

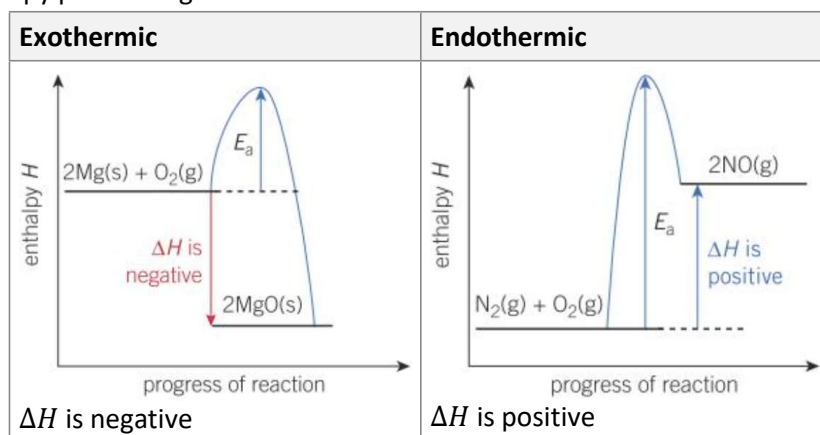
## 3.2 Physical chemistry

### 3.2.1 Enthalpy changes

- Definitions

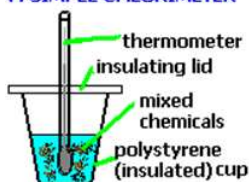
Term	Definition
<b>Enthalpy / <math>H</math></b>	Measure of heat energy in a chemical system
<b>Chemical system</b>	The atoms, molecules or ions making up the chemicals
<b>Activation energy / <math>E_a</math></b>	The minimum energy required for a reaction to take place
<b>Standard state</b>	The physical state of a substance under standard conditions
<b>Enthalpy change of reaction / <math>\Delta_r H</math></b>	The enthalpy change associated with a stated equation in the <b>molar quantities shown in a chemical equation</b>
<b>Enthalpy change of formation / <math>\Delta_f H</math></b>	The enthalpy change that takes place when <b>1 mole of a compound</b> is formed from its elements
<b>Enthalpy change of combustion / <math>\Delta_c H</math></b>	The enthalpy change that takes place when <b>1 mole of a substance</b> reacts completely with oxygen (complete combustion)
<b>Enthalpy change of neutralisation / <math>\Delta_{\text{neut}} H</math></b>	The enthalpy change that accompanies the reaction of an acid by a base to form <b>1 mole of <math>\text{H}_2\text{O}_{(l)}</math></b>
<b>Enthalpy change of solution / dissolution</b>	The enthalpy change when <b>1 mole of a substance</b> is completely dissolved in water
<b>Hess's Law</b>	The enthalpy change in a chemical reaction is independent of the route it takes

- (standard ... = under standard conditions : 298 K & 100 kPa, with all reactants and products in their standard states)
- Enthalpy change
  - $\Delta H = H(\text{products}) - H(\text{reactants})$
  - Can be positive (endothermic) or negative (exothermic)
- Conservation of energy
  - When a chemical reaction involving an enthalpy change takes place heat energy is transferred between the system and the surroundings
    - System = chemicals
    - Surroundings = apparatus, lab, etc. (everything that is not the system)
    - universe = system + surroundings
- Types of reactions
  - Exothermic reaction
    - Energy transferred from the system to the surroundings
  - Endothermic reaction
    - Energy transferred from the surroundings to the system
- Enthalpy profile diagrams

