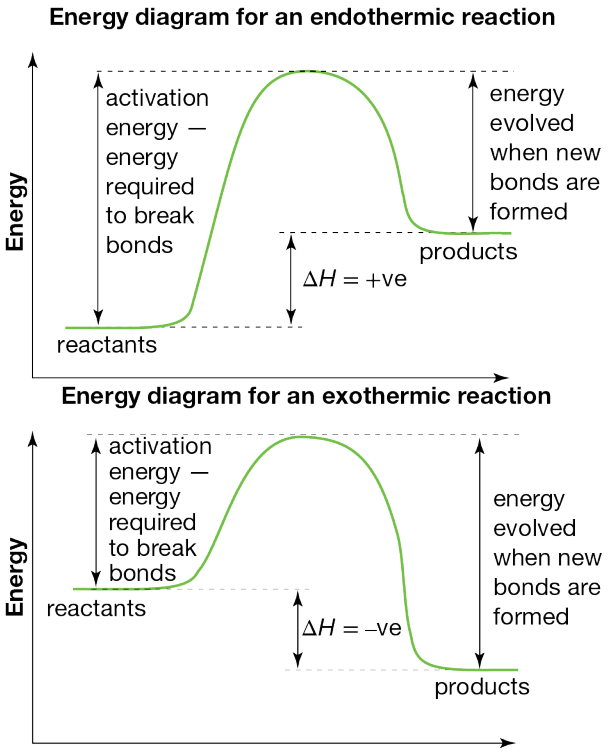
Rates and Equilibria

Energy profile diagrams

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

- 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

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

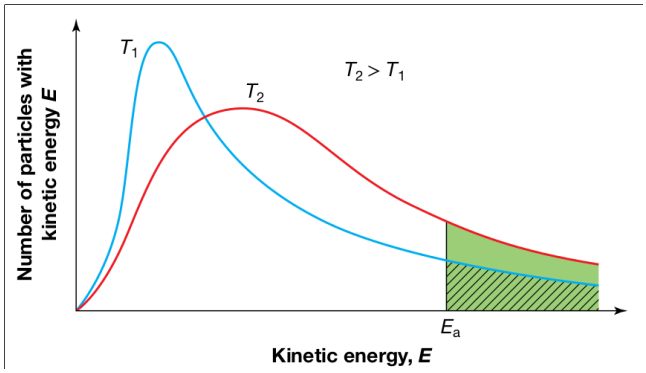


Ways to increase rate of reaction:

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

Kinetic energy

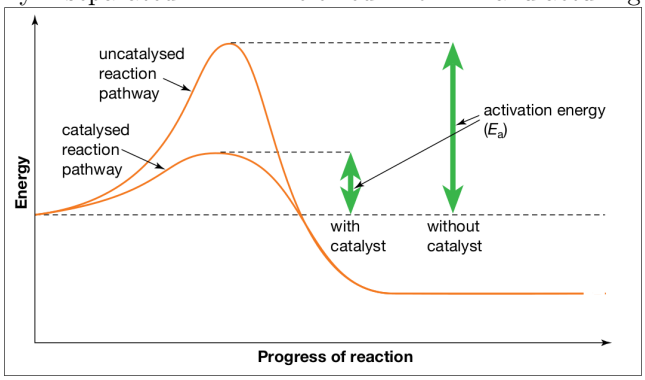
Temperature - measure of *avg* kinetic energy of particles. Over time each particle will eventually have enough energy to overcome E_A.
Note same distribution indicates same temperature.



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.

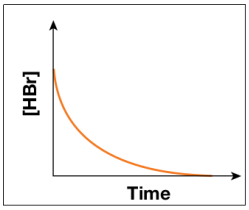


Many catalysts involve transition elements.
Haber process (ammonia producition) - enzymes are catalysts for one reaction each. Adsorption (bonding on surface) forms ammonia NH_3

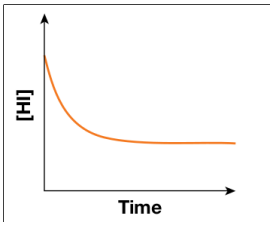
Equilibrium systems

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.

States (not in course)

- **Homogeneous** - all states are the same
- **Heterogeneous** - states are different

Equilibrium constant K_c

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

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

More generally, for reactants $n_i\mathrm{R}_i$ and products $m_i\mathrm{P}_i$:

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

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*

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. $\Delta V < 0 \implies$ [Σparticles] ↑, therefore system reacts in direction that produces less particles
2. $\Delta V > 0 \implies$ [Σparticles] ↓, therefore system reacts in direction that produces more particles
3. n(left) = n(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

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

Acid/base equilibria

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

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

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

When a weak acid is diluted:

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