Intensive note (Topic 13: Industrial chemistry)

Synthetic products

Raw materials → (chemical processes) → Bulk chemicals → (chemical processes) → Synthetic products

Example 1	N_2, H_2	NH_3	NH_4NO_3, $(NH_4)_2SO_4$ fertilizer
Example 2	*Petroleum	Polyethene, nylon, polyester, aspirin	Plastics, shoes, cloths, drugs
Example 3	D-glucose	L-ascorbic acid	^Vitamin C tablets

* Detergent is also a synthetic product made from petroleum

^ Vitamin C can also be obtained from natural sources (fruits). It is still necessary to synthesize vitamin C in industry as it solves the problems of inadequate supply of vitamin C from natural sources.

Rate law

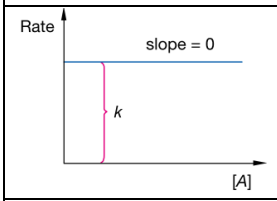
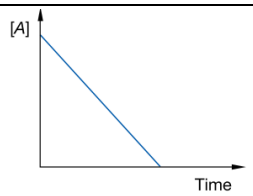
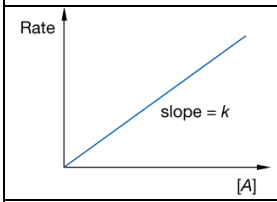
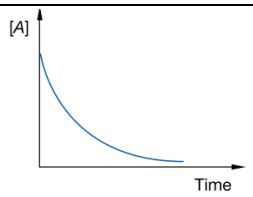
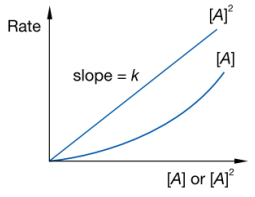
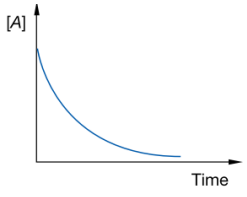
Consider the following reaction

$$A(g) + 2B(g) \rightarrow C(g) + 2D(g)$$

Rate equation of the above reaction can be expressed as:

$$\text{Rate} = \mathbf{k}[A(g)]^{\mathbf{a}}[B(g)]^{\mathbf{b}}$$

- [A(g)] is the concentration of reactant A while [B(g)] is the concentration of reactant B.
- **a** is the order of reaction with respect to A(g) while **b** is the order of reaction with respect to B(g). They specify the relationships between the concentrations of reactants A and B and the rate of reaction.
- The values of **a** and **b** are determined experimentally. (**a** and **b** can be any integers or fractions)
- The values of a and b are NOT necessarily equal to the stoichiometric coefficients. (i.e. **a** may not be 1 and **b** may not be 2)
- **k** is the rate constant of the reaction. It is a fixed value at a constant temperature. It usually increases with time.
- The overall order of the reaction is the sum of the powers on the concentration terms in the rate equation. (i.e. **a** + **b**)

<table>
<tr><th colspan="4">Zeroth order reaction (Rate = k)</th></tr>
<tr><td> 
</td><td>Rate is independent of [A]
y-intercept = k
Unit of k = mol dm^{-3} s^{-1}</td><td> 
</td><td>[A] decreases uniformly over time. This shows that rate is independent of [A]
Slope = rate of reaction</td></tr>
<tr><th colspan="4">First order reaction (Rate = k[A])</th></tr>
<tr><td> 
</td><td>From the graph, it is a straight line passes through origin.
This shows that rate is directly proportional to [A]
Slope = k
Unit of k = s^{-1}</td><td colspan="2"> 
</td></tr>
<tr><th colspan="4">Second order reaction (Rate = k[A]^2)</th></tr>
<tr><td> 
</td><td>For rate vs [A], it is a parabolic curve passing through origin.
For rate vs [A]^2, it is a straight line passes through origin. This shows that rate is directly proportional to [A]^2
Slope = k (for Rate vs [A]^2)
Unit of k = mol^{-1} dm^3 s^{-1}</td><td colspan="2"> 
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Determining rate equations by method of initial rate

3 trials of an experiment were performed under the same experimental conditions to study the kinetics of the following reaction:

$$2A(aq) + 2B(aq) \rightarrow 2C(aq) + D(aq)$$

Trial	Initial [A(aq)] / mol dm^{-3}	Initial [B(aq)] / mol dm^{-3}	Initial rate of formation of D(g) / mol dm^{-3} s^{-1}
1	0.0836	0.202	0.26×10^{-4}
2	0.0836	0.404	1.04×10^{-4}
3	0.0418	0.404	0.52×10^{-4}

(a) Deduce the order of reaction with respect to A(aq) and that with respect to B(aq).

Answer: Let the rate equation be: Rate = $k[A(aq)]^x[B(aq)]^y$. By substituting the given data into the rate equation,

$0.26 \times 10^{-4} = k(0.0836)^x(0.202)^y$ ..... (1)

$1.04 \times 10^{-4} = k(0.0836)^x(0.404)^y$ ..... (2)

$0.52 \times 10^{-4} = k(0.0418)^x(0.404)^y$ ..... (3)

Dividing (1) by (2),

$$\frac{0.26 \times 10^{-4}}{1.04 \times 10^{-4}} = \left(\frac{0.202}{0.404}\right)^y$$

$$y = 2$$

Therefore the order of reaction with respect to B is 2.

Dividing (2) by (3),

$$\frac{1.04 \times 10^{-4}}{0.52 \times 10^{-4}} = \left(\frac{0.0836}{0.0418}\right)^x$$

$$x = 1$$

Therefore the order of reaction with respect to A is 1.

Alternatively

From trial 1 and 2, at the same initial concentration of [A(aq)], the initial rate increases by a factor of 4 when [B(aq)] is doubled. Therefore the order of reaction with respect to B is 2.

From trial 2 and 3, at the same initial concentration of [B(aq)], the initial rate decreases by a factor of 2 when [A(aq)] is halved. Therefore the order of reaction with respect to A is 1.

(b) Calculate the rate constant at the experimental temperature.

Answer: Rate = $k[A(aq)][B(aq)]^2$. Substitute the results of Trial 1 into the rate equation,

$(0.26 \times 10^{-4}) = k(0.0836)(0.202)^2$

$k = 7.6 \times 10^{-3}$ mol^{-2} dm^6 s^{-1}

Unit of k: [mol dm^{-3} s^{-1}] = k[mol dm^{-3}][mol dm^{-3}]^2 k = mol^{-2} dm^6 s^{-1}

(c) Explain why 'method of initial rate' is commonly used in the study of the kinetics of a reaction

Answer: As initial concentrations of reactants are all known.

