

Unit

7

AP Chemistry

Equilibrium

Dynamic equilibrium · Q and K · ICE tables · Le Châtelier's principle · Solubility · Common ions

Unit 1

7–9%
Atomic
structure

Unit 2

7–9%
Compound
structure

Unit 3

18–22%
Substances
and
mixtures

Unit 4

7–9%
Chemical
reactions

Unit 5

7–9%
Kinetics

Unit 6

7–9%
Thermo-
chemistry

Unit 7

7–9%
Equilibrium

Unit 8

11–15%
Acids and
bases

Unit 9

7–9%
Thermo-
dynamics,
electro-
chemistry

Unit 7 is 7–9% of the multiple-choice section. It also turns up in the free-response section most years, as a short question or as parts of a long one.

7.1 Equilibrium

7.2 Direction of
reaction

7.3 Q and K

7.4 Calculating K

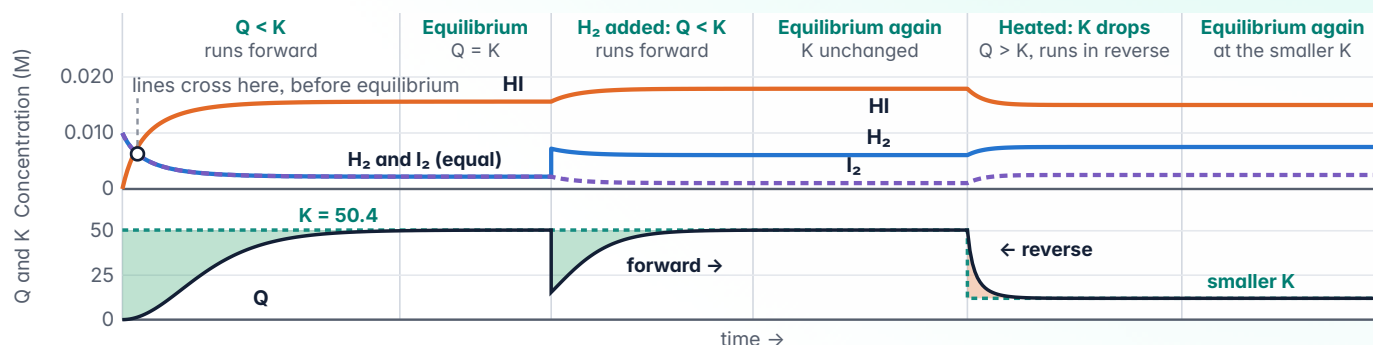
7.5 Magnitude of
K

7.6 Properties of K

7.7 ICE tables

7.8
Representations

7.9 Le Châtelier

7.10 Q and Le
Châtelier7.11 Solubility
equilibria7.12 Common-ion
effect

■ Q is below K, so the reaction runs forward ■ Q is above K, so it runs in reverse — Q — K (lower graph)

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, starting with no HI. The top graph shows concentrations and the bottom one shows Q and K. Where every line is flat, both reactions are still running at equal rates. Heating lowers K because the forward reaction is exothermic; the drop is drawn larger than it really is.

What the exam asks most

- Write an expression for K_c , K_p or K_{sp} (K_{sp} is K for a solid dissolving). Put products over reactants and raise each one to the power of its coefficient. Leave out solids and pure liquids. Use square brackets (mol/L) for K_c and K_{sp} , and partial pressures for K_p (c for concentration, p for pressure). **7.3**

7.11

- Say which way a change shifts a reaction, and why. State what the change does to Q (or, for a temperature change, to K), compare Q with K, and give the direction. Naming Le Châtelier's principle alone earns no credit. **7.9** **7.10**

- Calculate K from data or from a particle diagram. Use only equilibrium amounts; if one is missing, get it from the change row of an ICE table (Initial, Change, Equilibrium). Turn moles into molarity, and particle counts into molarity or pressure, before you substitute. **7.4** **7.7** **7.8**

- Find a molar solubility or a K_{sp} , or decide whether a solid forms. Write the dissolving equation first. After mixing two solutions, find each ion's diluted concentration, then compare Q with K_{sp} : a solid forms if $Q > K_{sp}$. One of the salt's own ions already in the water lowers the solubility but not K_{sp} . **7.11** **7.12**

Not on the exam

- Converting a K_c value into a K_p value, or the reverse.
- Equilibrium calculations for a gas dissolved in a liquid, such as CO_2 in a sealed soda.
- Solubility rules, except one you do need: all Na^+ , K^+ , NH_4^+ and NO_3^- salts dissolve.

On the equation sheet

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \text{ for } a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

It also gives $P_A = P_{\text{total}} \times X_A$, where X_A is the mole fraction of A. It gives no K_{sp} expression.

Know by heart

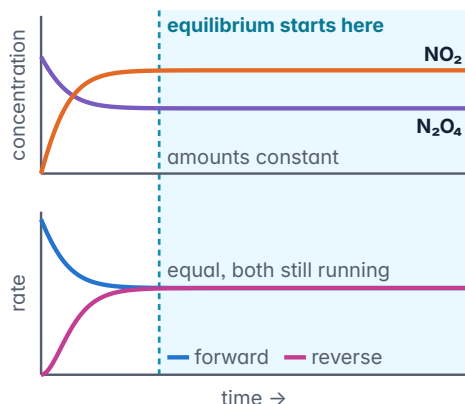
- If $Q < K$, the reaction runs forward until $Q = K$; if $Q > K$, it runs in reverse.
- Only a temperature change changes K. Concentration and volume changes can change Q, never K.
- Reversing an equation gives $1/K$, multiplying its coefficients by n gives K^n , and adding two equations multiplies their K values.
- In pure water, $K_{sp} = s^2$ for a salt with one cation per anion, like AgCl, and $4s^3$ for one like CaF_2 (one Ca^{2+} , two F^-). s is the molar solubility in mol/L.

