How far? The extent of chemical change

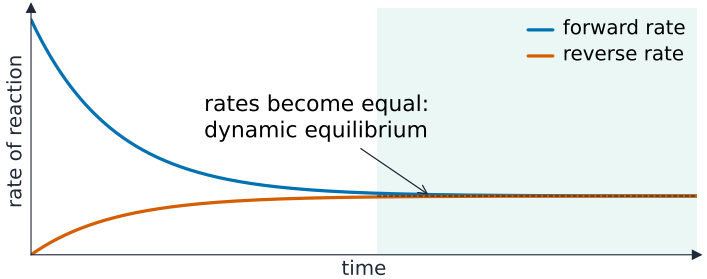
Reactivity 2.3 · SL and AHL

Why does a sealed bottle of cola stay fizzy?

Net composition can become constant while both reactions continue.

- CO_2 leaves the drink and dissolves back at equal rates.
- Open the bottle and the gas escapes; the drink goes flat.
- This unit: dynamic balance, equilibrium constants and controlled disturbances.

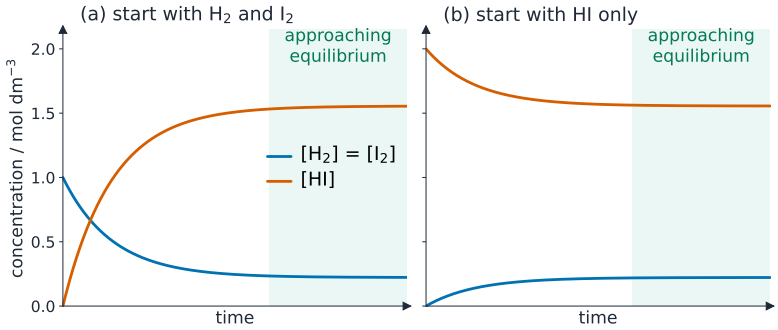
Dynamic equilibrium



equal forward and reverse rates; constant composition at fixed conditions

Both reactions keep going; their changes cancel.

The same equilibrium from both sides



Same elemental inventory, temperature and volume: same equilibrium; supplied K = 49.

A physical equilibrium has two phases

> A constant macroscopic signal does not mean particles have stopped.

- In a sealed flask, $Br_2(l) \rightleftharpoons Br_2(g)$.
- At fixed temperature, evaporation and condensation rates match.
- Opening a carbonated bottle lowers the CO_2 partial pressure; dissolved gas is lost overall.

Check: what is true at equilibrium?

Your turn

Which statement is true for every dynamic equilibrium?

A. The concentrations of reactants and products are equal.

B. The forward and reverse reactions have stopped.

C. The forward and reverse rates are equal.

D. The mixture is mainly products.

The equilibrium law

- Products on top, reactants underneath; coefficients become powers.
- Use equilibrium concentrations; keep the equation and concentration convention fixed.

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

for $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$

Calculating K_c

1. **Expression.** Supplied equilibrium at 700 K: $H_2 + I_2 \rightleftharpoons 2HI$; $[HI] = 0.14$, $[H_2] = [I_2] = 0.020$ mol dm^{-3}.
2. **Substitute.** $K_c = [HI]^2/([H_2][I_2]) = 0.14^2/(0.020 \times 0.020) = 49$
3. **Reverse equation.** $1/49 = 0.020$

Decision

$K_c = 49$

What the size of K tells you

Value of K	**Equilibrium mixture**
$K \gg 1$	Large product/reactant ratio
$K > 1$	Products favoured
$K = 1$	Equal numerator and denominator
$K < 1$	Reactants favoured
$K \ll 1$	Very small product/reactant ratio

Same K, different concentrations

1. **Mixture one.** A $\rightleftharpoons$ B: [A] $= 0.20$, [B] $= 0.60$; $K_c = 3.0$.
2. **Mixture two.** [A] $= 0.40$, [B] $= 1.20$; $K_c = 3.0$ again.
3. **Interpret.** The ratio is fixed at this temperature, not each concentration separately.

Decision

K alone does not set a universal percentage **yield**.

Le Chatelier's principle

Change	**Shift**	K
add reactant	to the right	same
compress at fixed T	fewer gas coefficients	same
higher temperature	endothermic way	changes
catalyst	none	same

Pure phases and dissolved substances

> A dissolved component is not a separate pure liquid phase.

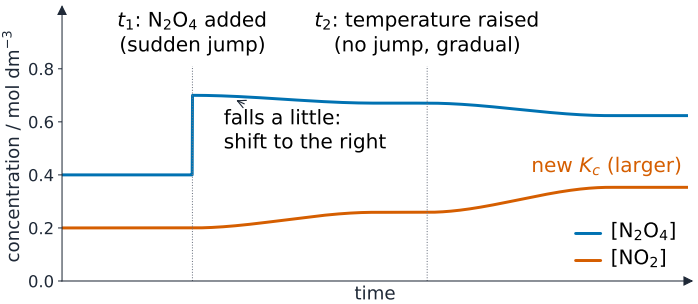
- $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$: omit the pure solid terms while both phases remain.
- Adding bulk solid does not change the equilibrium CO_2 level; exhaustion removes that phase constraint.
- $CO_2(g) \rightleftharpoons CO_2(aq)$: higher gas partial pressure favours dissolution.