Reaction between $Na_2S_2O_3$ and dilute acid

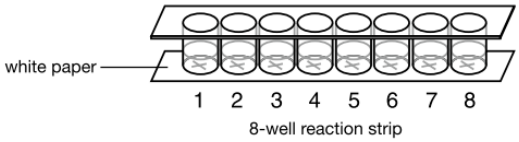
Consider the reaction between sodium thiosulphate ($Na_2S_2O_3$) and dilute sulphuric acid (H_2SO_4)

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l) + S(s)$$

An 8-well reaction strip was used in the experiment. Different wells of the reaction strip were filled with different contents according to the table below.

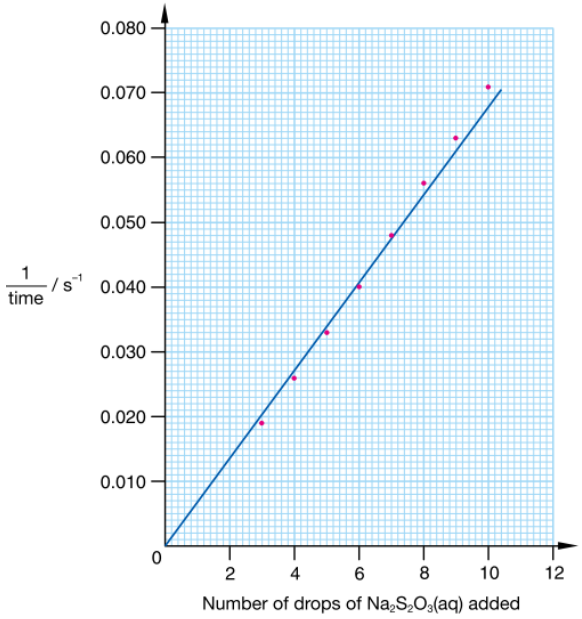
Well number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
No. of drops of 0.15 M $Na_2S_2O_3$(aq)	10	9	8	7	6	5	4	3
No. of drops of 1.0 M H_2SO_4(aq)	2	2	2	2	2	2	2	2
No. of drops of H_2O(l)	0	1	2	3	4	5	6	7
Time taken for the cross to be 'blotted out' by the S(s) / s	14	16	18	21	25	30	38	52

- Different numbers of drops of distilled water added to the wells of reaction strip. This can make the total volume of the reaction mixture the same in all wells for fair comparisons.
- The above reaction produces a creamy yellow precipitate of S(s). The solution turns turbid and reduces the amount of light transmitted through the solution.
- The cross under the 8-well reaction strip will disappear from our vision as enough S(s) forms to 'blot out' the cross



- As the total volume of solution was the same in all the wells, the initial concentration of $S_2O_3^{2-}(aq)$ was proportional to the number of drops of the solution added.
- $[H^+(aq)]$ is much greater than $[S_2O_3^{2-}(aq)]$ in each trials. This can ensure that $[H^+(aq)]$ was more or less constant throughout the reaction, and $[S_2O_3^{2-}(aq)]$ would be the only factor to be varied in the experiment.

Experimental results:



- The faster the reaction, the shorter is the time taken to 'blot out' the cross. As the formation of a very small amount of sulphur is sufficient to blot out the cross, the initial rate can be expressed as

$$\textbf{initial rate} \propto \frac{1}{\text{time taken to 'blot out' the cross}}$$

- As the graph gives a straight line passing through the origin, the reaction is first order with respect to $S_2O_3^{2-}(aq)$.
- Since $[H^+(aq)]$ is much higher than $[S_2O_3^{2-}(aq)]$, the rate law can be written as rate = $k'[S_2O_3^{2-}(aq)]$, where $k' = k[H^+(aq)]$

Determining rate equations by log[initial rate] vs log[initial concentration] graph

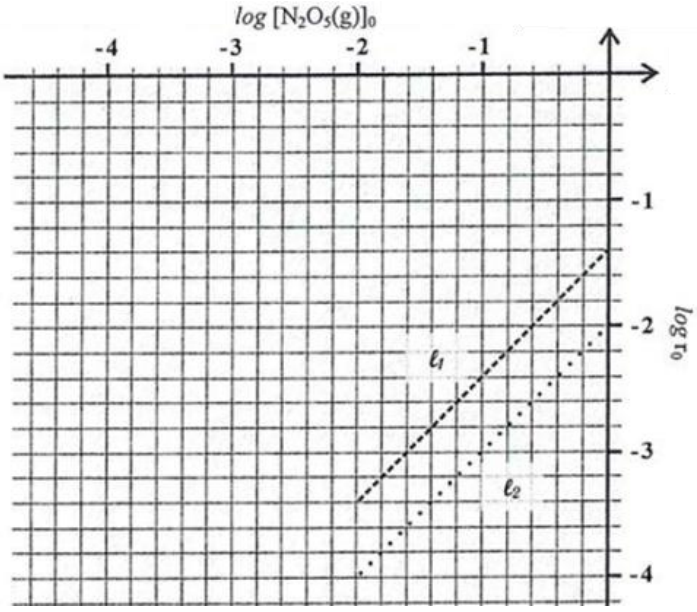
Example 1

Two sets of experiments were performed to study the chemical kinetics of the decomposition of $N_2O_5(g)$:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

For each set of the experiments, the variation of log r_0 with log $[N_2O_5(g)]_0$ was plotted and both of them got a straight line as shown in the graph below:

	Representing	Unit
$[N_2O_5(g)]_0$	Initial concentration of $N_2O_5(g)$	mol dm^{-3}
r_0	Initial rate of decomposition of $N_2O_5(g)$	mol dm^{-3} s^{-1}
l_1	Straight lint obtained at 360 K	---
l_2	Straight lint obtained at 345 K	---



(a) Given that l_1 and l_2 have the same slope, what can you deduce in terms of chemical kinetics?

Answer: Order of reaction is not affected by temperature change.

(b) From l_1, deduce the order of reaction with respect to $N_2O_5(g)$.

Answer: Let rate = $k[N_2O_5]^a$ where x is the order of reaction with respect to N_2O_5

$\boxed{\log(\text{rate})} = \underline{\log(\mathbf{k})} + \underline{\mathbf{a}}\ \boxed{\log[N_2O_5]}$

By $\boxed{y} = \underline{c} + \underline{m}\ \boxed{x}$, **a** = slope of l_1 (i.e. m)

$$\mathbf{a} = \frac{[(-3.4) - (-1.4)]}{[(-2) - (0)]}$$

$$\mathbf{a} = 1$$

(c) From l_1, deduce the rate constant for the reaction at 360 K.