7.1 Introduction to equilibrium

Seal some water in a bottle and the level drops for a while, then holds. Molecules still evaporate and condense, but at equal rates, so nothing you can see changes. Dissolving a salt, acid–base reactions and redox reactions can all reach the same kind of balance.

⚡ What is true at equilibrium

- Reactants and products are **both present**.
- Their concentrations and partial pressures stay constant, and they are usually not equal to each other.
- The forward and reverse reactions keep running at the **same rate**. That is why chemists call equilibrium dynamic.
- Measurable properties such as color, pressure and pH hold steady.



The flask starts with only N_2O_4 . The forward rate falls because N_2O_4 is being used up, and the reverse rate rises because NO_2 is building up.

⚠ Exam trap

- Thinking equilibrium means equal amounts.** It means the amounts stop changing. In the graph above, NO_2 ends well above N_2O_4 , and both then stay where they are.
- Saying the reaction has stopped.** Both reactions are still running, at the same rate. Write "the forward and reverse rates are equal" instead.
- Marking equilibrium where two concentration curves cross.** At a crossing the amounts are equal for an instant but still changing. In the graph above, they cross well before the dashed line, where equilibrium starts.

7.2 Direction of reversible reactions

Which way a reaction goes overall depends only on which rate is bigger right now.

Rates right now	Change	Q and K
forward > reverse	forward →	$Q < K$
reverse > forward	← reverse	$Q > K$
forward = reverse	equilibrium	$Q = K$

📖 What a catalyst does

It speeds up both directions by the same factor, so equilibrium arrives **sooner** with the **same amounts** and the same K.

🔗 Evidence that both reactions keep running

Drop crystals of PbI_2 made with radioactive iodide into a saturated PbI_2 solution. The solution soon turns radioactive while its concentration stays the same, because ions keep leaving the solid and landing back on it.

🔗 Describe equilibrium in words

The rate of the forward reaction **equals** the rate of the reverse reaction, so the concentrations stay **constant**.

For a physical change, name both processes, such as evaporating and condensing.

🔗 Quick check

A syringe of brown NO_2 and colorless N_2O_4 has kept the same shade for an hour. Has the reaction stopped?

Answer: No. NO_2 molecules pair up and N_2O_4 molecules split at the same rate, so the amounts, and the color, stay constant.

7.3 Reaction quotient and equilibrium constant

Fill the balanced equation's expression with the concentrations or pressures **right now** and you get the reaction quotient, Q. At equilibrium, Q equals the equilibrium constant, K.

📖 On the equation sheet

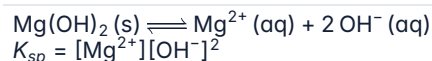
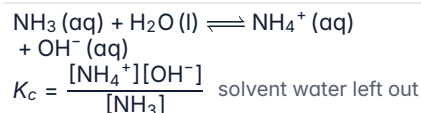
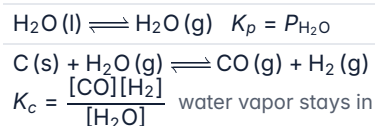
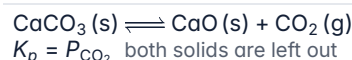
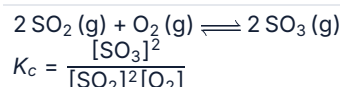
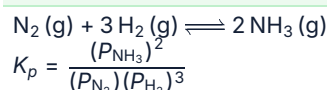
$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

K is the same for every starting mixture. Different starting amounts end at different concentrations, but at one temperature they all give the same K.

📖 How to write K or Q

- Products on top, reactants on the bottom.**
- Each coefficient becomes a power, and the terms multiply.**
- Leave out solids (s) and pure liquids (l).** Keep gases (g) and dissolved species (aq). Liquid water used as the solvent is left out, but water vapor goes in.
- Use square brackets (mol/L) for K_c and partial pressures for K_p .** Never mix the two in one expression.
- Write K without units.** Each K value belongs to one temperature.

Equations and their expressions



⚠ Exam trap

Each of these wrong ways to write K_{sp} for $\text{Mg}(\text{OH})_2$ loses the point.

$(\text{Mg}^{2+})(\text{OH}^-)^2$	Parentheses. Only square brackets mean mol/L.
$[\text{Mg}^{2+}][2\text{OH}^-]$	The coefficient 2 belongs in the power: $[\text{OH}^-]^2$.
$\frac{[\text{Mg}^{2+}][\text{OH}^-]^2}{[\text{Mg}(\text{OH})_2]}$	The solid is left out, so nothing goes on the bottom.
$[\text{Mg}][\text{OH}]^2$	No charges, so it names atoms instead of the ions in solution.

🔗 Quick check

Write K_p for baking soda breaking down: $2\text{NaHCO}_3(\text{s}) \rightleftharpoons \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

Answer: $K_p = (P_{\text{CO}_2})(P_{\text{H}_2\text{O}})$. Both solids are left out, and the water stays in because it is a gas here.

7.4 Calculating the equilibrium constant

K comes from amounts measured at equilibrium. Write the K expression first, since it is often worth a point by itself. Then substitute equilibrium amounts only, in mol/L for K_c or atm for K_p . If only one amount was measured, an ICE table gives you the rest.

Worked example

$P_4(g) \rightleftharpoons 2 P_2(g)$ at 1600 K in a rigid container. It starts with 0.470 atm of P_4 and no P_2 . At equilibrium, $P_{P_2} = 0.630$ atm. Find K_p .

	P_{P_4} (atm)	P_{P_2} (atm)
I	0.470	0
C	-x	+2x
E	0.470 - x	2x = 0.630

1 $x = 0.315$, so $P_{P_4} = 0.470 - 0.315 = 0.155$ atm

$$2 \quad K_p = \frac{(0.630)^2}{0.155}$$

$$K_p = 2.56$$

Worked example

A 2.00 L flask holds 0.0320 mol NO_2 and 0.0840 mol N_2O_4 at equilibrium. Find K_c for $2 NO_2 \rightleftharpoons N_2O_4$.

