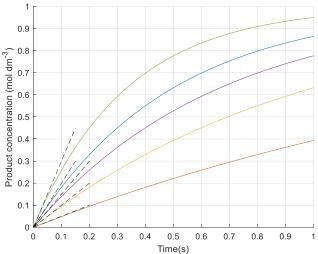
# **Industrial Chemistry**

# Rate equation

For any reaction with:

$$X \to Products$$

We would like to investigate how the rate of reaction varies with the initial concentration of X. We can repeat the experiment multiple times, each trial with a different concentration of X and plot graphs that can help us to find the rate of reaction.



In particular we are interested in the *initial rate of reaction* since the reaction conditions and reactant concentrations are clearly known. The initial rate can be deduced from calculating the slope of the tangent line to the curve at t = 0s. The graph can also tell us the unit of rate of reaction, which is mol dm<sup>-3</sup> s<sup>-1</sup>.

Generally we have the following rate equation for some reaction  $A+B+C \rightarrow Products$ :

$$Rate = k[A]^x[B]^y[C]^z$$

To investigate the effect of the concentration of one reactant, we can hold the concentration of the other two reactants constant, hence giving us:

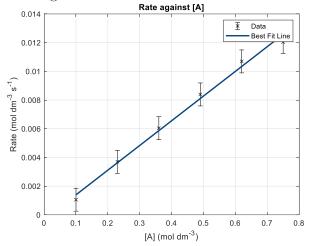
$$Rate = k'[A]^x$$
, where  $k' = k[B_0]^y[C_0]^z$ 

#### First Order Reaction

The rate of reaction of a first order reaction (wrt the reactant) is directly proportional to the concentration of the reactant. i.e.,

$$Rate = k[A]$$

Plotting out a curve of rate against concentration, we should obtain a straight line passing through the origin.



Concentration [A] (mol dm <sup>-3</sup> )	Rate (mol $dm^{-3} s^{-1}$ )
0.100	0.00105
0.230	0.00369
0.360	0.00603
0.490	0.00839
0.620	0.01069
0.750	0.01204

To find out k, we can calculate the slope of the graph. Here the best fit line has a slope m = 0.0172. The unit of the rate constant can be found by directly dividing the unit of rate (mol dm<sup>-3</sup> s<sup>-1</sup>) with the unit of [A] (mol dm<sup>-3</sup>).

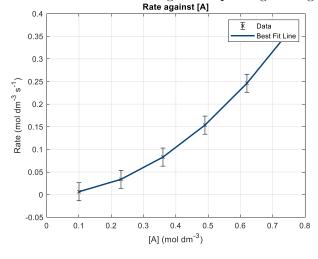
$$k = m = \frac{\Delta \ Rate}{\Delta t} = 0.0172 \ \left(\frac{\text{mol dm}^{-3} \ \text{s}^{-1}}{\text{mol dm}^{-3}}\right) = 0.0172 \ \text{s}^{-1}$$

#### Second order reaction

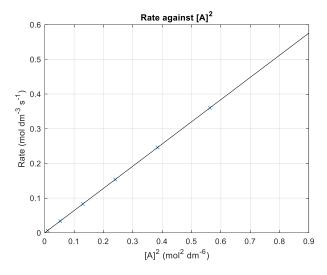
This time, the rate of reaction is directly proportional to the **square** of the concentration of the reactant, i.e.

$$Rate = k[A]^2 = kx$$
, if  $x = [A]^2$ 

A direct plot of rate against [A] would lead to a quadratic curve, so we can plot rate against [A]<sup>2</sup> instead to obtain a straight line passing through the origin.