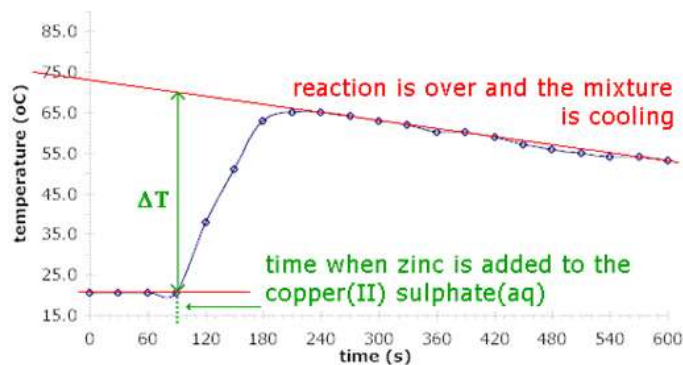


- \* The activation energy can normally be omitted when there are > 1 energy changes
- Standard conditions
  - Shown with symbol  $\ominus / ^\circ$
  - Standard pressure = **100 kPa /  $1 \times 10^5 \text{ N m}^{-2}$  / 1 atm**
  - Standard temperature = **298 K / 25 °C**
  - Standard concentration = **1 mol dm<sup>-3</sup> / 1 M**
  - Substances will be in their **normal physical states**
- Measuring energy changes
  - Use the equation  $q = mc\Delta T$
  - Energy change for the **system** =  $-q$
- Determine enthalpy change of combustion
  - Measure certain volume of water, pour water into beaker
  - Record initial temperature of water using a thermometer
  - Add fuel to spirit burner + weigh spirit burner and fuel together
  - Place spirit burner under beaker + light the burner
  - Stir water with thermometer
  - Extinguish flame after about 3 mins
  - Immediately record water temperature
  - Re-weigh spirit burner
  - Work out the mass of fuel burnt hence the amount of fuel burnt in moles
  - Work out energy change with  $q = mc\Delta T$
  - Enthalpy change of combustion =  $-\frac{q}{n}$
- Reasons for inaccuracies
  - Heat loss to surroundings  $\rightarrow$  less exothermic than expected
  - Incomplete combustion fuel (black layer soot on calorimeter)  $\rightarrow$  less exothermic than expected
  - Non-standard conditions  $\rightarrow$  more or less exothermic than expected
  - Evaporation of fuel
    - Less exothermic
    - Seems to have used more fuel than actual
    - Weigh the spirit burner before
    - Extinguish the spirit burner ASAP after the experiment
- Determine enthalpy change of reaction
  - Carry out reaction in polystyrene cup with thermometer clamped so that it stands in it
  - Surroundings = the reaction solution (may assume density and specific are close to those of water)
  - Enthalpy change of neutralisation
    - Make one reactant excess so the amount of water formed is fixed
    - In theory all acid and alkali should **release the same amount of energy** but in reality it isn't due to the different strengths of acid / alkali species

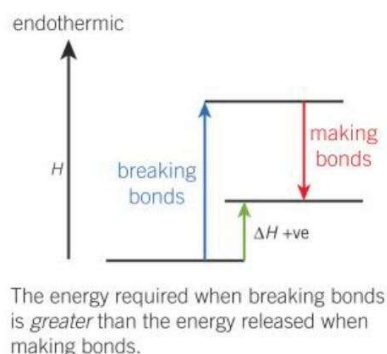
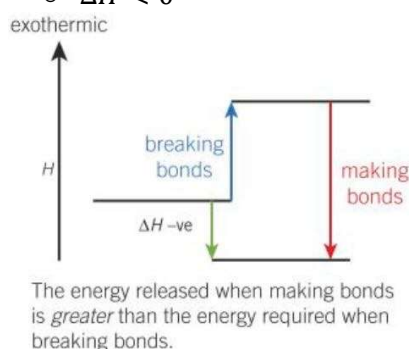
A SIMPLE CALORIMETER



- Cooling curve correction
  - Add one reactant to the polystyrene cup
  - Take temperature of the solution every 30s until temperature stays constant
  - Add the other reactant + stir
  - Measure temperature every 30s until temperature has fallen for several mins
  - Plot a graph of temperature against time
  - Extrapolate cooling curve section back to when second reactant added
  - Find the theoretical  $\Delta T$  at that point of time



- Average bond enthalpy
  - The enthalpy change when **1 mole** of a bond is broken in the **gas state**
  - Limitations: actual bond enthalpy can vary depending on the chemical environment of the bond
- Endothermic / exothermic
  - Endothermic
    - Bond breaking is endothermic
    - More energy required when breaking bonds than energy released when making bonds
    - $\Delta H > 0$
  - Exothermic
    - Bond formation is exothermic
    - More energy released when making bonds than energy required when breaking bonds
    - $\Delta H < 0$