1 Divide by 2.00 L: 0.0160 M NO_2 and 0.0420 M N_2O_4

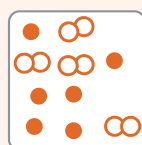
$$2 \quad K_c = \frac{0.0420}{(0.0160)^2}$$

$$K_c = 164$$

Exam trap

- **Putting moles into K_c .** K_c needs mol/L. In the flask above, moles give $0.0840/(0.0320)^2 = 82.0$. With concentrations, the top is divided by 2.00 and the bottom by $2.00^2 = 4.00$, so the right answer is twice as big: 164.
- **Putting starting amounts into K.** K uses the equilibrium (E) row only. Using the starting 0.470 atm of P_4 above gives $(0.630)^2/0.470 = 0.844$ instead of 2.56.

K from a particle diagram



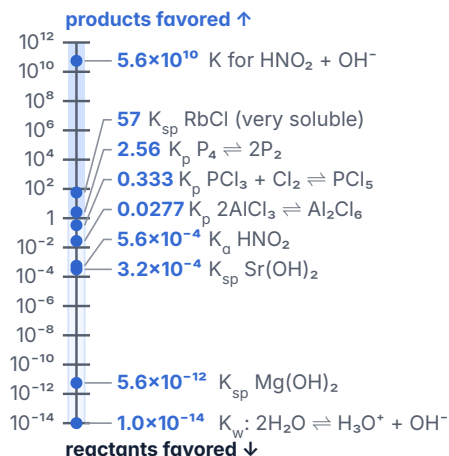
2.00 atm total

● NO_2 ○○ N_2O_4 , for
 $2 NO_2 \rightleftharpoons N_2O_4$ at another temperature
 $NO_2: \frac{6}{10} \times 2.00 = 1.20$ atm
 $N_2O_4: \frac{4}{10} \times 2.00 = 0.800$ atm
 $K_p = \frac{0.800}{(1.20)^2} = 0.556$

Each species' pressure is its share of the particles times the total pressure. If a question says each particle stands for 1.00 atm instead, the counts are the pressures, and you still square the NO_2 term.

7.5 Magnitude of the equilibrium constant

The size of K tells you what the mixture contains once it reaches equilibrium.



These K values all come from AP Chemistry questions, each at its own temperature. K_a is K for an acid and K_w is K for water (both in Unit 8); K_{sp} is K for a solid dissolving.

$K \gg 1$ (much larger than 1) mostly products, so treat the reaction as complete

K near 1 both sides in measurable amounts

$K \ll 1$ (much smaller than 1) mostly reactants; very little product forms

Exam trap

- **Thinking a large K means a fast reaction.** K only tells you how far a reaction goes. Hydrogen and oxygen can sit mixed for years even though K for making water is enormous; how fast they react is kinetics (Unit 5).
- **Thinking $K = 1$ means equal amounts.** $K = 1$ only means the top and the bottom of the expression are equal. For $A \rightleftharpoons 2 B$, 0.250 M A and 0.500 M B give $K = 0.500^2/0.250 = 1.00$, with twice as much B as A.

7.6 Properties of the equilibrium constant

When you rewrite an equation, its K changes in fixed ways, and Q follows the same rules. For $2 NO_2 \rightleftharpoons N_2O_4$, $K = 164$:

Do this to the equation	New K (for this example)
Reverse it	$1/K$ (6.10×10^{-3})
Double every coefficient	K^2 (2.69×10^4)
Halve every coefficient	$\sqrt{K}$ (12.8)
Add two equations	$K_1 \times K_2$

These rules mirror Hess's law from Unit 6: where enthalpy changes (ΔH) add, K values multiply.

Worked example

K_a of HNO_2 is 5.6×10^{-4} and $K_w = 1.0 \times 10^{-14}$. Find K for $HNO_2 + OH^- \rightleftharpoons NO_2^- + H_2O$.

- 1 $HNO_2 + H_2O \rightleftharpoons NO_2^- + H_3O^+$ K_a
- 2 K_w belongs to $2 H_2O \rightleftharpoons H_3O^+ + OH^-$. Reverse it: $H_3O^+ + OH^- \rightleftharpoons 2 H_2O$ $1/K_w$
- 3 Add them (H_3O^+ and one H_2O cancel): $K = \frac{5.6 \times 10^{-4}}{1.0 \times 10^{-14}}$

$K = 5.6 \times 10^{10}$, so the reaction goes essentially to completion

Exam trap

- **Adding K values when you add equations.** ΔH values add, but K values multiply. With $K_1 = 4.0$ and $K_2 = 25$, the overall K is 100, not 29.
- **Making K negative when you reverse an equation.** K is a ratio of positive amounts, so it is never negative. Reversing takes the reciprocal: K = 164 becomes $1/164 = 6.10 \times 10^{-3}$.
- **Doubling K when you double the coefficients.** Doubling them squares K instead: $164^2 = 2.69 \times 10^4$.

How combining equations is asked

You get two or three equations with K values and a target equation. Reverse any equation whose species are on the wrong side (take $1/K$), multiply its coefficients if needed (raise K to that same power n), then add the equations and multiply the K values. Write the combination, such as $K = K_1/K_2$, and the final number.

7.7 Calculating equilibrium concentrations

Given K and the starting amounts, an ICE table (Initial, Change, Equilibrium) finds every equilibrium amount.

The ICE table, step by step

- Find the direction.** Compare Q with K . If no gaseous or dissolved product is present yet, $Q = 0$ and the reaction runs forward.
- Initial row:** the starting molarities or pressures. Divide moles by liters to get molarity.
- Change row:** one unknown, x , times each coefficient, with a minus sign on the side being used up.
- Equilibrium row = Initial + Change.** Only this row goes into K .
- Solve for x .** If the K expression is a square over a square, take the square root of both sides. If K is tiny, drop x where it is subtracted from a starting amount, then check it is under 5% of that amount. Otherwise use the quadratic formula.
- Answer from the equilibrium row.** x is how far the reaction went; the answers are the amounts in that row.