Concentration [A] (mol dm <sup>-3</sup> )	Rate (mol $\mathrm{dm}^{-3}\mathrm{s}^{-1}$ )
0.100	0.00641
0.230	0.0338
0.360	0.0829
0.490	0.153
0.620	0.246
0.750	0.360

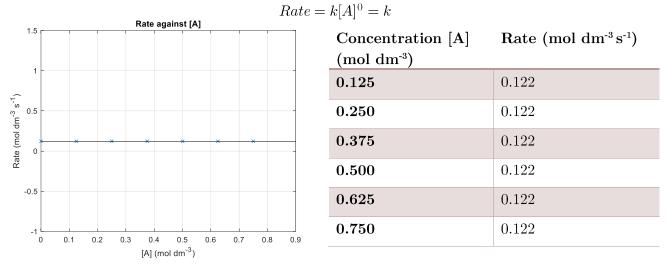


Once again the slope of the line in the rate against  $[A]^2$  graph can be used to find the rate of reaction. For this curve, m = 0.64. Once again, pay attention to the units.

$$k = m = \frac{\Delta \ Rate}{\Delta([A]^2)} = 0.64 \ (\frac{\text{mol dm}^{-3} \ \text{s}^{-1}}{\text{mol}^2 \ \text{dm}^{-6}})$$
$$k = 0.64 \ \text{mol}^{-1} \ \text{dm}^3 \ \text{s}^{-1}$$

#### Zeroth order reaction

This is a special case as k does not depend on [A], it is said the order of reaction wrt A is zero.



It is quite trivial to find that the value of k is 0.122 mol dm<sup>-3</sup> s<sup>-1</sup>.

# N-order reaction – A general method

Suppose you are given a bunch of data with no clear pattern, i.e. hard to know if it is linear, quadratic, cubic, etc. You can easily find the rate of reaction with respect to that reactant by plotting a log-log graph. Going back to the rate equation.

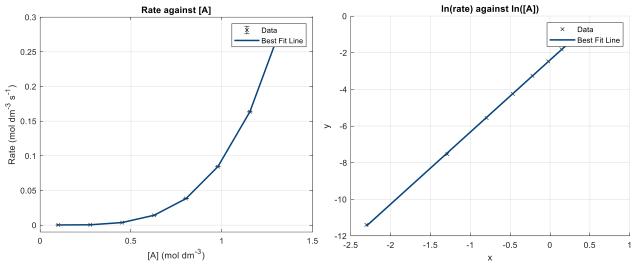
$$Rate = k[A]^m$$

Taking log on both sides, (the base of logarithm doesn't matter here so you can use ln as well)

$$\log Rate = m \log([A]) + \log(k)$$

This gives us a linear equation, with the slope of the graph being the order of the reaction wrt to A. k can also be directly found from this expression since the  $\log(k) = y$ -intercept.

[A] (mol dm <sup>-3</sup> )	Rate (mol dm <sup>-3</sup> s <sup>-1</sup> )	$\ln([A])$	ln(Rate)
0.10	$1.12 \cdot 10^{-5}$	-2.3026	-11.3934
0.27	0.000532	-1.2884	-7.5388
0.45	0.00381	-0.7953	-5.5677
0.62	0.0142	-0.4666	-4.2524
0.80	0.0382	-0.2196	-3.2643
0.97	0.0843	-0.0217	-2.4726
1.15	0.1633	0.1435	-1.8121
1.33	0.287	0.2852	-1.2453



From the log plot,

$$m = 3.93 \approx 4$$
 
$$c = \ln k = -2.40 \Rightarrow k = 0.091$$

The order wrt to [A] is 4 while the rate constant,  $k = 0.091 \text{ mol}^3 \text{ dm}^9 \text{ s}^{-1}$ . For a quick check of your answers, you can use *linear regression* mode on your own calculator.

#### Multiple-trial approach to determine order and rate constant

A more common question type comes by asking you to determine the order and rate constant by comparing results from different trials.

Trial	[A] (mol dm <sup>-3</sup> )	[B] (mol dm <sup>-3</sup> )	Rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
1	0.1	0.1	0.07
2	0.1	0.5	0.35
3	0.3	0.1	0.63

 $Rate = k[A]^a[B]^b$ 

#### General steps:

- Choose one reactant to be your variable while hold others constant and find two trials that correspond to the case.
- Divide through to get a ratio of your variable reactant raise to the power of its order and compare it with the ratio of the two resulting rates.
- Repeat this for all reactants
- Substitute in trial conditions and reaction orders to determine rate constant.