- Calculating enthalpy change from average bond enthalpies
  - $\Delta_r H = \Sigma(\text{bond enthalpies in reactants}) - \Sigma(\text{bond enthalpies in products})$
- Hess's Law
  - Working out enthalpy change using Hess's Law
    - Using enthalpy change of formation:  $\Delta_r H = \Sigma \Delta_f H \text{ products} - \Sigma \Delta_f H \text{ reactants}$
    - Using enthalpy change of combustion:  $\Delta_r H = \Sigma \Delta_c H \text{ reactants} - \Sigma \Delta_c H \text{ products}$

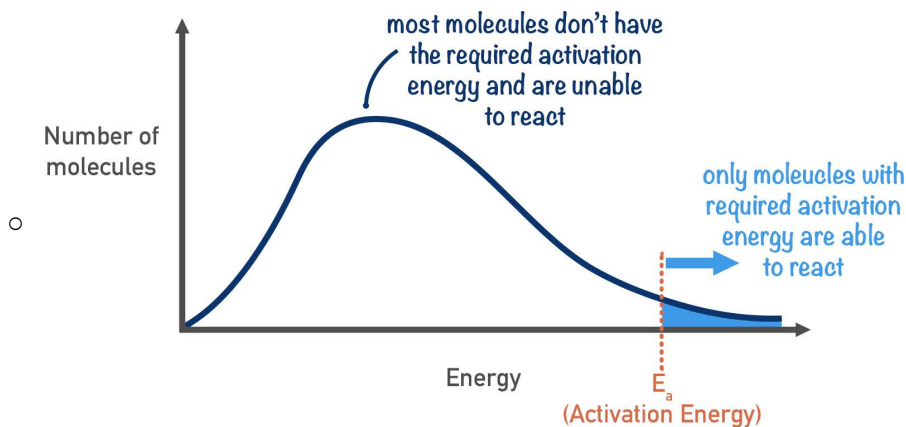
### 3.2.2 Reaction rates

- Definitions

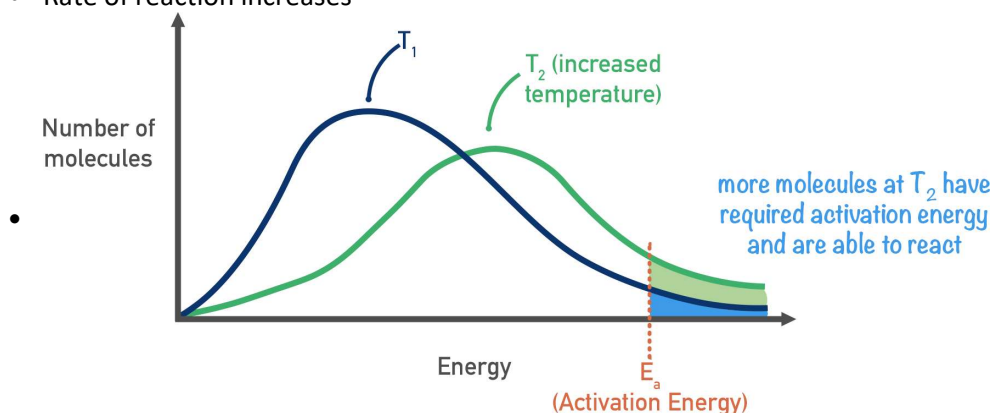
Term	Definition
• <b>Intermediate</b>	A species formed during a reaction that reacts further and is not present in the final products

- Rate of reaction
  - Measures how fast a reactant is being used up / a product is being formed
  - $\text{rate} = \frac{\text{change in concentration}}{\text{time}}$  (units =  $\text{mol dm}^{-3} \text{s}^{-1}$ )
- The collision theory
  - Two reacting particles must **collide** with the **correct orientation** and have **sufficient energy** to overcome the activation energy barrier of the reaction
  - Most collisions between particles are unsuccessful and **do not** result in a chemical reaction
- Effect of change in concentration / pressure on rate of reaction
  - Increase concentration / pressure = increase in rate of reaction