Worked example

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, $K_c = 50.4$. It starts with 0.0100 M H_2 and 0.0100 M I_2 . Find every equilibrium concentration.

	$[\text{H}_2]$	$[\text{I}_2]$	$[\text{HI}]$
I	0.0100	0.0100	0
C	$-x$	$-x$	$+2x$
E	$0.0100 - x$	$0.0100 - x$	$2x$

- There is no HI yet, so $Q = 0 < K$ and the reaction runs forward.
- $50.4 = \frac{(2x)^2}{(0.0100 - x)^2}$, and both sides are perfect squares.
- Square-root both sides:
 $7.10 = \frac{2x}{0.0100 - x}$, so $x = 0.00780$
- Put x back into the E row. Check:
 $0.0156^2 / 0.0022^2 \approx 50 \checkmark$

$$[\text{HI}] = 0.0156 \text{ M}; [\text{H}_2] = [\text{I}_2] = 0.0022 \text{ M}$$

Worked example

$\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$, $K_c = 3.8 \times 10^{-5}$. It starts with 0.0100 M I_2 . Find $[\text{I}]$.

- E row: $[\text{I}_2] = 0.0100 - x$ and $[\text{I}] = 2x$
- K is tiny, so $0.0100 - x \approx 0.0100$:
 $\frac{4x^2}{0.0100} = 3.8 \times 10^{-5}$, so $x = 3.1 \times 10^{-4}$
- Check: x is 3% of 0.0100, under the usual 5% rule of thumb.

$$[\text{I}] = 2x = 6.2 \times 10^{-4} \text{ M}$$

Either starting side gives the same equilibrium



Both graphs show concentration against time. From 0.0200 M HI alone, the reaction can only run in reverse, and it ends at the same concentrations because both flasks hold the same atoms.

Worked example

$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, $K_c = 0.0420$. It starts with 0.100 M PCl_5 . Find every equilibrium concentration.

- E row: $[\text{PCl}_5] = 0.100 - x$ and $[\text{PCl}_3] = [\text{Cl}_2] = x$
- $\frac{x^2}{0.100 - x} = 0.0420$, so $x^2 + 0.0420x - 0.00420 = 0$
- Quadratic formula with $a = 1$, $b = 0.0420$, $c = -0.00420$:
 $x = \frac{-0.0420 + \sqrt{0.01856}}{2} = 0.0471$.
The other root is negative, so throw it out.

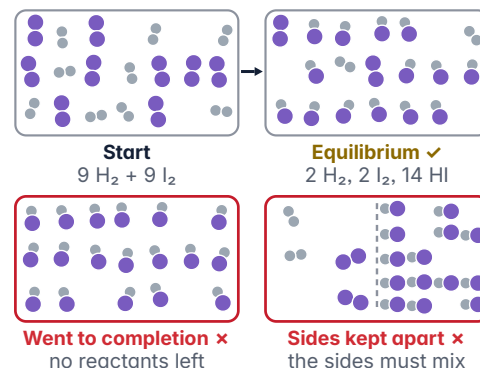
$$[\text{PCl}_3] = [\text{Cl}_2] = 0.0471 \text{ M}; [\text{PCl}_5] = 0.0529 \text{ M}$$

Exam trap

- Reporting x as the answer.** x only tells you how far the reaction went. In the HI example, $x = 0.00780$, but $[\text{HI}] = 2x = 0.0156 \text{ M}$ and $[\text{H}_2] = 0.0100 - x = 0.0022 \text{ M}$.
- Changing HI by x instead of $2x$.** Two HI form for every H_2 used, so the change row is $-x$, $-x$, $+2x$.
- Using the small- x shortcut when K isn't small.** In the PCl_5 example, x is 47% of 0.100 M. Dropping it would give $x = \sqrt{0.0420 \times 0.100} = 0.0648$, far from 0.0471.

7.8 Representations of equilibrium

An equilibrium particle diagram shows reactants and products together, in numbers that make $Q = K$, with every starting atom still there.



● H ● I. The correct box keeps all 18 H and 18 I atoms, and its $Q = 14^2 / (2 \times 2) = 49$ is close to K .

When particle counts can go straight into Q or K

Counts go straight into Q only when the powers on top and bottom add to the same number (2 and 2 for HI), so the box volume cancels. Otherwise convert to molarity or pressure first.

Worked example

A 2.0 L box contains 10 NO_2 and 8 N_2O_4 particles, and each particle stands for 0.0010 mol. Find K_c for $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ at a different temperature.

- $[\text{NO}_2] = 10(0.0010)/2.0 = 0.0050 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.0040 \text{ M}$
- $K_c = 0.0050^2 / 0.0040$. The raw counts would give $10^2/8 = 12.5$, which is wrong.

$$K_c = 6.3 \times 10^{-3}$$

Exam trap

- Drawing the box as if the reaction went to completion.** At equilibrium some of every reactant is left, so 18 HI from 9 H_2 and 9 I_2 is wrong. With counts in the ICE table, $(2x)^2 / (9 - x)^2 = 50.4$ gives $x = 7$: 2 H_2 , 2 I_2 and 14 HI.

Quick check

At another temperature, $K = 2.0$ for $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$. An equilibrium box holds 4 H_2 and 2 I_2 . How many HI should you draw?

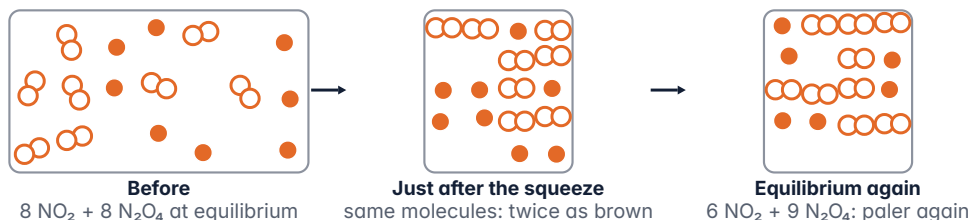
Answer: Call the number of HI n :
 $n^2 / (4 \times 2) = 2.0$, so $n = 4$.

