole

**SOLVED EXAMPLE 06** — $PCl_5$ DISSOCIATION

$PCl_5$ is 50% dissociated at 1 atm total pressure. Find Kp.

SOLUTION

1. α = 0.5.
2. $K_p = (0.5)^2 \times 1 / (1 - 0.25) = 0.25 / 0.75$.

ANSWER Kp ≈ 0.33 atm.

KEY IDEA

**Lowering the total pressure increases** α for any dissociation that increases the number of gas moles: from $\alpha \approx \sqrt{(K_p/P)}$, α rises as P falls. K itself does not change.

CHECK YOURSELF

C3 Q = 0.5 and K = 2.0. Which direction does the reaction go?

C4 Why does adding more $CaCO_3(s)$ not shift $CaCO_3 \rightleftharpoons CaO + CO_2$?

*Answers at the end of the chapter.*

SECTION H

# Le Chatelier's principle

H

*Disturb an equilibrium and it shifts to partly undo the disturbance.*

| Change | Shift | Does K change? |
|---|---|---|
| Add a reactant / remove a product | Forward | No |
| Add a product / remove a reactant | Backward | No |

| Change | Shift | Does K change? |
|---|---|---|
| Increase pressure (decrease volume) | Toward fewer gas moles | No |
| Decrease pressure | Toward more gas moles | No |
| Add inert gas at constant volume | No shift (partial pressures unchanged) | No |
| Add inert gas at constant pressure | Toward more gas moles (volume grows) | No |
| Raise temperature | In the endothermic direction | **Yes** — K rises for endothermic, falls for exothermic |
| Add a catalyst | No shift; equilibrium reached sooner | No |

KEY IDEA

**Temperature is the only thing that changes K.** Everything else changes Q and the system moves back to the same K.

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

- **High pressure** (about 200 atm) favours the side with fewer moles (2 vs 4) → more $NH_3$.
- **Low temperature** favours the exothermic forward reaction, but is too slow — so a compromise of about 700 K is used.
- **Iron catalyst** with molybdenum promoter speeds up the approach to equilibrium; it does not change the yield at equilibrium.
- $NH_3$ is liquefied and removed, pulling the equilibrium forward.

SOLVED EXAMPLE 07 — PREDICTING SHIFTS

For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H < 0$, what happens to the amount of $SO_3$ when (a) pressure is increased, (b) temperature is increased, (c) argon is added at constant volume?

SOLUTION

1. (a) 3 gas moles → 2: higher pressure favours $SO_3$.
2. (b) Forward is exothermic: heating favours the backward reaction, and K falls.
3. (c) Partial pressures of the reacting gases do not change.

ANSWER (a) More $SO_3$. (b) Less $SO_3$. (c) No change.

SECTION I

# K, $\Delta G^\circ$ and temperature

I

*The thermodynamics behind K.*

$$\Delta G^\circ = -2.303\ RT \log K$$

$K > 1 \Leftrightarrow \Delta G^\circ < 0;\ K = 1 \Leftrightarrow \Delta G^\circ = 0;\ K < 1 \Leftrightarrow \Delta G^\circ > 0$

$$\log (K_2 / K_1) = [\Delta H^\circ / (2.303\ R)] \times [(T_2 - T_1) / (T_1\ T_2)]$$

van't Hoff equation; R = 8.314 J $K^{-1}$ $mol^{-1}$ here, $\Delta H^\circ$ in J

**SOLVED EXAMPLE 08** — VAN'T HOFF

The equilibrium constant of a reaction doubles when the temperature rises from 300 K to 310 K. Find $\Delta H^\circ$. (log 2 = 0.301)

SOLUTION

1. $\log 2 = [\Delta H^\circ / (2.303 \times 8.314)] \times [10 / (300 \times 310)]$.
2. $\Delta H^\circ = 0.301 \times 19.147 \times 9300$ J.

ANSWER $\Delta H^\circ \approx +53.6$ kJ $mol^{-1}$ — positive, as expected when K rises with temperature.