Answer: $\boxed{\log(\text{rate})} = \underline{\log(\mathbf{k})} + \underline{\mathbf{a}}\ \boxed{\log[N_2O_5]}$

By $\boxed{y} = \underline{c} + \underline{m}\ \boxed{x}$, log(**k**) = y-intercept (i.e. c)

$\log(\mathbf{k}) = -1.4$

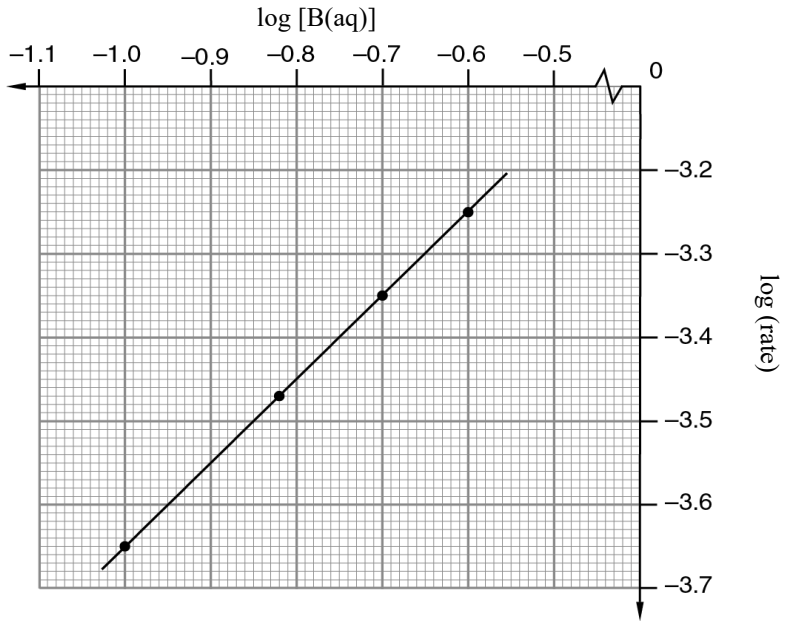
$\mathbf{k} = 10^{-1.4} = 0.0398\ s^{-1}$

Example 2

The following equation represents the alkaline hydrolysis of ethyl ethanoate.

$$A(aq) + B(aq) \rightarrow C(aq) + D(aq)$$

Several trials of an experiment were carried out at the same temperature to determine the rate equation of the above reaction. The graph below shows the results of the experiment.



The rate equation can be written as:

$$\text{rate} = k[A(aq)]^m[B(aq)]^n$$

where **k** is the rate constant and **m** and **n** are the order of reaction with respect to A(aq) and that to B(aq). When [A(aq)] is kept constant, the rate equation becomes: rate = **k'**[B(aq)]$^{\mathbf{n}}$, where **k'** is a constant value equal to **k**[A(aq)].

(a) Suggest how [A(aq)] can be kept constant. Explain your answer.

Answer: Use a large excess of A(aq). Since [A(aq)] is much higher than [B(aq)], [A(aq)] changes only a little at the start of the reaction. [A(aq)] can be considered as constant.

(b) Determine the order of reaction with respect to B(aq).

Answer: rate = **k'**[B(aq)]$^{\mathbf{n}}$

log(rate) = log(**k'**) + **n** log[B(aq)] (n = slope of the straight line)

Slope of the line = $\frac{-3.25 - (-3.65)}{-0.60 - (-1.00)}$

= 1 (The order of reaction with respect to B(aq) is 1)

Arrhenius equation

$\log(k) = \log(A) - \frac{Ea}{2.3R}(\frac{1}{T})$	$\log\left(\frac{k_1}{k_2}\right) = -\frac{Ea}{2.3\ R}(\frac{1}{T_1} - \frac{1}{T_2})$
- R = 8.31 J mol^{-1} K^{-1} - Unit of Ea should be J mol^{-1} - Unit of T should be in K (℃ + 273 = K)	

Example 1

The rate constant of a certain reaction at 25 °C is k_1 and the rate constant of the reaction at 35 °C is k_2. If the ratio of k_2 to k_1 is 1.9 : 1.0, calculate the activation energy of the reaction, in kJ mol^{-1}.

$$\log\left(\frac{k_1}{k_2}\right) = -\frac{Ea}{2.3\ R}(\frac{1}{T_1} - \frac{1}{T_2})$$

$$\log\left(\frac{1.0}{1.9}\right) = -\frac{Ea}{2.3 \times 8.31}(\frac{1}{25+273} - \frac{1}{35+273})$$

$$Ea = 48.9\ \text{kJ mol}^{-1}$$

Example 2

The activation energy of a certain reaction is 160 kJ mol^{-1}. Calculate the ratio of the rate constant at 1500 K (k_1) to the rate constant at 1200 K (k_2) for this reaction.

$$\log\left(\frac{k_1}{k_2}\right) = -\frac{Ea}{2.3\ R}(\frac{1}{T_1} - \frac{1}{T_2})$$

$$\log\left(\frac{k_1}{k_2}\right) = -\frac{160 \times 1000}{2.3 \times 8.31}(\frac{1}{1500} - \frac{1}{1200})$$

$$\frac{k_1}{k_2} = 24.8$$

$k_1 : k_2 = 24.8 : 1$

Example 3

The rate constant of a certain reaction at 30 ℃ and x ℃ are 6.5 x 10^8 mol^{-1} dm^3 s^{-1} and 7.0 x 10^8 mol^{-1} dm^3 s^{-1} respectively. If the activation energy of a certain reaction is 11.5 kJ mol^{-1}, calculate the value of x.

$$\log\left(\frac{k_1}{k_2}\right) = -\frac{Ea}{2.3\ R}(\frac{1}{T_1} - \frac{1}{T_2})$$

$$\log\left(\frac{6.5 \times 10^8}{7.0 \times 10^8}\right) = -\frac{11.5 \times 1000}{2.3 \times 8.31}(\frac{1}{30+273} - \frac{1}{x+273})$$

