09 Chemical Equilibria

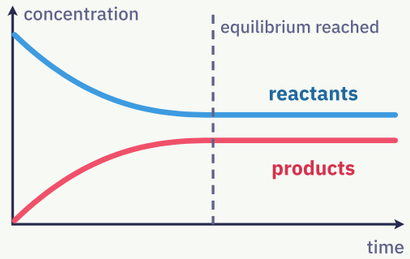


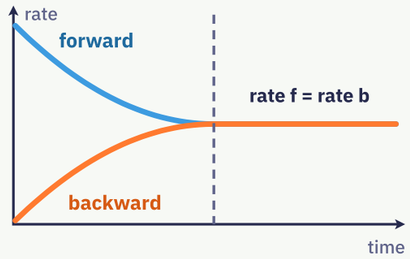
1 Dynamic Equilibrium

DEFINITION **Reversible reaction**: a reaction that takes place in both the _____ and _____ directions (⇌)

DEFINITION **Dynamic equilibrium**: the state in a reversible reaction where the rate of the forward reaction _____ the rate of the backward reaction, such that there is _____ in the concentrations of reactants and products, in a _____.

DEFINITION **Closed system**: no matter is lost to or gained from the surroundings





- At equilibrium, [reactants] and [products] are _____, but usually **not equal**, both reactions are still occurring
- The same equilibrium is reached whether we start from the reactants or the products
- In an open system, products _____, so the reaction goes to completion.

2 Equilibrium Constants

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

	Expression	Units	Use for
K_c	$\frac{[C]^c[D]^d}{[A]^a[B]^b}$	$(\text{mol dm}^{-3})^{(c+d)-(a+b)}$	species in solution or gas, as concentrations
K_p	$\frac{p_C{}^c\, p_D{}^d}{p_A{}^a\, p_B{}^b}$	$(\text{atm or Pa})^{(c+d)-(a+b)}$	_____, as partial pressures

- **Partial pressure**: $p_A = x_A \times p_{total}$, where the mole fraction $x_A = n_A \div n_{total}$
- **Heterogeneous** equilibria: leave out _____, _____ and the _____, as their concentrations are constant
- $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$: K_c = _____, K_p = _____

NOTE K is changed **only by temperature**. Concentration, pressure and catalysts do not change K. K says nothing about how **fast** equilibrium is reached.

Size of K	Position of equilibrium	Equilibrium mixture
$K \gg 1$	lies to the _____	mostly products
$K \ll 1$	lies to the _____	mostly reactants

3 Calculations with K

ICE table: Initial, Change, Equilibrium. Convert equilibrium moles to concentration (÷ V) or partial pressure before substituting into K.

I: initial amounts → **C: change, in mole ratio** → **E: equilibrium amounts** → **÷ V (or p) → into K**

3.1 Find K_c from equilibrium amounts

WORKED EXAMPLE

$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$

To make the ester ethyl ethanoate, 2.0 mol of ethanoic acid and 2.0 mol of ethanol are mixed. At equilibrium, 1.33 mol of water is present and the total volume is 0.500 dm^3. Find K_c.

	CH_3CO_2H	C_2H_5OH	ester	H_2O
I / mol	2.0	2.0	0	0
C / mol	_____	−1.33	+1.33	+1.33
E / mol	0.67	0.67	1.33	1.33

Divide each by 0.500 dm^3 to get concentrations:

$$K_c = \frac{(1.33/0.500)(1.33/0.500)}{(0.67/0.500)(0.67/0.500)} = \text{_____ (no units)}$$

Water is a product here, not the solvent, so it is included. V cancels, but working must still show concentrations.

3.2 Find K_p from initial partial pressures

WORKED EXAMPLE

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

In the Contact process, SO_2 (1.00 atm) and O_2 (0.50 atm) reach equilibrium in a vessel of fixed volume at 675 K. The total pressure at equilibrium is 1.01 atm. Find K_p.

- At fixed volume and temperature, partial pressure ∝ moles, so the ICE table can use **pressures**
- Let **x** atm of O_2 react: SO_2 falls by **2x**, and SO_3 rises by **2x** (mole ratio 2 : 1 : 2)

	SO_2	O_2	SO_3
I / atm	1.00	0.50	0
C / atm	−2x	−x	+2x
E / atm	_____	_____	_____

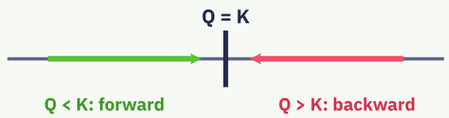
Total: $(1.00 - 2x) + (0.50 - x) + 2x = 1.01 \rightarrow x = 0.49$

$$K_p = \frac{p_{SO_3}{}^2}{p_{SO_2}{}^2\, p_{O_2}} = \frac{(0.98)^2}{(0.02)^2(0.01)} = \text{_____}$$

4 Le Chatelier's Principle

DEFINITION **Le Chatelier's Principle**: if a change is made to a system in dynamic equilibrium, the position of equilibrium shifts so as to _____ (minimise) that change and re-establish equilibrium.

