Equilibria:

$$A + B \longrightarrow C + D \qquad 30 \text{ Seconds}$$
$$A + B \longrightarrow C + D \qquad 90 \text{ Seconds}$$
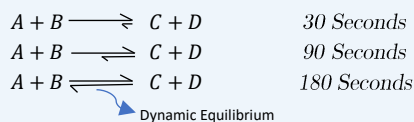$$A + B \rightleftharpoons C + D \qquad 180 \text{ Seconds}$$

Dynamic Equilibrium

Features of a dynamic equilibrium:
- **Rate of forward reaction** is **equal** to **rate of backward reaction.**
- Concentrations of reactants and products **remain constant** (not the same).
- Note: dynamic equilibria can only be achieved in a **closed system** i.e. nothing gets/ in /out of system.

Le Chataliers principle: states that when an established equilibrium is disturbed, the equilibrium shifts in the direction to reduce the disturbance.

Factors (disturbances) that affect position of equilibrium:
- Temperature
- Concentration/Pressure

Common terms used:
Equilibrium position shifts/lies to the right: more products than reactants.
Equilibrium position shifts/lies to the left: more reactants than products.

Effect of Temperature on Equilibrium

Increasing the temperature, the system would counteract this disturbance by shifting to reduce the temperature. This will **favour the endothermic reaction** (absorbs/uses heat energy thus decreasing temperature).

Decreasing the temperature, the system would counteract the disturbance by shifting to increase the temperature. This will **favour the exothermic reaction** (releases heat energy thus increasing temperature).

E.g.1 :

$$A + B \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} C + D \qquad\qquad \Delta H = -150 KJ/mol$$
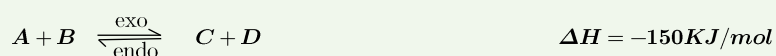
Increasing the Temperature:
- System tries to counteract by decreasing the temperature.
- This favours the endothermic reaction (reaction uses heat which reduces temp).
- Hence, equilibrium shifts to the left.

Decreasing the Temperature:
- System tries to counteract by increasing the temperature.
- This favours the exothermic reaction (releases heat which increases temp).
- Hence, equilibrium shifts to the right.

Effect of Pressure on Equilibrium

Increasing the pressure, the system counteracts this disturbance by shifting to decrease the pressure. This will favour the side with **fewer gaseous moles.**

Decreasing the pressure, the system counteracts this disturbance by shifting to increase the pressure. This will favour the side with **more gaseous moles.**

E.g.2 :

$$2A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)}$$

| 3 gaseous moles | 4 gaseous moles |
| Low Pressure | High Pressure |
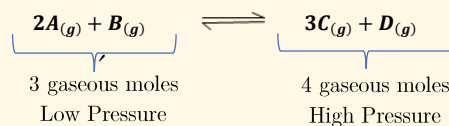
Increasing the Pressure:
- System tries to counteract by decreasing the Pressure.
- This favours the side with fewer gaseous moles.
- Hence, equilibrium shifts to the left.
- Yield of C+D decreases.

Decreasing the Pressure:
- System tries to counteract by increasing the Pressure.
- This favours the side with more gaseous moles.
- Hence, equilibrium shifts to the right.
- Yield of C+D increases.

Effect of Catalyst on Equilibrium

A catalyst has **no effect** on the position of the equilibrium but **speeds up the rate at which equilibrium is achieved**. It has no effect, as a catalyst will affect both the forwards and backward reaction equally.

Equilibrium Reactions in Industry

Haber Process

$$N_{2\,g} + 3H_{2\,g} \rightleftharpoons 2NH_{3\,g} \qquad\qquad \Delta H = -92 KJ/mol$$
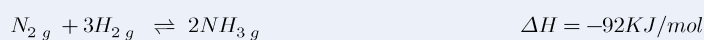
- Compromise conditions: 450°C, 200 atm, Fe Catalyst
- Compromise between yield and rate. Low temperatures provide higher yield, but slow rate. Higher pressures provide greater yield, however dangerous and expensive.