Using the above table, we first consider trial 1 and 3 to find the order with respect to A

$$\frac{{\rm k}[A_3]^a[B_3]^b}{{\rm k}[A_1]^a[B_3]^b} = \frac{0.63}{0.07}$$
$$\left(\frac{[A_3]}{[A_1]}\right)^a = 3^a = 9$$
$$\implies a = 2$$

Then consider trials 1 and 2 to find the order with respect to B

$$\frac{k[A_2]^a[B_2]^b}{k[A_1]^a[B_1]^b} = \frac{0.35}{0.07}$$
$$\left(\frac{[B_2]}{[B_1]}\right)^b = 5^b = 5$$
$$\implies b = 1$$

Therefore, the order of the reaction wrt A is 2 and the order of reaction wrt b is 1.

We thus have our rate equation as follows:

$$Rate = k[A]^2[B]$$

Considering trial 1 again to determine k:

$$k[A_1]^2[B_1] = 0.07$$
  
 $k = 70 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ 

#### Checkpoint

1. Consider the following reaction,

$$\mathbf{W}_{(aq)} + \mathbf{X}_{(aq)} + \mathbf{Y}_{(aq)} \rightarrow \mathbf{Z}_{(aq)}$$

A series of experiments was done to determine the rate equation of the reaction.  $\mathbf{X}_{(aq)}$ ,  $\mathbf{Y}_{(aq)}$ ,  $\mathbf{Z}_{(aq)}$  and water were mixed in a beaker. The results were recorded in the table below:

Emponimons	Volume of 1.0 M	Volume of 1.0 M	Volume of 1.0 M	Volume of	Initial rate
Experiment	W(aq) (cm <sup>3</sup> )	X(aq) (cm3)	Y(aq) (cm <sup>3</sup> )	water (cm³)	(mol dm <sup>-3</sup> s <sup>-1</sup> )
1	10.0	10.0	10.0	20.0	6.20 x 10 <sup>-3</sup>
2	15.0	8.0	10.0	17.0	9.30 x 10 <sup>-3</sup>
3	18.0	10.0	10.0	12.0	1.12 x 10 <sup>-2</sup>
4	10.0	5.0	15.0	20.0	?

a. i. Calculate the molarity (concentration) of  $\mathbf{W}_{(aq)}$  in experiment 1 and experiment 2 after mixing  $\mathbf{X}_{(aq)}$ ,  $\mathbf{Y}_{(aq)}$ ,  $\mathbf{Z}_{(aq)}$  and water in the beaker. (2 marks)

$$\begin{split} [W_{(aq)}]_1 &= (1*0.01)/(0.05) = 0.2 \ M \\ [W_{(aq)}]_2 &= (1*0.015)/(0.05) = 0.3 \ M \end{split}$$

ii. Hence state the function of water in these experiments (2 marks) Water is added so the volume of the mixture in each experiment is the same to ensure a fair test.

b. Deduce the order of reaction with respect to  $\mathbf{W}_{(aq)}$ 

Consider trials 1 and 3  $Rate = k[W]^a[X]^b[Y]^c$ 

(2 marks)

$$\frac{k[0.36]^{a}[0.16]^{b}[0.2]^{c}}{k[0.2]^{a}[0.2]^{b}[0.2]^{c}} = \frac{11.2}{6.20}$$
$$\frac{[0.36]^{a}}{[0.2]^{a}} = (1.8)^{a} = 1.806$$
$$a = 1$$

c. Deduce the order of reaction with respect to  $\mathbf{X}_{(aq)}$ 

(2 marks)

Consider trials 1 and 2

$$\frac{\sqrt{[0.3]^a[0.16]^b[0.2]^c}}{\sqrt{(0.2)^a[0.2]^b[0.2]^c}} = \frac{9.3}{6.2}$$
$$\frac{\frac{3}{2}(0.8)^b = \frac{3}{2}}{(0.8)^b = 1}$$
$$b = 0$$

d. i. Given the order of reaction with respect to Y(aq) is 2. Calculate the rate constant and write the rate equation for the reaction with the value of the rate constant.  $Rate = k[W][Y]^2$  Consider trial 1 (3 marks)