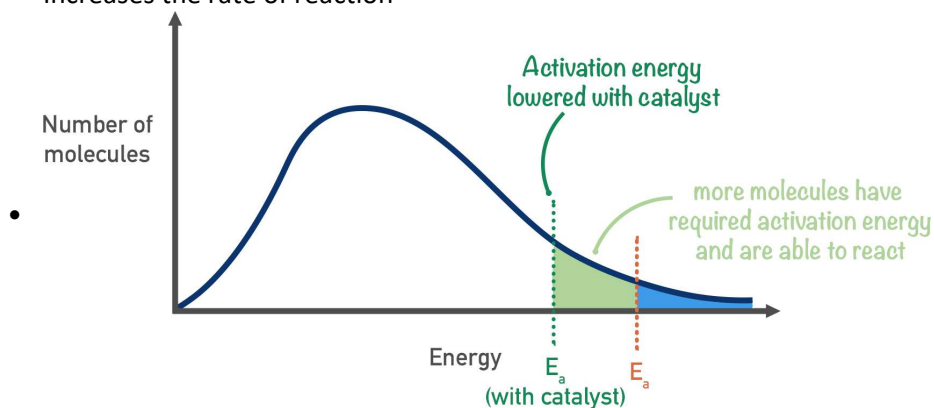
- Increases the number of particles in the same volume
  - The particles are closer together and collide **more frequently**
  - In a given period of time** there will be **more effective collisions**
  - (The proportion of collisions that are successful does not change)
- Measuring rates of reaction by amount of gas produced
  - Reactant added to conical flask + bung replaced
  - Initial volume of gas recorded
  - Catalyst added + bung replaced, start stopwatch
  - Volume of gas recorded at regular intervals until reaction is complete (no more gas produced)
  - Graph of total volume of gas produced against time plotted
  - Gradient of tangent at  $t = 0$  is the initial rate
- Measuring rates of reaction by mass loss
  - Add reactants to conical flask on a balance
  - Mass is recorded initially & at regular intervals until no more mass lost
  - Plot a graph of mass against time
  - Gradient of tangent at  $t = 0$  is the initial rate
- Catalyst
  - Increases the rate of reaction without being used up by the overall reaction
  - Allowing a reaction to proceed via a different route with **lower activation energy**
  - May react with a reactant to form an intermediate or provide a surface on which the reaction can take place
- Types of catalysts
  - Homogenous
    - The catalyst is in the **same physical state** as the reactants
  - Heterogeneous
    - The catalyst is in a **different physical state** from the reactants
- Economic importance of catalysts
  - Obtain industrial products faster
    - Increase profit
  - Operate industrial processes at lower temperatures and pressures
    - Reduce the amount of energy needed
    - Less electricity / fossil fuels used
- Problems of catalysts
  - Catalysts do not last forever and need to be replaced periodically
    - Waste need to be disposed of responsibly
    - Many catalysts are toxic and need to be disposed of very carefully to prevent damage to the environment
- Boltzmann distribution
  - Not all molecules in a substance have the same amount of energy
  - Particles to the right of the  $E_a$**  have enough energy to react
  - Distribution graph
    - Area under curve = total number of molecules
    - Peak = most probable energy of a molecule
    - No molecules have zero energy (**graph starts at origin**)
    - No maximum energy for a molecule (**the curve does not meet the x-axis at high energy**)
    - The shape is **positively skewed**



- Effect of change in temperature on Boltzmann distribution
  - Graph: higher temperature = lower peak, peak shifted to the right
  - Larger area to the right of  $E_a \rightarrow$  More molecules have energy  $\geq E_a$**  (major effect)
  - A greater proportion of collisions will lead to a reaction
  - More frequent collisions as the molecules gain more KE and are moving faster (minor effect)
  - Rate of reaction increases



- Effect of catalyst on Boltzmann distribution
  - Larger area to the right of  $E_a \rightarrow$  a greater proportion of molecules now have an energy  $\geq$  the lower activation energy
  - A greater proportion of collisions will lead to a reaction
  - Increases the rate of reaction



