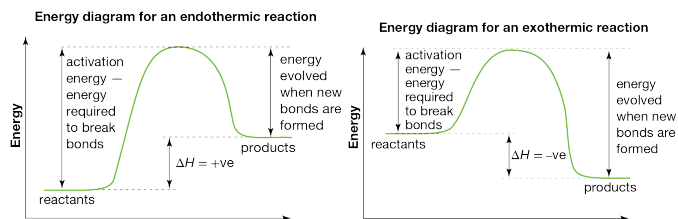# Rates and Equilibria

Energy

Enthalphy

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Endothermic (products > reactants, $\Delta H > 0$)
**Exothermic** (reactants > products, $\Delta H < 0$)

Activation energy E_A

$$E_A = E_{\text{max}} - E_{\text{initial}}$$

- Energy always needed to initiate reaction (break bonds of reactants)
- Reactant particles must collide at correct angle, energy etc
- Most collisions are not fruitful
- Energy must be greater than or equal to E_A

Kinetic energy

- **Temperature** - measure of *avg* kinetic energy of particles. Over time each particle will eventually have enough energy to overcome E_A
- Note same distribution indicates same temperature
- ↑ rate with ↑ T mainly caused by ↑ E_K ⟹ greater collision force
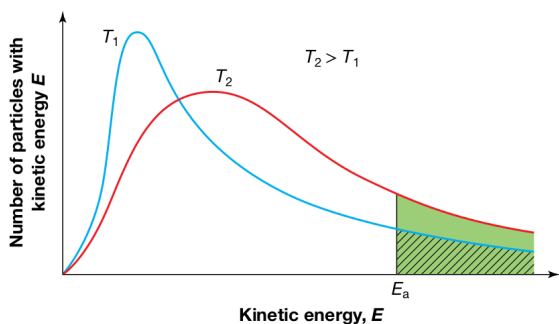
Rates

Ways to increase rate of reaction:

1. Increase surface area
2. Increase concentration/pressure
3. Increase temperature

Catalysts

- alternate reaction pathway, with lower E_A
- increased rate of reaction
- involved in reaction but regenerated at end
- does not alter K_c or extent of reaction
- attracts reaction products
- removal/addition of catalyst does not push system out of equilibrium

Homogenous catalyst: same state as reactants and products, e.g. Cl* radicals.
Hetrogenous catalyst: different state, easily separated. Preferred for manufacturing.
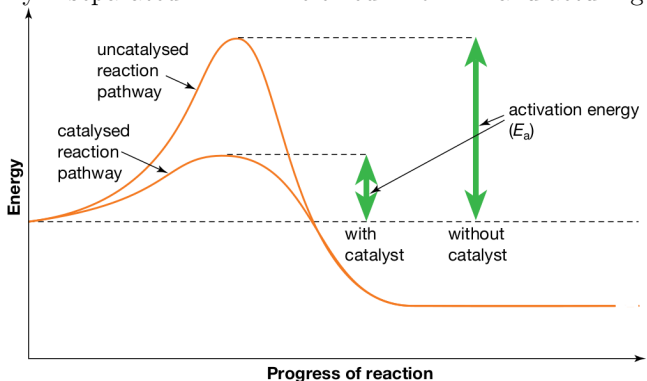
- Many catalysts involve transition elements
- **Solid catalysts** - particles around catalyst with high surface energy *adsorb* gas molecules, lowering E_A
- **Haber process** (ammonia production) - enzymes are catalysts for one reaction each. Adsorption (bonding on surface) forms ammonia NH_3.

Equilibrium systems

Equilibrium - the stage at which quantities of reactants and products remain unchanged

Reaction graphs - exponential/logarithmic curves for reaction rates with time (simultaneous curves forward/back)

	Complete reaction - all reactant becomes product
	Incomplete reaction - goes both ways and reaches equilibrium

- All reactions are equilibrium reactions, but extent of backwards reaction may be negligible
- Double arrow indicates equilibrium reaction
- At equilibrium, rate of forward reaction = rate of back reaction.

- Approaching equilibrium, forward rate > back rate

Equilibrium constant K_c

For $\alpha A + \beta B + ... \rightleftharpoons \chi X + \psi Y + ...$:

$$K_c = \frac{[\text{X}]^\chi \cdot [\text{Y}]^\psi \cdot ...}{[\text{A}]^\alpha \cdot [\text{B}]^\beta \cdot ...}$$

More generally, for reactants $n_i R_i$ and products $m_i P_i$:

$$K_c = \frac{\prod\limits_{i=1}^{|P|} [P_i]^{m_i}}{\prod\limits_{i=1}^{|R|} [R_i]^{n_i}} \mid i \in \mathbb{N}^*$$

Indicates extent of reaction
If value is high ($> 10^4$), then [products] > [reactants]
If value is low ($< 10^4$), then [reactants] > [products]

- **K_c depends on direction that equation is written (L to R)**
- If K_c is small, equilibrium lies *to the left*
- aka *equilibrium expression*
- For reverse reaction, use $K_c' = \frac{1}{K_c}$
- For coefficients, use $K_c' = K_c^n$

Reaction constant (quotient) Q

Proportion of products/reactants at a give time (specific K_C). If $Q = K_c$, then reaction is at equilibrium.

Le Châtelier's principle

> Any change that affects the position of an equilibrium causes that equilibrium to shift, if possible, in such a way as to partially oppose the effect of that change.

Changing volume / pressure

1. $\Delta V < 0 \implies [\Sigma\text{particles}] \uparrow$, therefore system reacts in direction that produces less particles
2. $\Delta V > 0 \implies [\Sigma\text{particles}] \downarrow$, therefore system reacts in direction that produces more particles
3. $n(\text{left}) = n(\text{right})$ (volume change does not disturb equilibrium)

Changing temperature

Only method that alters K_c.

Changing temperature changes kinetic energy. System's response depends on whether reaction is exothermic or endothermic.

- Exothermic - increase temp decreases K_c
- Endothermic - increase temp increases K_c

Time-concentration graph: smooth change

Changing concentration

- Decreasing "total" concentration of system causes a shift towards reaction which produces more particles

Yield

$$\text{yield } \% = \frac{\text{actual mass obtained}}{\text{theoretical maximum mass}} \times 100$$

- Yield may be lower than expected due to equilibrium reaction (incomplete)
- $\uparrow$ yield $\equiv$ forward rxn; $\downarrow$ yield $\equiv$ back rxn
- *Rate-yield conflict*: rxn is slower at eq. point further to RHS
- This is ameliorated by catalysts, high pressure and removal of product

Acid/base equilibria

Strong acid: $\text{HA} \longrightarrow \text{H}^+ + \text{A}^-$
Weak acid: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

For weak acids, dilution causes increase in % ionisation.
$\therefore [\text{HA}] \propto 1 \div \%$ ionisation
(see 2013 exam, m.c. q20)

$$\% \text{ ionisation} = \frac{[\text{H}^+]}{[\text{HA}]} \times 100$$

When a weak acid is diluted:

- amount of H_3O^+ increases
- equilibrium shifts right
- overall $[\text{H}_3\text{O}^+]$ decreases
- therefore pH increases