SECTION J

# Exam trap gallery

J

*Where marks are lost in equilibrium.*

✗ TRAP 01 · WHAT STUDENTS WRITE
At equilibrium the reactions stop.

✓ WHAT IS ACTUALLY CORRECT
Both continue at equal rates (dynamic equilibrium).

WHY Isotope-labelling experiments show exchange continues.

✗ TRAP 02 · WHAT STUDENTS WRITE
Include $CaCO_3$ and CaO in Kc.

✓ WHAT IS ACTUALLY CORRECT
Pure solids and liquids are left out: Kc = $[CO_2]$.

WHY Their concentrations are constant.

✗ TRAP 03 · WHAT STUDENTS WRITE
Use R = 8.314 in $Kp = Kc(RT)^{\Delta n}$ with atm.

✓ WHAT IS ACTUALLY CORRECT
Use 0.0821 L atm $K^{-1}$ $mol^{-1}$ (or 0.0831 for bar).

WHY R must match the pressure and volume units.

| ✗ TRAP 04 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| Increasing pressure changes K. | Only temperature changes K; pressure changes Q. |
| **WHY** The system shifts back to the same K. | |

| ✗ TRAP 05 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| A catalyst increases the yield at equilibrium. | A catalyst only gets there faster. |
| **WHY** It speeds forward and backward reactions equally. | |

| ✗ TRAP 06 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| Adding inert gas always shifts the equilibrium. | At constant volume: no shift. At constant pressure: shifts toward more gas moles. |
| **WHY** Only partial pressures of reacting gases matter. | |

| ✗ TRAP 07 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| Doubling an equation doubles K. | K is squared. |
| **WHY** Concentrations are raised to the new coefficients. | |

| ✗ TRAP 08 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| Q > K means the reaction goes forward. | Q > K: backward. Q < K: forward. |
| **WHY** Too many products already present. | |

MEMORY HOOK

"**Solids and liquids sit out**" — never in K.

"**Kp = Kc (RT) to the Δn**" — gas moles products minus reactants.

"**Only heat moves K.**"

"**Q small, go forward; Q big, go back.**"

SECTION K

# Practice MCQs

K

*Levels: Easy, Moderate, Tough.*

**Q01** At equilibrium: [EASY]

(a) both reactions stop

(b) forward rate = backward rate

(c) concentrations of reactants and products are equal

(d) K = 1

**Q02** For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, Kp equals: [EASY]

(a) $p(CO_2)$
(b) $p(CO_2)/p(CaCO_3)$
(c) $1/p(CO_2)$
(d) $p(CaO) \times p(CO_2)$

**Q03** Kp = Kc for: [EASY]

(a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(c) $H_2 + I_2 \rightleftharpoons 2HI$
(d) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