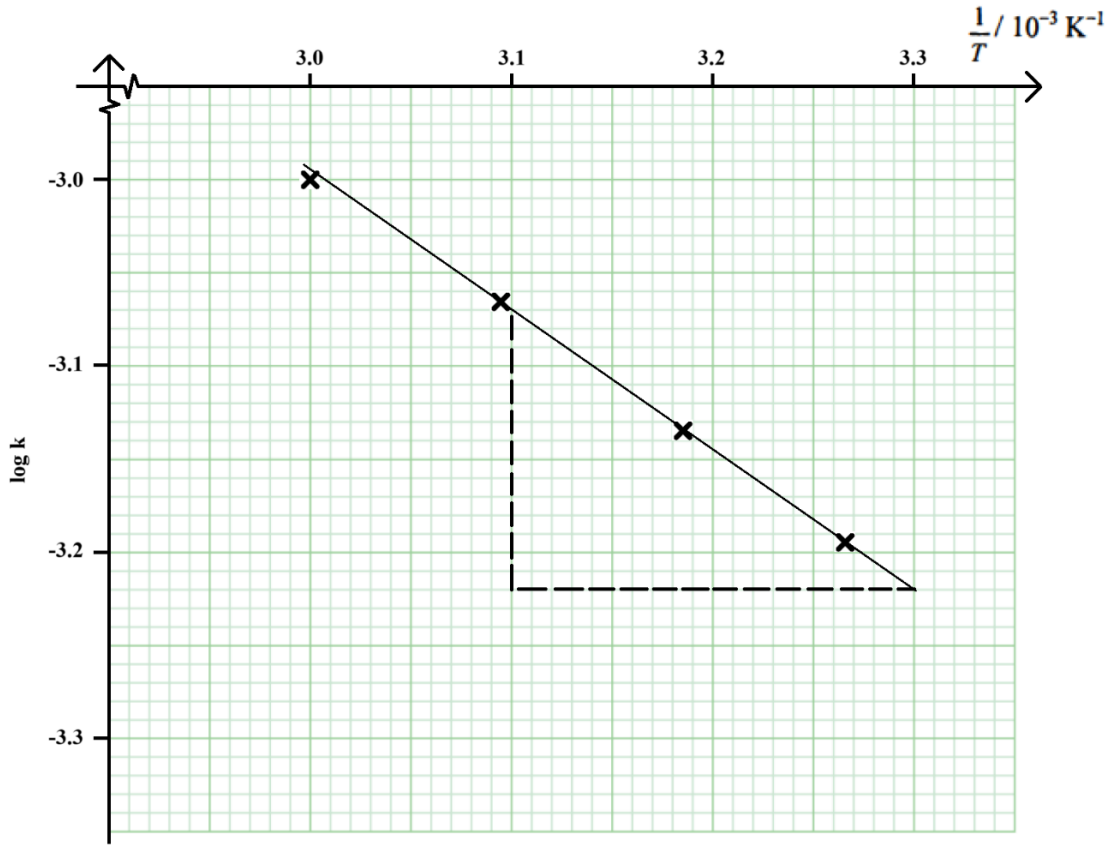
$$x = 35$$

Determining E_a by log(k) vs 1/T graph

Consider the following reaction:

$$A(aq) + 2\ B(aq) \rightarrow C(aq) + D(aq)$$

In a chemical kinetics experiment, the rate constants (k) of a reaction at various temperatures (T) were determined. The graph below shows the plot of log k against 1/T.



(a) By using the dotted lines in the graph above, deduce the activation energy of this reaction. (R = 8.31 J K^{-1} mol^{-1})

Answer:

$$\log(k) = \log(A) - \frac{Ea}{2.3R}\left(\frac{1}{T}\right)$$

From the graph, slope of the graph = $-\frac{Ea}{2.3R}$

$$\frac{[(-3.07) - (-3.22)]}{[(3.1) - (3.3)](10^{-3})} = -\frac{Ea}{2.3R}$$

$$Ea = 14300\ J\ mol^{-1}$$

(b) It is given that the order of reaction with respect to A(aq) and B(aq) are 0 and 2 respectively. From the graph above, deduce the rate constant of the above reaction at 331 K with correct unit.

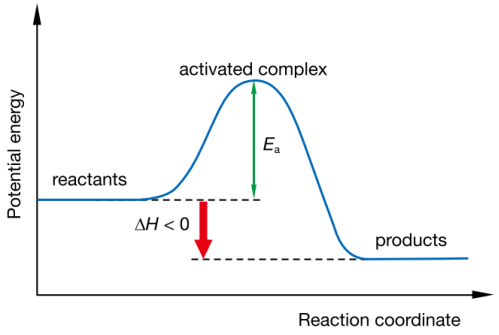
Answer: When temperature = 331, 1/T = 3.02 x 10^{-3}, log k = -3.01

k = 9.77 x 10^{-4} mol^{-1} dm^3 s^{-1}

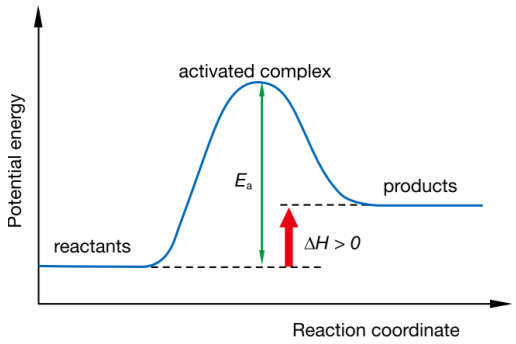
Energy profile

Activation energy (E_a) is the minimum energy possessed by the colliding reactant particles in order that a chemical reaction can occur

Exothermic vs endothermic reaction



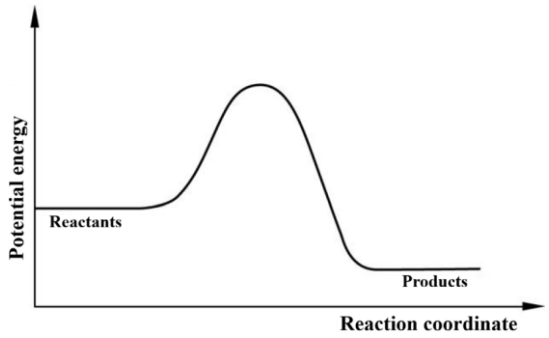
Exothermic reaction (single step)



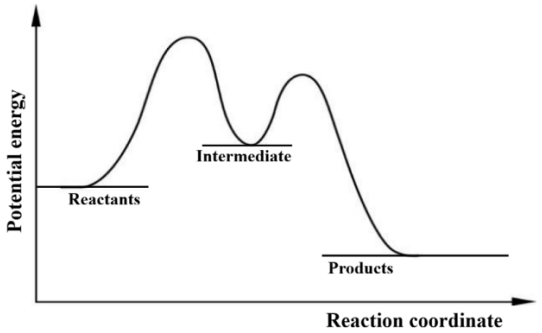
Endothermic reaction (single step)

- Activated complex contains partially broken and partially formed bonds. It is highly unstable and can never be isolated.
- Activation energy (E_a) is the difference in energy between the reactants and the activated complex.
- Enthalpy change (ΔH) is the difference in energy between the reactants and the products.
- If the reaction is reversible and the **activation energy of the forward reaction** is **Ea**, then the **activation energy of the backward reaction** will be (**Ea** – **ΔH**).