Hydration of Ethane to form Ethanol

$$C_2H_{4\,g} + H_2O_{(g)} \rightleftharpoons C_2H_5OH_{\,g} \qquad\qquad \Delta H = -46 KJ/mol$$
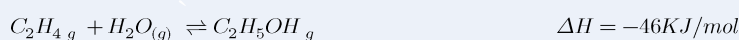
- Compromise conditions: 300°C, 65 atm, H_3PO_4 catalyst
- Low temperature provides higher yield, but rate is slow. High pressures causes ethene to polymerise (form polyethene), expensive and dangerous.

Production of Methanol

$$CO_{\,g} + H_{2(g)} \rightleftharpoons CH_3OH_{\,g} \qquad\qquad \Delta H = -91 KJ/mol$$
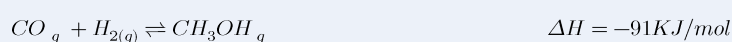
- Compromise Conditions: 230°C, 10 atm.

Equilibrium Constant

For a general equilibrium reaction such as the below:
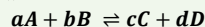
$$aA + bB \rightleftharpoons cC + dD \qquad where\ a, b, c, d = stochiometric\ ratio\ \ A, B = reactants\ \ C, D = products$$

The K_C expression can be derived as follows:

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{Products}{Reactants} \qquad\qquad where\ K_c = Equilibrium\ Constant$$

The equilibrium constant for a reaction indicates the position of the equilibrium at a given temperature. K_c is **only** affected by **temperature**.
The larger the equilibrium constant (K_c), the further the equilibrium lies to the right (product side) and vice versa.

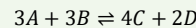### Deriving K_c Expressions and units.

E.g 1

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
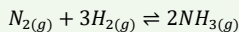
$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Units:

$$K_c = \frac{(moldm^{-3})^2}{(moldm^{-3})(moldm^{-3})^3} = \frac{(moldm^{-3})^2}{(moldm^{-3})^4} = \frac{1}{(moldm^{-3})^2}$$

$$K_c = mol^{-2}dm^6$$

E.g.2

$$3A + 3B \rightleftharpoons 4C + 2D$$

$$K_C = \frac{[C]^4[D]^2}{[A]^3[B]^3}$$

Units:

$$K_c = \frac{(moldm^{-3})^4(moldm^{-3})^2}{(moldm^{-3})^3(moldm^{-3})^3} = \frac{(moldm^{-3})^6}{(moldm^{-3})^6} = no\ units$$

Calculating Equilibrium Constants

Example 3

0.5 moles of Phosphorus Pentachloride was allowed to decompose in a vessel of 5dm³. At equilibrium 0.08 moles of Chlorine was present. Calculate K_C and units?

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial Moles	0.5		0		0
Reacted or Formed	-0.08		$+0.08$		$+0.08$
Equilibrium Moles	0.42		0.08		0.08
Equilibrium Conc($\frac{moles}{volume}$)	$\frac{0.42}{5} = 0.084$		$\frac{0.08}{5} = 0.016$		$\frac{0.08}{5} = 0.016$

Initially moles of product will be 0, as at time=0.

1 mol of Chlorine formed in the equation which represents 0.08 mol.

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.016 \text{ x } 0.016}{0.084} = 3.05 \text{ x}10^{-3}\ moldm^{-3}$$

Example 4

0.6 moles of Dinitrogen tetroxide wass allowed to decompose in a vessel of 5dm³. At equilibrium 25% of the dinitrogen tetroxide had decomposed.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial Moles	0.6		0
Reacted or Formed	-0.15		$+0.30$
Equilibrium Moles	0.45		0.30
Equilibrium Conc $\left(\frac{moles}{volume}\right)$	$\frac{0.45}{5} = 0.09$		$\frac{0.30}{5} = 0.06$

Calculations:
1) Moles of N_2O_4 decomposed: 25% of 0.6 moles= 0.15 moles.
2) 1 mol of N_2O_4 reacted= 0.15 moles.
3) 2 moles of NO_2 formed= 2 x 0.15= 0.30

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.06)^2}{0.09} = 0.04\ moldm^{-3}$$