### 3.2.3 Chemical equilibrium

- Definitions

Term	Definition
Dynamic equilibrium	When the rates of forward and backward reactions are equal

- Dynamic equilibrium conditions
  - In a **closed system** for **reversible reactions**
  - The rate of the forward reaction is equal to the rate of the reverse reaction
  - The amount of reactants and products are constant

- Effect of concentration changes on position of equilibrium
  - Increase in concentration of reactants / decrease in concentration of products
    - Rate of forward reaction increases
    - Equilibrium shifts to the right, more products formed
  - Increase in concentration of products / decrease in concentration of reactants
    - Rate of backward reaction increases
    - Equilibrium shifts to the left, more reactants formed
- Effect of changes in temperature on position of equilibrium
  - Increase in temperature
    - Favours the endothermic reaction
  - Decrease in temperature
    - Favours the exothermic reaction
  - (Equilibrium shifts to ..., there are more ..., less ..., the yield ...)
  - \* Forward and backward reactions have the same magnitude of enthalpy change but opposite signs
- Effect of changes in pressure on position of equilibrium
  - Increasing the pressure
    - ... is favoured because it reduces the number of moles of gas in the mixture (fewer moles of gas on that side)
    - Shift the position of equilibrium to side with fewer moles of gas
    - Reduces the pressure of the system
  - Decreasing the pressure
    - ... is favoured because it increases the number of moles of gas in the mixture (more moles of gas on that side)
    - Shift the position of equilibrium to side with more moles of gas
    - Increases the pressure of the system
- Effect of catalyst on equilibrium
  - Increases the rate of both forward and reverse reactions in an equilibrium **by the same amount**
  - **Do not** change the position of equilibrium
  - Allow equilibrium to be **achieved faster**
- Investigating changes in position of equilibrium
  - Observe colour change
  - Change in concentration
    - Add more reactants / products to the mixture
  - Change in temperature
    - Heat using boiling water bath
    - Cool using iced water
- Haber process
  - $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$  (Forward = exothermic)
  - Lower temperature
    - Higher yield of product
    - Rate may be too slow that equilibrium may not be established
    - Not used
  - High pressure
    - Increases yield & forces molecules closer together
    - Increases concentration + reaction rate
    - Requires very strong container + large quantity of energy → higher cost
    - Failure of steelwork / seals could lead to hot gases (including toxic ammonia) leaking → endangering the workforce and the surrounding area → safety concerns
  - Operate under compromise conditions of 400-500°C, 100-200 atm and iron catalysts
    - Gives a reasonable rate without shifting the equilibrium position too far away from ammonia and back to the reactants
    - Iron catalyst: increases the rate so lower temperatures can be used and operating cost is lowered
    - Only about 15% of the reactants is converted to ammonia, but  $\text{H}_2$  and  $\text{N}_2$  are recycled

repeatedly so nearly all reactants are eventually converted

- Industrial process conditions
    - Lower temperature / pressure: rate might be too slow
    - Higher temperature / pressure: safety risk / high cost / high energy use
  - The equilibrium constant /  $K_c$ 
    - For reaction  $aA + bB \rightleftharpoons cC + dD$
    - $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
    - $[\ ]$  = concentration of ...
    - $[A]$ ,  $[B]$ ,  $[C]$ ,  $[D]$  = equilibrium concentration of the reactants and products of this equilibrium
    - **Only solutions** should appear in the equation for  $K_c$ 
      - Include liquid if they have a similar amount to the solutions
  - Value of  $K_c$ 
    - $< 1$ 
      - Position of equilibrium is towards the LHS
      - Greater concentration for reactants
    - $= 1$ 
      - Position of equilibrium is halfway between reactants and products
    - $> 1$ 
      - Position of equilibrium is towards the RHS
      - Greater concentration for products
  - Effect of temperature change on  $K_c$ 
    - Forward reaction is exothermic
      - $K_c$  decreases when temperature increases
    - Forward reaction is endothermic
      - $K_c$  increases when temperature increases
- \* If the direction of reaction is not specified take it as the forward reaction by default