Single-step vs multi-steps reaction



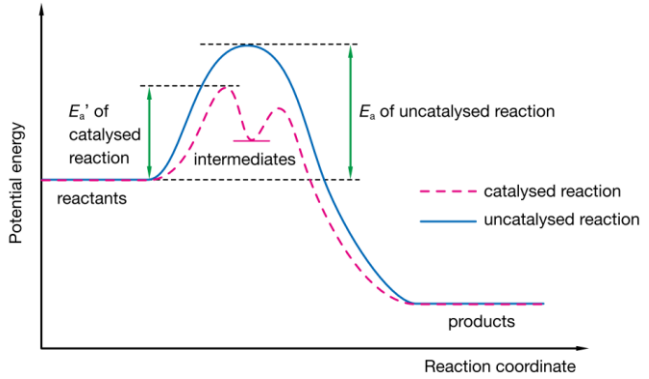
Exothermic reaction (**single step**)



Exothermic reaction (**two steps***)

* First step has a higher E_a (proceeds more slowly). It is the rate-determining step (it determines the overall reaction rate)

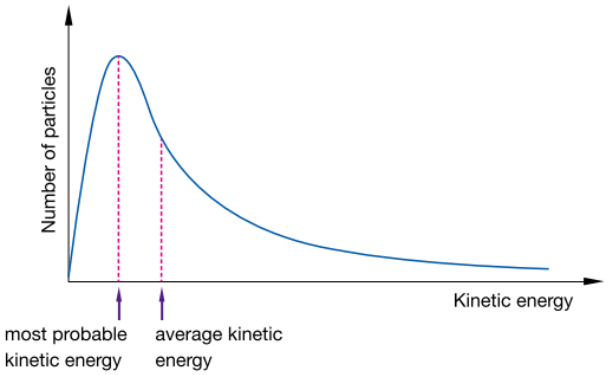
Uncatalyzed vs catalyzed reaction



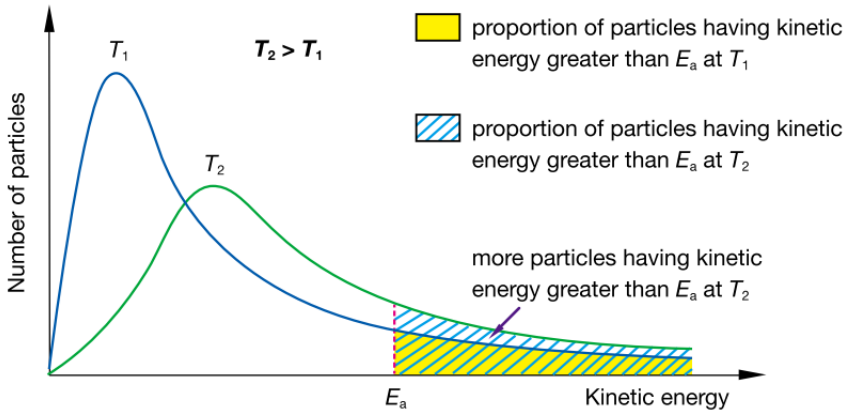
- The activation energy of the original reaction pathway remains unchanged. (Catalyst only provides an alternative reaction pathway with lower Ea. It does not 'change' the Ea of the original pathway)
- The enthalpy change of the reaction remain unchanged. (Refer to Hess's Law)
- Usually most of the catalyzed reactions involve at least two steps

Maxwell-Boltzmann distribution

- It shows the distribution of kinetic energies of the molecules in a gaseous system at a given temperature
- Area under the curve represents the number of particles in the gaseous system
- The kinetic energy corresponding to the maximum point on the curve represents the **most probable kinetic energy**.
- The curve is asymmetric. The **average kinetic energy** is always on the **right** of the **most probable kinetic energy**.

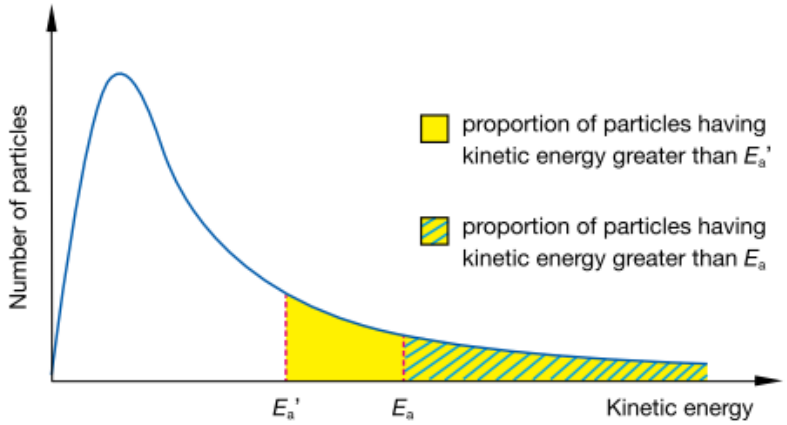


Effect of temperature change on reaction rate



As the temperature increases, the average K.E. of the particles increases. There is a larger proportion of particles having K.E. greater than the E_a. This increases the frequency of effective collisions. Hence, the reaction rate increases.

Effect of catalyst on reaction rate



In the presence of a catalyst, the reaction proceeds through an alternative pathway with lower E_a. There is a larger proportion of particles having K.E. greater than the E_a. This increases the frequency of effective collisions. Hence, the reaction rate increases.