- **$Q_c < K_c$**: too few products → _____ reaction favoured, POE shifts right
- **$Q_c = K_c$**: system is at _____, no net change
- **$Q_c > K_c$**: too many products → _____ reaction favoured, POE shifts left

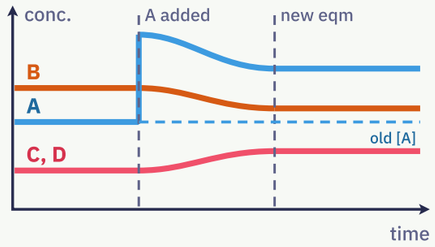


Q has the same expression as K but uses concentrations at any moment.

4.1 Concentration: $A + B \rightleftharpoons C + D$

Adding A

1. POE shifts _____ to consume some of the added A
2. Forward reaction is favoured
3. [A] ↓ (but stays higher than before), [B] ↓, [C] and [D] ↑
4. K_c _____

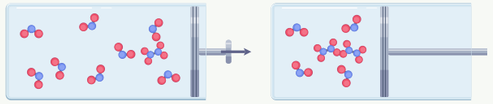


Removing a product, e.g. D: POE shifts right to produce more D.

4.2 Pressure: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

Decreasing volume (pressure ↑)

1. Pressure ↑ → POE shifts to the side with _____ _____ to reduce the pressure
2. 2 mol gas → 1 mol gas: POE shifts _____
3. Brown colour becomes _____ (after first darkening as all gases are compressed)



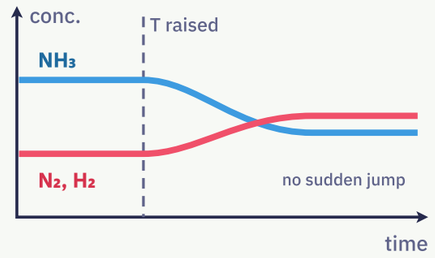
NOTE Special cases

- Equal moles of gas on both sides ($2HI \rightleftharpoons H_2 + I_2$): _____
- Inert gas at **constant volume**: partial pressures unchanged → no shift
- Inert gas at **constant pressure**: volume ↑, partial pressures ↓ → POE shifts to _____ gas particles

4.3 Temperature: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $\Delta H = -92$ kJ mol^{-1}

Increasing temperature

1. POE shifts _____
2. The _____ backward reaction is favoured to absorb the excess heat
3. [NH_3] ↓ → K_c _____

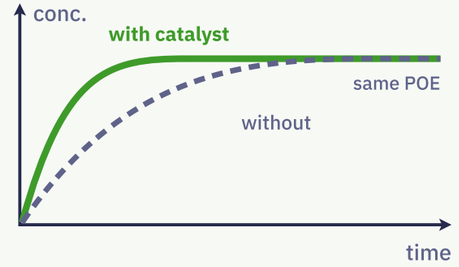


T ↑ favours the endothermic direction, T ↓ favours the exothermic direction. Only temperature changes K.

4 Le Chatelier's Principle (continued)

4.4 Catalyst

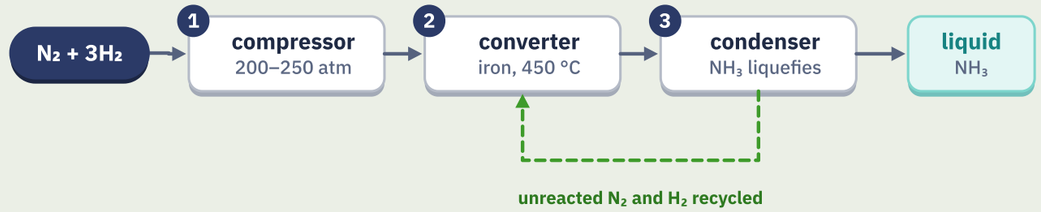
1. Rates of forward and backward reactions increase _____
2. E_a of both directions lowered by the same amount
3. k_f and k_b increase by the same factor
4. $K_c = \frac{k_f}{k_b}$ → no effect on POE or K
5. Equilibrium is only reached _____



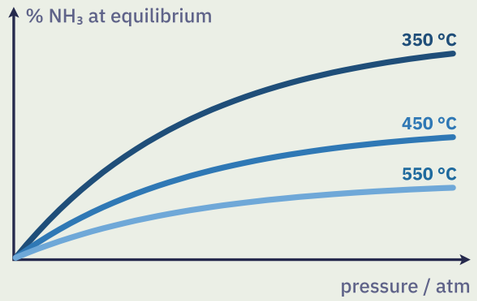
5 The Haber Process

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92$ kJ mol^{-1}

The plant



Yield of NH_3 at equilibrium



- Yield of NH_3 at equilibrium **rises with pressure** and **falls with temperature**
- 200–250 atm and about 450 °C are a _____ between yield, rate and cost

Temperature: _____

- Forward reaction exothermic: low T shifts POE right → higher yield
- But at low T, rate is too _____
- Moderate T: reasonable yield in a reasonable time

Pressure: _____

- 4 mol gas → 2 mol gas: high p shifts POE right → higher yield, also faster rate
- But very high p needs costly, thick-walled plant

Catalyst: _____

- Shortens the time to reach equilibrium, yield unchanged
- Cheaper than other catalysts (e.g. Ru)
- NH_3 is _____ _____ and removed: POE shifts right, unreacted N_2 and H_2 recycled