7.9 Introduction to Le Châtelier's principle

Disturb an equilibrium and it shifts in the direction that **partly** undoes the disturbance. If you add N_2 to the ammonia reaction below, some of the added N_2 is used up, but not all of it.

Change	What it changes	Shift	For $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$, $\Delta H^\circ < 0$
Add a reactant or remove a product (gas or dissolved)	Q falls below K	forward →	Add N_2 , or remove NH_3 : more NH_3 forms.
Add a product or remove a reactant (gas or dissolved)	Q rises above K	← reverse	Add NH_3 : some of it breaks down.
Compress (smaller volume)	Q, if the gas moles on each side differ	toward fewer gas moles	4 mol of gas on the left, 2 on the right: forward.
Expand (larger volume)	Q, if the gas moles on each side differ	toward more gas moles	Reverse.
Raise the temperature	K itself	toward the endothermic side	K falls, so $Q > K$: less NH_3 .
Lower the temperature	K itself	toward the exothermic side	K rises, so $Q < K$: more NH_3 .
Dilute a solution with water	Q, if the dissolved particles on each side differ	toward more dissolved particles	For ammonia in water, $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ shifts forward.
Add a catalyst, an inert gas at constant volume, or more solid	nothing	no shift	A catalyst only makes equilibrium arrive sooner.

In the table: ■ runs forward (Q now below K) ■ runs in reverse (Q now above K)



● NO_2 ○ N_2O_4 , squeezed to half the volume in a syringe. NO_2 is a brown gas and N_2O_4 is colorless, so the color shows how much NO_2 is packed into the space. It fades after the squeeze because pairs of NO_2 join into N_2O_4 , the side with fewer gas moles. All 24 N atoms are still there.

Spotting the change on a graph



● NO_2 ■ N_2O_4

All three show $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$, which is exothermic in the forward direction. The heated mixture is kept at constant volume.

Asked what caused a change at time t

Name the change and support it with the graph: "At time t, $[\text{NO}_2]$ jumps while $[\text{N}_2\text{O}_4]$ does not, so NO_2 was added. Q dropped below K, so some of the added NO_2 then reacted to form N_2O_4 ."

A catalyst or an inert gas at constant volume is never the answer: neither one changes any concentration.

When nothing shifts, say why

$\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ has 2 mol of gas on each side, so halving the volume leaves $Q = K$. There is no shift, and the moles of HI stay the same.

Signs you can see that an equilibrium shifted

Color Pink $\text{Co}(\text{H}_2\text{O})_6^{2+} + 4 \text{Cl}^- \rightleftharpoons \text{blue } \text{CoCl}_4^{2-} + 6 \text{H}_2\text{O}$ is endothermic. Heat it, or add Cl^- , and it turns blue.

Color In $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{FeSCN}^{2+}$, the FeSCN^{2+} ion is blood red. Add either reactant ion and the red deepens.

pH $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$. Add NH_4Cl and $[\text{OH}^-]$ falls, so the pH drops.

Heat A shift in the exothermic direction warms an insulated flask.

Worked example

A red solution of $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{FeSCN}^{2+}$ is at equilibrium. A few drops of AgNO_3 are added, and white solid AgSCN forms. What happens to the color, and why?

- 1 Ag^+ pulls SCN^- out of the solution as solid AgSCN , so $[\text{SCN}^-]$ falls.
- 2 $Q = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]}$ rises above K, because its denominator got smaller.
- 3 The reaction runs in reverse: some FeSCN^{2+} breaks apart until $Q = K$ again.

Less FeSCN^{2+} , so the red color fades

Exam trap

- **Naming a catalyst or an inert gas as the change that made more product.** A catalyst speeds both directions equally, and an inert gas added at constant volume doesn't change any partial pressure. Neither changes Q or K, so neither shifts the equilibrium.
- **Getting the heat direction backward.** Treat heat as a product of an exothermic reaction. Heating $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$ ($\Delta H^\circ < 0$) lowers K, so the mixture shifts back toward N_2 and H_2 and less NH_3 is left.

Quick check

For $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$, $\Delta H^\circ > 0$. Which change gives more moles of NO_2 : adding a catalyst, halving the volume, raising the temperature, or adding argon at constant volume?

Answer: Only **raising the temperature**, because K grows for an endothermic reaction. Halving the volume favors N_2O_4 , the side with fewer gas moles, and the other two change nothing.

7.10 Reaction quotient and Le Châtelier's principle

Le Châtelier's principle tells you which way an equilibrium shifts. Comparing Q with K explains why, and that explanation is what earns the point.

What changes Q , and what changes K

- Adding or removing a gas or dissolved substance changes Q . A volume change does too, unless both sides have the same number of gas moles. Neither one changes K .
- Temperature is the only thing that changes K . For an endothermic forward reaction, heating makes K bigger; for an exothermic one, heating makes K smaller.
- Halving the volume at constant temperature doubles every partial pressure, which multiplies Q by $2^{\Delta n}$. Here Δn is the moles of gas on the product side minus the moles on the reactant side. When $\Delta n = 0$, Q doesn't change.

Worked example

$N_2 + 3 H_2 \rightleftharpoons 2 NH_3$ is at equilibrium with 0.30 atm N_2 , 0.50 atm H_2 and 0.20 atm NH_3 . The volume is halved at constant temperature. Which way does it shift?

- 1 $K_p = \frac{0.20^2}{0.30 \times 0.50^3} = 1.1$
- 2 Every pressure doubles:
 $Q = \frac{0.40^2}{0.60 \times 1.00^3} = 0.27$, which is $K/4$ ($\Delta n = 2 - 4 = -2$)
- 3 The total pressure jumps from 1.00 to 2.00 atm, then falls as 4 mol of gas react to make 2.

$Q < K$, so it shifts forward. The total pressure ends between 1.00 and 2.00 atm.