Catalyst

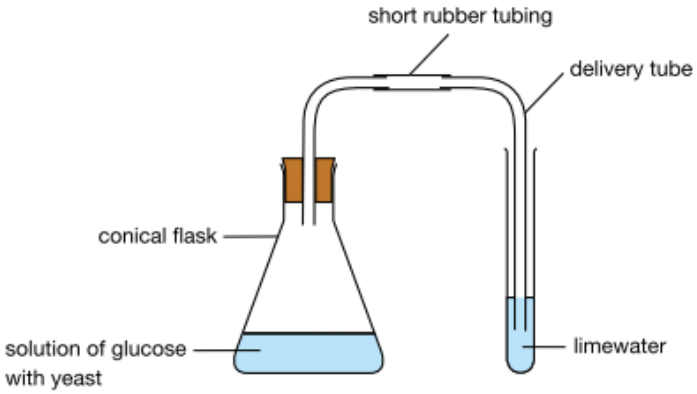
Characteristics of catalyst:

1. They are used in very small amounts.
2. They are very selective in action.
   (A particular catalyst may change the rate of only one specific reaction.)
3. The catalytic effect of a solid catalyst can be improved by increasing its surface area.
   (Powdered / finely divided solid catalyst has a larger area of active sites)
4.. They remain chemically unchanged at the end of reaction.
   (Catalyst may participate in chemical reactions, but will be regenerated at the end of reaction)
5. They can be poisoned by impurities.
   (This happens because the active sites on the catalyst surface are occupied by impurities, making them catalytically inactive)
   (That's why frequent replacement of catalysts in industrial processes are needed)

- For catalyst on reversible reactions, it only shortens the time needed to reach equilibrium. Catalyst can increase the forward rate and backward rate to the same extent. Therefore it has NO effect on equilibrium position and yield of reaction.

Enzyme

Example: Fermentation of glucose to give ethanol and carbon dioxide



- Enzymes are biological catalysts that can increase the rate of reaction.
- Zymase (an enzyme) in yeast catalyses the conversion of glucose into ethanol and carbon dioxide

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

- At high temperatures and extreme pH, enzymes in yeast are denatured and lose their functions.
- The concentration of ethanol produced cannot exceed 15% as ethanol is toxic to yeast. Ethanol with higher concentration can be obtained by distillation.

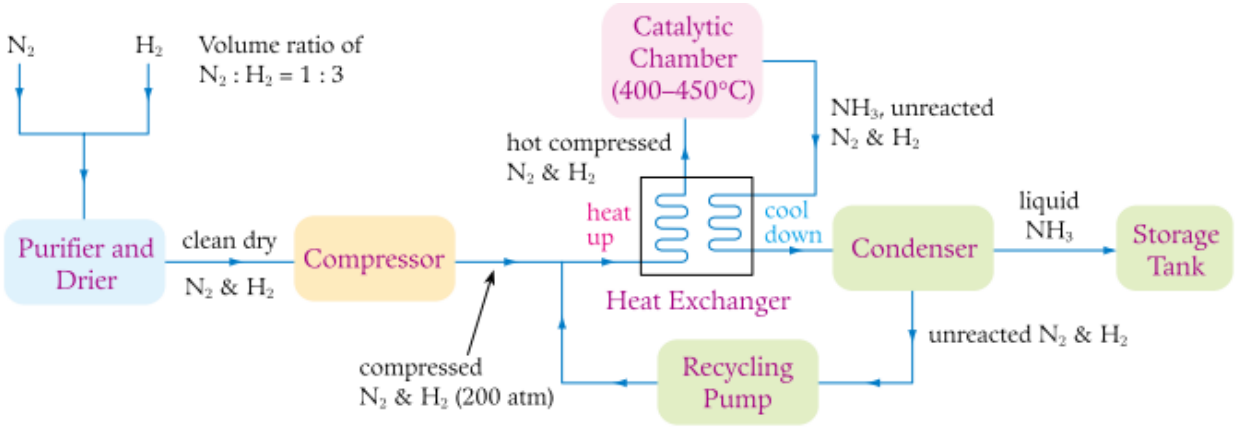
Haber Process

- H_2 can be obtained by the following methods:

  1. Cracking of naphtha
  2. Electrolysis of brine
  3. Steam-methane reforming (from natural gas)

Equation	ΔH	Catalyst	Temperature (℃)	Pressure (atm)
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\ H_2(g)$	> 0	NiO	700 – 1000	30

- N_2 can be obtained from fractional distillation of liquid air



Equation	ΔH	Catalyst	Temperature (℃)	Pressure (atm)
$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$	< 0	Finely divided Fe	400 – 450	200

- N_2 and H_2 should be purified as the impurities may poison the catalyst (Fe) in catalytic chamber.

- The gaseous mixture leaving the catalytic chamber is very hot. This mixture goes to the heat exchanger, which heats up the incoming N_2 and H_2 while the mixture gets cooled down. This process saves energy.

- NH_3 can be obtained by cooling the gaseous mixture to -33.3°C. NH_3 is condensed and separated out while the unreacted N_2 and H_2 are recycled to save chemicals.

- Unreacted N_2 and H_2 are recycled to save chemicals. This can also increase the overall conversion percentage of N_2 and H_2.

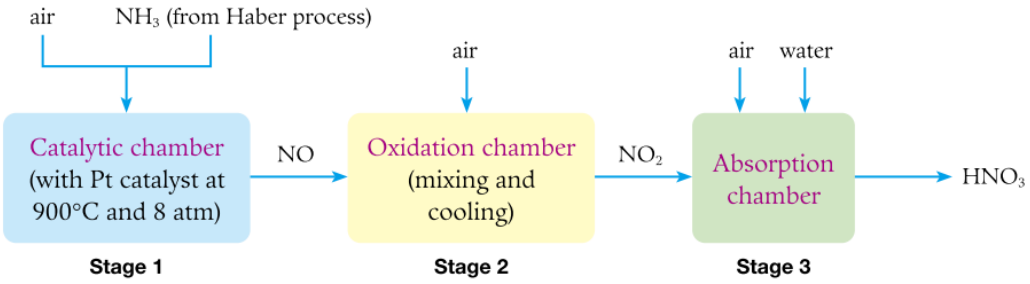
- In the Haber process, the product mixture is removed from the reaction chamber before reaching the yield of about 20%. It takes a long time for the system to reach equilibrium. By allowing the gaseous mixture to leave the catalytic chamber before reaching the yield of about 20% ammonia, the total amount of $NH_3(g)$ produced per unit time increases.

Why is the pressure in Haber process not set at 1 atm?	Number of moles of gases on the reactant side is greater than that of product side, low pressure will shift the equilibrium position to the left and reduce the yield of NH_3. A high pressure also increases the concentration of the gaseous mixture and speeds up the reaction.
Why is the pressure in Haber process not set at 1000 atm?	Cost in construction and maintenance of pipelines and reaction chambers that can withstand a high pressure will be very high.
Why is the temperature in Haber process not set at 25 °C?	The reaction rate will be too slow
Why is the temperature in Haber process not set at 1000 °C?	Forward reaction is exothermic. High temperature will shift the equilibrium position to the left and reduce the yield of NH_3.
Why is finely divided iron added?	The activation energy of Haber process is very high (large amount of energy is needed to break N≡N bond). The iron catalyst can speed up the reaction. Finely divided form of iron increases the surface area of the catalyst, and thus improves its catalytic effect.