Compression or inert gas?

> Specify what changed; total pressure alone is insufficient.

- $N_2 + 3H_2 \rightleftharpoons 2NH_3$: compression at fixed temperature favours ammonia.
- Adding ideal inert gas at fixed volume leaves reacting concentrations unchanged: no shift.
- At fixed total pressure, inert addition expands the mixture; the conditions differ.

Temperature changes K



$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, forward endothermic · fixed volume; invented data

At fixed volume: addition jumps; heating changes K and the final mixture.

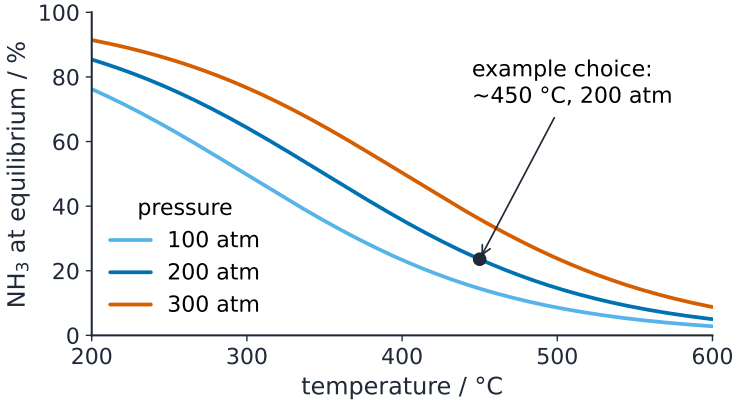
Check: making methanol

Your turn

For these ideal gases, which change raises the equilibrium methanol yield?

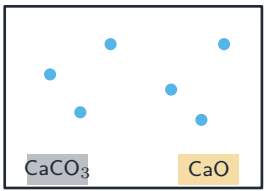
A. Raising temperature
B. Compressing at fixed temperature
C. Adding a catalyst at fixed temperature
D. Expanding at fixed temperature

The Haber process

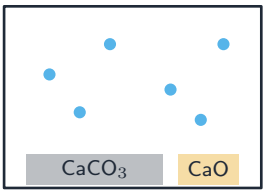


Invented trends show the **yield**/rate trade-off; these are not plant data.

Solids do not appear in K_p



less $CaCO_3$

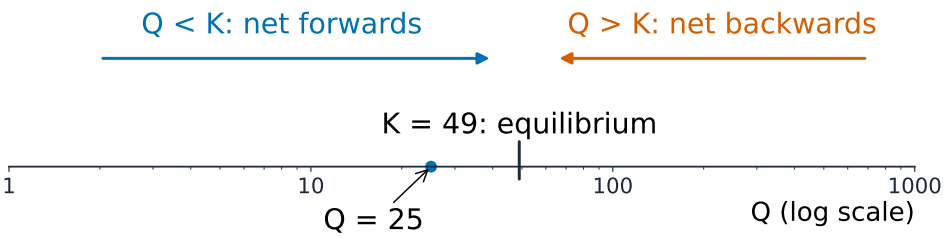


more $CaCO_3$

same temperature and volume: same p_{CO_2} while both solids remain; $K_p = p_{CO_2}$

$$K_p = p_{CO_2}$$

AHL: The reaction quotient



$Q < K$, so the mixture reacts forwards.

AHL: Find the same equilibrium by a square root

1. **Set up.** Initially $[H_2] = [I_2] = 1.00$, $[HI] = 0$; equilibrium $1 - x$, $1 - x$, $2x$.
2. **Use the constant.** $49 = (2x)^2/(1 - x)^2$ gives $7 = 2x/(1 - x)$.
3. **Solve without early rounding.** $x = 7/9$; $[HI] = 14/9 \approx 1.56$, reactants $= 2/9 \approx 0.222$ mol dm^{-3}.

Decision

Unrounded substitution returns $K = 49$ exactly.