Consider trial 1

$$6.2 \cdot 10^{-3} (mol \ dm^{-3} s^{-1}) = k[0.2][0.2]^2 (mol \ dm^{-3})^3$$

$$k = 0.775 \frac{(mol \ dm^{-3} s^{-1})}{mol^3 \ dm^{-9}} = 0.775 \ mol^{-2} \ dm^6 \ s^{-1}$$

ii. Determine the initial rate of Experiment 4.

$$R_4 = k[0.2][0.3]^2 = 0.0140 \text{ mol dm}^{-3} \text{ s}^{-1}$$

2. Comment on the following statement.

"An increase in concentration of reactants must result in an increase in reaction rate."

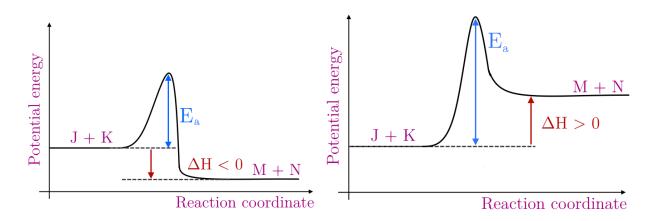
The statement is incorrect. For a zeroth order reaction, the rate of reaction is independent of the concentration of reactants.

# Energy profiles and activation energy

### Energy profile

We can illustrate the energy levels throughout a reaction using an energy profile.

$$J+K\to M+N$$



The ending line (signaling completion of rection) will be lower than the starting line when the reaction is exothermic, i.e.  $\Delta H < 0$ . It will be higher than the starting line when the reaction is endothermic, i.e.  $\Delta H > 0$ .

The activation energy  $(E_a)$  is defined as the minimum amount of kinetic energy required for the reaction to proceed from its reactant stage to the product stage. In terms of the graph, it can be seen as the energy difference between the reactants and the peak of the energy curve.

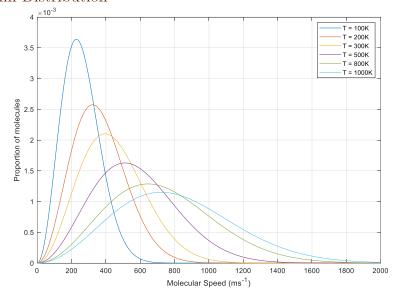
Molecules possessing kinetic energy equal to or greater than  $E_a$  will be able to have an effective collision and hence react. Therefore, when more molecules have sufficient kinetic energy, the frequency of effective collisions will increase, leading to a higher rate of reaction.

What is interesting is that we can use this graph to not only deduce the activation energy of the forward reaction  $(J + K \to M + N)$ , but also for the backward reaction  $(M + N \to J + K)$ , provided that the reaction is reversible. Using the previous definition – "energy difference between the reactants and the peak of the energy curve", we can get the following expression to calculation  $E_a$  of the backward reaction.

$$E_{a(backward)} = E_{a(forward)} - \Delta H$$

Thus, if the reaction is exothermic  $E_{a(backward)} > E_{a(forward)}$  as  $-\Delta H > 0$ . Inversely, if the reaction is endothermic,  $E_{a(backward)} < E_{a(forward)}$  with  $-\Delta H < 0$ . You can verify this by looking at the energy profiles corresponding to endothermic and exothermic reactions.