Fertilizer

- Fertilizer (e.g. NH_4NO_3, $(NH_4)_2SO_4$, $(NH_2)_2CO$) is important to plants as they can increase crop yields.

Manufacture of ammonium sulphate / ammonium nitrate from nitric acid:



Stage 1 Catalytic oxidation of ammonia

Equation	ΔH	Catalyst	Temperature (°C)	Pressure (atm)
$4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(g)$	< 0	Pt	900	8

Stage 2 Oxidation of nitrogen monoxide

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Stage 3 Formation of nitric acid

$$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$$

Stage 4 Formation of ammonium fertilizer

$$HNO_3(aq) + NH_3(aq) \rightarrow NH_4NO_3(aq)$$

$$H_2SO_4(aq) + 2NH_3(aq) \rightarrow (NH_4)_2SO_4(aq)$$

Manufacture of urea

$$2NH_3(aq) + CO_2(g) \rightarrow H_2NCOO^-NH_4^+(aq) \text{ (Ammonium carbamate)}$$

$$H_2NCOO^-NH_4^+(aq) \rightarrow H_2O(l) + (H_2N)_2CO(aq) \text{ (Urea)}$$

Chloroalkali

- Electrolysis of brine (concentrated NaCl(aq)) produces three important chemicals, NaOH(aq), $Cl_2(g)$ and $H_2(g)$.

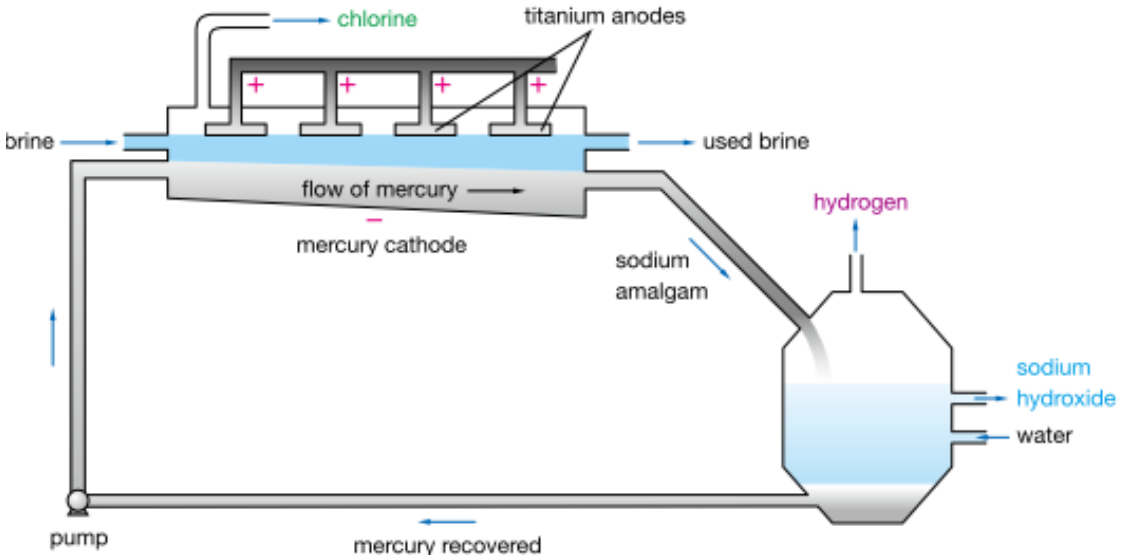
$$2NaCl(aq) + 2H_2O(l) \rightarrow H_2(g) + Cl_2(g) + 2NaOH(aq)$$

Products	Hydrogen	Chlorine	Sodium hydroxide
Uses	1. Making margarine 2. Making ammonia 3. As rocket fuel	1. Sterilizing swimming pool 2. Making polyvinyl chloride (PVC)	1. Making soap 2. Making drain cleaner 3. Neutralizing acidic effluent from factory
	Making hydrochloric acid		Making chlorine bleach

Traditional electrolytic cells are not used to prepare NaOH(aq), $Cl_2(g)$ and $H_2(g)$. It is because:

1. The hydrogen and chlorine formed would give an explosive mixture. They can also react to form hydrogen chloride gas. ive.
2. The chlorine formed would react directly with the sodium hydroxide solution formed in the electrolytic solution.

A. Flowing mercury cell



At anode (Ti / Graphite): $[Cl^-(aq)]$ is much higher than $[OH^-(aq)]$. Due to concentration effect, $Cl^-(aq)$ ions are preferentially discharged to form $Cl_2(g)$.

$$2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$$

At cathode (Hg): $Na^+(aq)$ ions are preferentially discharged and the Na metal formed dissolves in Hg to form an alloy, sodium amalgam (Na/Hg).

$$Na^+(aq) + Hg(l) + e^- \rightarrow Na/Hg(l)$$

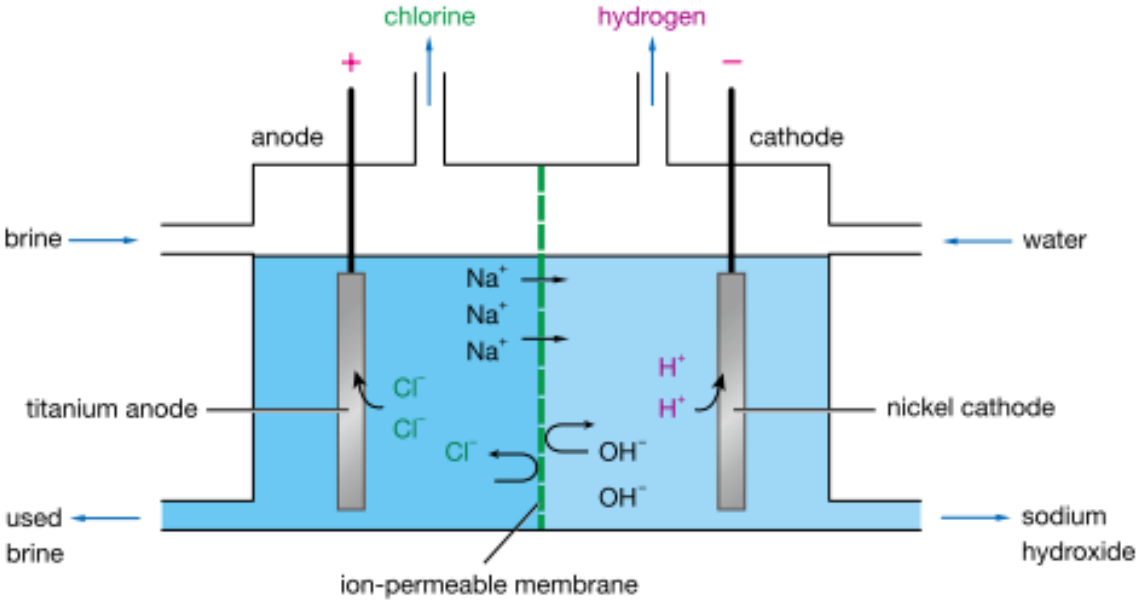
Na/Hg formed is carried away immediately. It flows into another tank and reacts with water inside to form NaOH(aq). $H_2(g)$ is also formed in this reaction