Sentences that earn the point, for the ammonia reaction

Halving the volume doubles every partial pressure, which makes $Q < K$. At constant temperature K doesn't change, so the reaction proceeds forward until $Q = K$.

The forward reaction is exothermic, so raising the temperature decreases K . Now $Q > K$, so the reaction proceeds in reverse until $Q = K$.

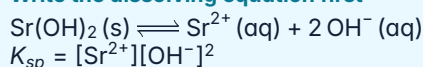
Exam trap

- Writing "by Le Châtelier's principle" as the whole explanation. It earns no credit on its own. Name the change, say what it does to Q or K , compare them, and give the direction.
- Saying a volume change can't shift anything because the temperature stayed the same. Constant temperature keeps K the same, but the volume change can still change Q , as in the ammonia example: Q fell to $K/4$.

7.11 Introduction to solubility equilibria

A saturated solution with solid on the bottom is an equilibrium: ions leave the crystal and land back on it at equal rates. Its K is the solubility product, K_{sp} .

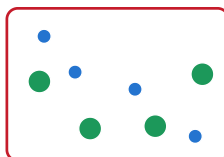
Write the dissolving equation first



As in any K , the solid is left out and the 2 becomes a power.



$Sr(OH)_2$ solution ✓
1 Sr^{2+} for every 2 OH^{-}



Equal numbers ✗
charges don't balance

● Sr^{2+} ● OH^{-} . If a question asks what is wrong with the right-hand box, name the 1 : 2 ratio of Sr^{2+} to OH^{-} . "The number of ions is wrong" is too vague.

Salt (ion ratio)	Ion concentrations in pure water*	K_{sp}
AgCl (1 : 1)	s and s	s^2
CaF_2 , $Mg(OH)_2$ (1 : 2)	s and 2s	$4s^3$
Ag_2CrO_4 (2 : 1)	2s and s	$4s^3$
$Al(OH)_3$ (1 : 3)	s and 3s	$27s^4$

*Only when the salt is the only source of these ions and nothing else reacts with them.

Quick check

A saturated $Mg(OH)_2$ solution in pure water has $[OH^{-}] = 2.2 \times 10^{-4}$ M. Find K_{sp} .

Answer: $[Mg^{2+}]$ is half of $[OH^{-}]$, 1.1×10^{-4} M, so $K_{sp} = (1.1 \times 10^{-4})(2.2 \times 10^{-4})^2 = 5.3 \times 10^{-12}$.

Molar solubility, s

- s is the moles of solid that dissolve per liter of saturated solution. Don't add up the ion concentrations to get it, and don't confuse it with K_{sp} .
- To compare how well salts dissolve, compare their s values. Comparing K_{sp} values works only when the salts have the same K_{sp} formula, such as two 1 : 1 salts.

Worked example

A saturated $Sr(OH)_2$ solution in pure water has $[Sr^{2+}] = 0.043$ M. Find K_{sp} .

- 1 Two OH^{-} for each Sr^{2+} : $[OH^{-}] = 2(0.043) = 0.086$ M
- 2 $K_{sp} = (0.043)(0.086)^2$, the same as $4s^3$ with $s = 0.043$

$$K_{sp} = 3.2 \times 10^{-4}$$

Worked example

0.0168 g of CaF_2 (78.08 g/mol) dissolves per liter of water. Find K_{sp} .

- 1 Change g/L to mol/L, keeping extra digits: $s = 0.0168/78.08 = 2.1516 \times 10^{-4}$ M
- 2 $K_{sp} = [Ca^{2+}][F^{-}]^2 = s(2s)^2 = 4s^3 = 4(2.1516 \times 10^{-4})^3$

$$K_{sp} = 3.98 \times 10^{-11}, \text{ which rounds to } 4.0 \times 10^{-11}$$

Worked example

K_{sp} of CaF_2 is 4.0×10^{-11} and of $AgCl$ is 1.8×10^{-10} . Which dissolves more?

- 1 CaF_2 : $4s^3 = 4.0 \times 10^{-11}$, so $s = \sqrt[3]{1.0 \times 10^{-11}} = 2.15 \times 10^{-4}$ M
- 2 $AgCl$: $s^2 = 1.8 \times 10^{-10}$, so $s = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5}$ M

CaF_2 , about 16 times more, even though its K_{sp} is smaller

Take a cube root

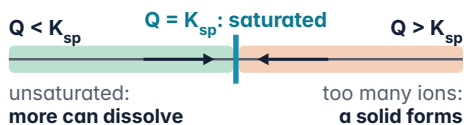
TI-84 Plus CE. Press **math** and choose 4, the cube root. Type 1.0, press **2nd**, **^** (EE, meaning $\times 10$ to the power) and **(-)** 11, close the bracket and press **enter**.

TI-Nspire CX. Press **ctrl**, **^** for the root template. Type 3 in the small box, press **tab**, type 1.0×10^{-11} and press **enter**.

Desmos. Type **cbt** and Desmos turns it into a cube-root sign. Type 1.0×10^{-11} inside it, and the answer (about 0.000215) appears.

Will a precipitate form?

Calculate Q from the ion concentrations in the mixture and compare it with K_{sp} .



Worked example

35.00 mL of 1.85×10^{-3} M $\text{Mg}(\text{NO}_3)_2$ is mixed with 50.00 mL of 2.80×10^{-4} M NaOH . K_{sp} of $\text{Mg}(\text{OH})_2$ is 5.61×10^{-12} . Does a precipitate form?