**Q04** The value of K changes with: [EASY]

(a) pressure
(b) concentration
(c) catalyst
(d) temperature

**Q05** If K for $A \rightleftharpoons B$ is 10, K for $B \rightleftharpoons A$ is: [EASY]

(a) 10
(b) 0.1
(c) -10
(d) 100

**Q06** For $N_2 + 3H_2 \rightleftharpoons 2NH_3$, Kp/Kc equals: [MODERATE]

(a) $(RT)^2$
(b) $(RT)^{-2}$
(c) RT
(d) 1

**Q07** If Q < K, the reaction: [MODERATE]

(a) is at equilibrium
(b) goes backward
(c) goes forward
(d) stops

**Q08** Increasing pressure on $2NO_2 \rightleftharpoons N_2O_4$ will: [MODERATE]

(a) increase $NO_2$
(b) increase $N_2O_4$
(c) have no effect
(d) change K

**Q09** For an exothermic reaction, raising temperature: [MODERATE]

(a) increases K
(b) decreases K
(c) does not affect K
(d) makes K = 1

**Q10** Adding argon at constant volume to $N_2 + 3H_2 \rightleftharpoons 2NH_3$: [MODERATE]

(a) shifts forward
(b) shifts backward
(c) no change
(d) increases K

**Q11** If K for $\frac{1}{2}A \rightleftharpoons B$ is 4, K for $A \rightleftharpoons 2B$ is: [MODERATE]

(a) 2
(b) 8
(c) 16
(d) 1/16

**Q12** $\Delta G^\circ$ for a reaction with K = 1 is: [MODERATE]

(a) negative
(b) positive
(c) zero
(d) infinite

**Q13** In $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, lowering the total pressure: [TOUGH]

(a) decreases α (b) increases α
(c) does not change α (d) changes Kp

**Q14** For $H_2 + I_2 \rightleftharpoons 2HI$ with Kc = 64, starting with 1 mol each in 1 L, [HI] at equilibrium is: [TOUGH]

(a) 0.8 M (b) 1.6 M
(c) 0.2 M (d) 1.0 M

**Q15** Adding inert gas at constant pressure to $PCl_5 \rightleftharpoons PCl_3 + Cl_2$: [TOUGH]

(a) shifts forward (b) shifts backward
(c) no change (d) increases Kp

## Answer key with explanations

Q01 **(b) forward rate = backward rate** — Dynamic balance.

Q02 **(a) $p(CO_2)$** — Solids are left out.

Q03 **(c) $H_2 + I_2 \rightleftharpoons 2HI$** — $\Delta n = 0$.

Q04 **(d) temperature** — Only temperature.

Q05 **(b) 0.1** — Reversed: 1/K.

Q06 **(b) $(RT)^{-2}$** — $\Delta n = -2$.

Q07 **(c) goes forward** — Needs more products.

Q08 **(b) increase $N_2O_4$** — Fewer moles on the right.

Q09 **(b) decreases K** — Backward (endothermic) direction favoured.

Q10 **(c) no change** — Partial pressures unchanged.

Q11 **(c) 16** — Doubled equation: $4^2$.

Q12 **(c) zero** — log 1 = 0.

Q13 **(b) increases α** — $\alpha \approx \sqrt{(Kp/P)}$.

Q14 **(b) 1.6 M** — x = 0.8, [HI] = 2x.

Q15 **(a) shifts forward** — Volume grows → toward more moles.

## Check-yourself answers

C1 $Kp = p(CO) \times p(H_2) / p(H_2O)$. Carbon is a solid.

C2 K = 1/4 = 0.25.

C3 Forward (Q < K).

C4 $CaCO_3$ is a solid; its "concentration" is constant and not in K.

QUICK REVISION

# One-page revision

*Read this page the night before the exam.*

## The constant

- $K_c = [C]^c[D]^d / [A]^a[B]^b$
- Leave out pure solids and liquids
- K changes only with T
- $K > 10^3$ products; $K < 10^{-3}$ reactants

## Kp and Kc

- $K_p = K_c (RT)^{\Delta n}$
- $\Delta n$ = gas moles products − reactants
- R = 0.0821 (atm) or 0.0831 (bar)
- $\Delta n = 0 \rightarrow K_p = K_c$

## Manipulating K

- Reverse → 1/K
- × n → K to the n
- ÷ 2 → √K
- Add equations → multiply K

## Q and ICE

- Q < K forward; Q > K backward
- I, C (in ratio), E → into K
- Perfect squares: take roots
- Small K: neglect x, then check

## Le Chatelier

- P up → fewer gas moles
- Inert gas: const V none; const P → more moles
- T up → endothermic side; K changes
- Catalyst: faster, no shift

## Dissociation and $\Delta G^\circ$

- $PCl_5$: $K_p = \alpha^2 P/(1 - \alpha^2)$
- $\alpha = (D - d)/[(n - 1)d]$
- $\Delta G^\circ = -2.303RT \log K$
- van't Hoff: $\log(K_2/K_1) = \Delta H^\circ/2.303R \times (T_2-T_1)/T_1T_2$

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