$$2\ Na/Hg(l) + 2\ H_2O(l) \rightarrow 2\ NaOH(aq) + H_2(g) + 2\ Hg(l)$$

The mercury formed is recovered and pumped back to the electrolytic cell.

- Disadvantages of flowing mercury cell:
  1. It uses toxic mercury
  2. It operates at a high voltage

B. Membrane cell



At anode (Ti): $[Cl^-(aq)]$ is much higher than $[OH^-(aq)]$. Due to concentration effect, $Cl^-(aq)$ ions are preferentially discharged to form $Cl_2(g)$, leaving excess $Na^+(aq)$ in anode compartment

$$2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$$

At cathode (Ni) $H^+(aq)$ is a stronger oxidizing agent than $Na^+(aq)$. $H^+(aq)$ ions are preferentially discharged to form $H_2(g)$, leaving excess $OH^-(aq)$ in cathode compartment.

$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$$

$$[OR\ 2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2\ OH^-(aq)]$$

- The ion-permeable membrane only allows $Na^+(aq)$, but not $Cl^-(aq)$ and $OH^-(aq)$ to pass through. The excess $Na^+(aq)$ ions in the anode compartment will move across the ion-permeable membrane to the cathode compartment to balance the excess negative charge there.

- Used brine in anode compartment is removed while pure NaOH(aq) can be obtained in cathode compartment without NaCl(aq) impurity.

Production of methanol

Importance of methanol:

1. As feedstock to produce chemicals
   - It is a one-carbon compound which can be a starting material to make other compounds with larger carbon numbers (e.g. Ethanoic acid, methanal, dimethyl ether)
2. As a fuel for motor vehicles
   - It is a liquid which can be easily transported. It can be blended into petrol to produce cleaner fuels.
3. As a fuel for fuel cell
4. For making biodiesel
   - It can be used to convert triglycerides in vegetable oils into biodiesel

Production of methanol

Stage 1 Production of syngas by steam reforming of natural gas (contains mainly methane)

Equation	ΔH	Catalyst	Temperature (°C)	Pressure (atm)
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\ H_2(g)$	> 0	NiO	700 – 1000	30

The gaseous mixture containing CO(g) and $H_2(g)$ is syngas.

Stage 2 Synthesis of methanol

Equation	ΔH	Catalyst	Temperature (°C)	Pressure (atm)
$CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$	< 0	Cu / ZnO / Al_2O_3	250	50 – 100

Note that the conversion of syngas to methanol requires CO(g) and $H_2(g)$ in a mole ratio of 1 : 2. However, the production of syngas gives CO(g) and $H_2(g)$ in a mole ratio of 1 : 3. $CO_2(g)$ is added to the gaseous mixture to increase the amount of CO(g) and decrease the amount of $H_2(g)$ via a shift reaction

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Stage 3 Purification of methanol

Crude methanol obtained can be purified by distillation

Advancement of the methanol production technology

1. Direct conversion of methane to methanol

$$CH_4(g) + \frac{1}{2}O_2(g) \xrightarrow[\sim 200^\circ C,\ 1\ atm]{\text{zeolite}} CH_3OH(\ell)$$

   - No by-products form in this reaction

2. Microbial reactions
   - Methane can be oxidized to methanol directly by some microbes (e.g. yeast and bacteria). These microbes contain enzymes which can catalyze the oxidation. The oxidation uses renewable feedstock and has higher energy efficiency.

3. New sources of renewable feedstock
   - Biomass and methane from landfill (renewable feedstock) can be converted to syngas, and then to methanol directly.

Green chemistry

1. **Waste prevention**
2. **Maximizing atom economy**

$$\text{Atom economy} = \frac{\text{total mass of atoms in the desired product}}{\text{total mass of atoms in the reactants used}} \times 100\%$$

Example: By using NaOCl, this chemical plant can produce hydrazine (H_2NNH_2) a propellant used in space vehicles:

$$NaOCl + 2NH_3 \rightarrow H_2NNH_2 + NaCl + H_2O$$

(a) Calculate the atom economy. (Relative atomic masses: H = 1.0, N = 14.0, O = 16.0, Na = 23.0, Cl = 35.5)

Answer: Atom economy = (1x2 + 14 + 14 + 1x2) / [(23 + 16 + 35.5) + 2(14 + 1x3)] x 100% = 29.5%

(b) Explain why a reaction with high atom economy does not necessarily have a high yield.

Answer: Calculation of atom economy is based on 100% yield. In fact, most reactions do NOT go to completion.

3. **Using less hazardous chemical synthesis**

Corrosive chemicals: H_2SO_4, HCl, NaOH, KOH

Toxic chemicals: CO, CH_3OH, halogens, KCN, HCN, Benzene, SO_2, H_2S, 2,4-DNPH, compounds of Pb and Hg.

4. **Producing safer chemical products**
5. **Using safer solvents and auxiliaries**
   - When solvent is needed, safer solvents (H_2O) is preferred
   - Solvent-free processes are greener than processes that require solvent
6. **Designing for energy efficiency**
   - Processes with lower operating temperatures and pressures are preferred
7. **Using renewable raw materials**

Renewable raw materials: Glucose, sugars, fats, biomass, lactic acid

8. **Reducing derivatives**
   - Processes that involve fewer steps are preferred. Generally, the more steps in an industrial process:
     1. The more chemicals are needed and eventually, more wastes are produced.
     2 The lower will be the overall yield.
9. **Using catalysts**
   - Catalyst can speed up the rate (and itself remains chemically unchanged at the end). Processes using catalyst can operate under moderate conditions.
10. **Designing degradable chemical products**
11. **Developing real-time analysis for pollution prevention**
12. **Minimizing the potential for chemical accidents**