- First find the diluted concentrations. The total volume is 85.00 mL:
 $[\text{Mg}^{2+}] = 1.85 \times 10^{-3} \times \frac{35.00}{85.00} = 7.62 \times 10^{-4}$ M and $[\text{OH}^-] = 2.80 \times 10^{-4} \times \frac{50.00}{85.00} = 1.65 \times 10^{-4}$ M
- $Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (7.62 \times 10^{-4})(1.65 \times 10^{-4})^2 = 2.07 \times 10^{-11}$

$Q < K_{sp}$, so $\text{Mg}(\text{OH})_2$ precipitates

Exam trap

- Using the concentrations from before mixing. Mixing dilutes both solutions. Multiply each concentration by its own volume over the total volume, as in step 1 above.
- Getting $[\text{OH}^-]$ wrong from $[\text{Sr}^{2+}]$. In saturated $\text{Sr}(\text{OH})_2$ with $[\text{Sr}^{2+}] = 0.043$ M, each formula unit releases two OH^- , so $[\text{OH}^-] = 2 \times 0.043 = 0.086$ M. Setting it equal to $[\text{Sr}^{2+}]$, or halving it, gives the wrong K_{sp} .
- Squaring $[\text{Sr}^{2+}]$ before doubling it. Double $[\text{Sr}^{2+}]$ to get $[\text{OH}^-]$, then square: $(0.043)(0.086)^2 = 3.2 \times 10^{-4}$. Writing $(0.043)(2)(0.043)^2$ gives half of that.
- Comparing powers of ten backward. 2.07×10^{-11} is larger than 5.61×10^{-12} , because 10^{-11} is ten times 10^{-12} . Compare the exponents first, then the numbers in front.

Quick check

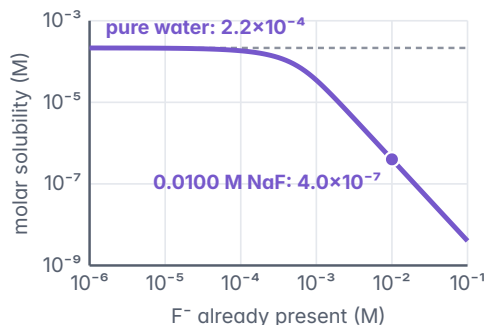
After mixing, $[\text{Ag}^+] = [\text{Cl}^-] = 1.0 \times 10^{-5}$ M. K_{sp} of AgCl is 1.8×10^{-10} . Does a precipitate form?

Answer:

$Q = (1.0 \times 10^{-5})(1.0 \times 10^{-5}) = 1.0 \times 10^{-10}$, which is less than K_{sp} . So no solid forms; the solution is unsaturated.

7.12 Common-ion effect

A salt dissolves **less** in water that already contains one of its ions. The ion that is already there makes Q reach K_{sp} after less of the salt has dissolved. K_{sp} itself does not change. This is Le Châtelier's principle applied to dissolving. The extra ion pushes the dissolving reaction back toward the solid.



CaF_2 in water that already contains F^- . K_{sp} is 4.0×10^{-11} at every point on the curve; only the solubility changes.

Worked example

What is the molar solubility of CaF_2 ($K_{sp} = 4.0 \times 10^{-11}$) in 0.0100 M NaF ?

	$[\text{Ca}^{2+}]$	$[\text{F}^-]$
I	0	0.0100 (from NaF)
C	+s	+2s
E	s	$0.0100 + 2s \approx 0.0100$

- $s(0.0100)^2 = 4.0 \times 10^{-11}$, so $s = \frac{4.0 \times 10^{-11}}{(0.0100)^2}$
- Check: $2s$ is tiny next to 0.0100, so dropping it was fine ✓

$s = 4.0 \times 10^{-7}$ M, about 540 times smaller than in pure water (2.15×10^{-4} M)

Worked example

Rank the molar solubility of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) in pure water, 0.10 M NaNO_3 , 0.10 M NaCl and 0.10 M CaCl_2 .

- NaNO_3 shares no ion with AgCl , so s is the same as in pure water: $s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}$ M
- 0.10 M NaCl gives $[\text{Cl}^-] = 0.10$ M: $s = 1.8 \times 10^{-10}/0.10 = 1.8 \times 10^{-9}$ M
- Each CaCl_2 releases two Cl^- , so $[\text{Cl}^-] = 0.20$ M: $s = 9.0 \times 10^{-10}$ M

Pure water = $\text{NaNO}_3 > \text{NaCl} > \text{CaCl}_2$

The explanation that earns the point

$[\text{OH}^-]$ is **lower** in a saturated solution of $\text{Sr}(\text{OH})_2$ in 0.10 M $\text{Sr}(\text{NO}_3)_2$ than in pure water. Sr^{2+} is a **common ion** that is already present, so less $\text{Sr}(\text{OH})_2$ dissolves before $Q = K_{sp}$, and **less OH^-** is released.

With $[\text{Sr}^{2+}] = 0.10 + s$ and $[\text{OH}^-] = 2s$, K_{sp} gives $4s^2(0.10 + s) = 3.2 \times 10^{-4}$. Its exact solution is $s = 0.0253$, so $[\text{OH}^-] = 0.051$ M here, against 0.086 M in pure water. Dropping s next to 0.10 fails on this one: it gives $s = 0.028$ M, which is 28% of 0.10.

Removing an ion has the opposite effect

Add HNO_3 to saturated $\text{Mg}(\text{OH})_2$ with solid present. H^+ reacts with OH^- to make water, so $[\text{OH}^-]$ falls and Q drops below K_{sp} . **More solid dissolves** until $Q = K_{sp}$ again. Write out each of those steps. "The acid reacts with the solid" on its own is too vague to earn the point.

Exam trap

- Saying the common ion lowers K_{sp} . It lowers the solubility, s . K_{sp} changes only with temperature. In 0.0100 M NaF , s for CaF_2 falls from 2.2×10^{-4} M to 4.0×10^{-7} M while K_{sp} stays 4.0×10^{-11} .
- Writing only "because of the common-ion effect." Name the common ion, say it is already present, and say what that does to how much dissolves, as in the sentences above.

Quick check

What is the molar solubility of $\text{Mg}(\text{OH})_2$ ($K_{sp} = 5.6 \times 10^{-12}$) in 0.10 M NaOH ?

Answer: $[\text{OH}^-] \approx 0.10$ M, so $s(0.10)^2 = 5.6 \times 10^{-12}$ and $s = 5.6 \times 10^{-10}$ M, against 1.1×10^{-4} M in pure water.