AHL: An ICE table

1. **Initial.** Invented homogeneous mixture: acid 1.00, ethanol 1.00, ester 0, water 0 mol; dry catalyst.
2. **Change.** -0.67, -0.67, $+0.67$, $+0.67$
3. **Equilibrium.** 0.33, 0.33, 0.67, 0.67

Decision

$K_c = 0.67^2/0.33^2 = 4.1$

AHL: When K is very small

1. **Assume.** $N_2 + O_2 \rightleftharpoons 2NO$, supplied $K_c = 4.0 \times 10^{-4}$; initial reactants each 0.50 mol dm^{-3}, no NO.
2. **Solve.** $[NO]^2 = 4.0 \times 10^{-4} \times 0.25 = 1.0 \times 10^{-4}$
3. **Check.** 0.005 used, 1% of 0.50

Decision

[NO] = 0.010 mol dm^{-3}

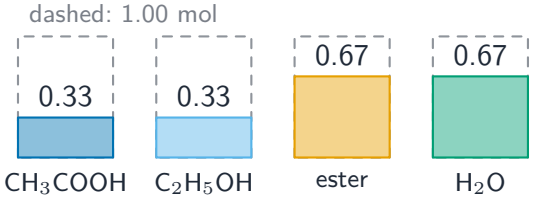
AHL: Reject an impossible approximation

1. **Tentative assumption.** A $\rightleftharpoons$ 2B, $K_c = 1.6 \times 10^{-5}$; initial [A] $= 10^{-8}$ mol dm^{-3}, no B.
2. **Prediction.** If A were unchanged, [B] $= \sqrt{1.6 \times 10^{-5} \times 10^{-8}} = 4.0 \times 10^{-7}$.
3. **Conservation test.** Even complete conversion gives [B] at most 2.0×10^{-8}; the prediction is impossible.

Decision

Small K alone does not validate negligible depletion.

Equilibrium in esterification



initial acid and alcohol 1.00 mol
change ∓ 0.67 mol

$$K_c = \frac{0.67^2}{0.33^2} = 4.1$$

(V cancels; invented data)

$K_c = 0.67^2/0.33^2 \approx 4.1$

When K is small

$[N_2]$ stays ≈ 0.50 (0.495)

$[O_2]$ stays ≈ 0.50 (0.495)

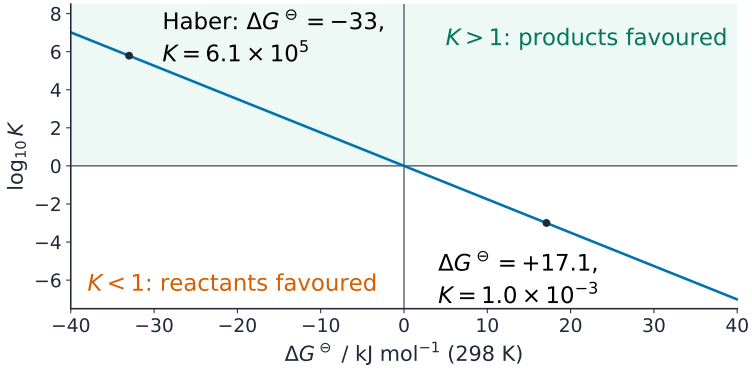
used: 0.005
$= 1\%$ of 0.50

$[NO]^2 \approx 4.0 \times 10^{-4} \times 0.50 \times 0.50 = 1.0 \times 10^{-4}$, so $[NO] = 0.010$

check: depletion small relative to each initial value, so the approximation holds

> So treat the reactant concentrations as unchanged

AHL: Gibbs energy and K



Convert kJ to J before using $\Delta G^\ominus = -RT \ln K$.

AHL: Calculate the thermodynamic constant

1. **Supplied standard value.** $\Delta G^{\ominus} = -33$ kJ mol^{-1} at 298 K for the Haber equation.
2. **Convert and calculate.** $\ln K = 33000/(8.31 \times 298) = 13.3259\ldots$.
3. **Antilogarithm.** $K \approx 6.1 \times 10^{5}$; retain guard digits until exponentiating.

Decision

This is the activity-based K, not an unconverted gas concentration quotient.

AHL: Actual and standard Gibbs energy

1. **Supplied mixture.** $\Delta G^{\ominus} = +5.00$ kJ mol^{-1}; $Q = 0.0100$ at 298 K.
2. **Actual reaction energy.** $\Delta_r G = 5000 + (8.31)(298)\ln(0.0100) \approx -6404$ J mol^{-1}.
3. **Direction.** Actual $\Delta_r G < 0$: net forward change, despite a positive standard value.

Decision

At equilibrium actual reaction **Gibbs energy** is zero; the standard value need not be.

Exam tips

State ΔH or count gas molecules before predicting a shift.

- Never write that the concentrations are equal.
- For the fixed equation: temperature changes K; compression can change composition.
- AHL. Compare Q with K before giving a direction.
- AHL. ICE changes follow the mole ratio.

Check yourself

Try these

Write K_c for $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$.

Predict the colour change on warming a rigid N_2O_4/NO_2 gas cell.

Explain the choice of 450 °C for the Haber process.

AHL. 2.00 mol SO_2 + 1.00 mol O_2 in 1.00 dm^3 give 1.60 mol SO_3; find K_c.