Enter powers of ten

TI-84 Plus CE. For 5.61×10^{-12} , type 5.61, press $\boxed{2\text{nd}} \boxed{[]}$ (EE), then $\boxed{(-)} \boxed{12}$. The screen shows 5.61E-12.

TI-Nspire CX. Type 5.61 $\boxed{\times} \boxed{10} \boxed{\wedge} \boxed{(-)} \boxed{12}$.
Desmos. Type 5.61*10^-12.

On both TI calculators, use the $\boxed{(-)}$ key for a negative sign, never the subtraction key.

Free-response questions on equilibrium

⊙ A free-response-style question on one equilibrium

$2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$, $\Delta H^\circ = -57 \text{ kJ/mol}$. Every part is at the same temperature except (d), which heats the flask.

The question	An answer that earns the point	What earns it, and what loses it
(a) Write the expression for K_c .	$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$	Put products over reactants, with the coefficient 2 as a power. Writing $[2\text{NO}_2]$, using parentheses, or using partial pressures loses it.
(b) A 2.00 L flask at equilibrium holds 0.0320 mol NO_2 and 0.0840 mol N_2O_4 . Calculate K_c .	0.0160 M and 0.0420 M, so $K_c = \frac{0.0420}{(0.0160)^2} = 164$	Show the expression with the values substituted, in mol/L. Putting in moles gives 82.0 and loses the point.
(c) Another flask holds 0.0200 M NO_2 and 0.0500 M N_2O_4 . Which way does it react?	$Q = \frac{0.0500}{(0.0200)^2} = 125$. $Q < K$, so it reacts forward and more N_2O_4 forms.	Calculate Q, compare it with K, then give the direction. A direction with no Q earns nothing.
(d) The flask from (b) is heated at constant volume. Does $[\text{NO}_2]$ increase, decrease or stay the same? Justify.	It increases. The forward reaction is exothermic, so heating lowers K. Now $Q > K$, so the reaction shifts in reverse and makes more NO_2 .	Give all three steps: the sign of ΔH° , what happens to K, then Q against K. "By Le Châtelier's principle it shifts left" on its own loses it.
(e) A catalyst is added to the flask from (b), which has not been heated. What happens to $[\text{N}_2\text{O}_4]$?	It stays the same. A catalyst speeds up both reactions equally, so Q still equals K and nothing shifts.	Say that both rates go up by the same factor. "The catalyst speeds up the reaction, so more N_2O_4 forms" loses it.

✍ What earns the point on other kinds of question

When the question says	Write this
"Using the particle diagram, calculate K_p "	Count each species. Its pressure is its share of the particles times the total pressure, or its count times the pressure each particle stands for. Raise each pressure to the power of its coefficient.
"Draw the missing particles"	Call the unknown count n, set Q equal to the value given, and solve for n. Keep every atom from the start and mix everything in one box. Never draw it as if the reaction went to completion.
"Will a precipitate form? Justify."	Find the concentrations after mixing, using the total volume. Calculate Q from the K_{sp} expression, write a sentence comparing Q with K_{sp} , then answer.
"Increase, decrease or remain the same?" after adding, removing or a volume change	Say whether it increases, decreases or stays the same, then what the change does to Q, how Q compares with K, and the direction. With equal moles of gas on each side, a volume change leaves $Q = K$, so nothing shifts.
"Explain what happened at time t" on a graph	If one line jumps, that substance was added or removed. If every line jumps, the volume changed. If nothing jumps but the lines bend smoothly, the temperature changed.
"Calculate the molar solubility" or K_{sp}	Write the dissolving equation, then each ion's concentration in terms of s from the formula (s and 2s for CaF_2 , s and s for AgCl), then the K_{sp} expression, and solve. Change g/L to mol/L first.
"Explain why it is less soluble" in a salt solution than in water	Name the common ion and say it is already present, so less of the salt dissolves and its other ion ends up lower than in pure water. An acid that removes OH^- has the opposite effect.

⚠ Sentences that lose points, and what to write instead

- Instead of "Le Châtelier: it shifts right," write "Adding H_2 , a reactant, makes $Q < K$, so the reaction proceeds forward until $Q = K$."
- Instead of "K increases because more product forms," write "K stays the same at constant temperature. Adding a reactant changed Q."
- Instead of "At equilibrium the reaction stops," write "At equilibrium the forward and reverse rates are equal."
- Instead of "The concentrations are equal," write "The concentrations are constant."
- Instead of "The solubility is K_{sp} ," write "For CaF_2 , $K_{sp} = 4s^3$, so $s = \sqrt[3]{K_{sp}/4}$."

Keep every digit in the middle of a calculation and round only the final answer. Rounding x partway through an ICE table can change the last digit of every answer.

📱 Keep every digit until the end

TI-84 Plus CE. After a result, press **sto→**

alpha **math** (the letter A) and **enter**.

Use it later as A: for 2x, type 2 **alpha**

math.

TI-Nspire CX. After a result, press **ctrl**

var (sto→), type a name such as x, and press **enter**. Type the name to use it later.

Desmos. Store a value by giving it a letter.

For x in the HI example, type a = 0.0100*sqrt(50.4)/(2 + sqrt(50.4)), then type 2a to get [HI]. Desmos keeps every digit.

🔗 Where Unit 7 comes back

Unit 3

Water in a closed container: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ has $K_p = P_{\text{H}_2\text{O}}$, the vapor pressure.

Unit 5

A catalyst speeds up both directions equally, so equilibrium arrives sooner with the same K.

Unit 6

The sign of ΔH° tells you which way heating shifts an equilibrium.

Unit 8

K_a (acids), K_b (bases) and K_w (water) are equilibrium constants. The pH of a weak acid comes from this unit's ICE table, and buffers work by Le Châtelier's principle.

Unit 9

K is linked to free energy: $K > 1$ exactly when $\Delta G^\circ < 0$.