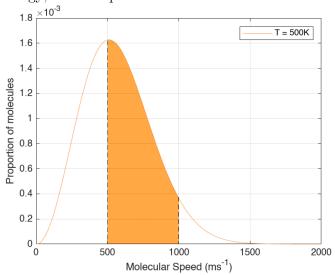
# Maxwell-Boltzmann Distribution



Molecules are not moving at uniform speeds. Instead, their speeds are distributed in a Maxwell-Boltzmann probability density function (pdf). The distribution is asymmetrical with a sharp peak near zero and a long tail that tends to zero. It can be seen that higher temperatures causes the peak to shift to the right but it becomes lower, resulting in a higher mean molecular kinetic energy/speed.

$$\int_0^\infty f(v)dv = 1$$

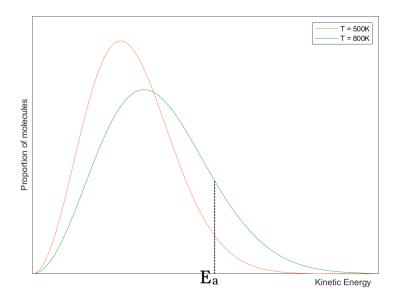
The area under the function at any temperature (measured in kelvins) is always equal to 1. In fact, the area under the function corresponds to the proportion of molecules with that range of molecular speed/molecular kinetic energy, which explains the fact above.



For instance, the orange area corresponds to the proportion of molecules with speeds from 500 ms<sup>-1</sup> to 1000 ms<sup>-1</sup>. To generalize this we can use the following integral.

$$P \ a \le v \le b \ = \int_a^b f(v') \, dv'$$

If you prefer to work without integrals, then you can always bear in mind that the larger the area under the curve, the more molecules that have that range of molecular speeds/molecular kinetic energy.



We now add in a vertical line that indicates  $E_a$  to explain why reaction rate is higher at high temperature conditions.

Clearly, the area under the curve and to the right of the line of the T=800K curve is larger than that of the T=500K curve, which is expected since the higher temperature results in a higher average molecular kinetic energy. More molecules have sufficient kinetic energy to react at 800K compared to at 500K, therefore effective collisions are more likely to occur, increasing the frequency of effective collisions, thereby increasing the rate of reaction.

Conditions for effective collisions:

- Molecules must possess kinetic energy equal to or greater than  $E_a$
- Molecules must collide at the right angle (not as important as the first)

# Checkpoint

1. With the aid of a Maxwell-Boltzmann distribution curve, suggest why an increase in temperature (from  $T_1$  to  $T_2$ ) can lead to an increase in the reaction rate of a gaseous reaction.

#### Arrhenius equation

Another way to quantify the increase in rate due to temperature is by using the Arrhenius equation to calculate the increase in k (rate constant) when temperature increases. The Arrhenius equation is given by:

$$k = A \, \exp\left(\frac{-E_a}{RT}\right)$$

A is a constant which changes for every reaction,  $E_a$  is the activation energy, R is the universal gas constant (~8.31 J mol<sup>-1</sup> K<sup>-1</sup>) and T is temperature (**MEASURED IN KELVINS!!!**). Logarithm is usually taken on both sides of the Arrhenius equation when analyzing, which gives us:

$$\ln k = \ln A - \frac{E_a}{RT} \text{ or } \log k = \log A - \frac{E_a}{2.3RT}$$

The ln version is preferred here as there is no need to divide by an extra 2.3. If we then consider the equation at two different temperatures, (note that  $E_a$  is unchanged with T)

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad ...(1)$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \qquad ...(2)$$

(1) – (2), giving us,

$$\Rightarrow \ln k_1 - \ln k_2 = \left\{ \ln A - \frac{E_a}{RT_1} \right\} - \left\{ \ln A - \frac{E_a}{RT_2} \right\}$$
$$\ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Now equipped with this version of the Arrhenius equation, we can find the activation energy of a reaction given rate constants at two temperatures.

Temperature (°C)	25	60
Rate constant $k$	0.00244	0.0255

Applying the equation derived above,

$$\ln\left(\frac{0.0255}{0.00244}\right) = \frac{E_a}{R} \left(\frac{1}{25 + 273} - \frac{1}{60 + 273}\right)$$
$$2.34 = \frac{E_a}{R} (3.52 \cdot 10^{-4})$$
$$E_a = \frac{2.34}{3.52 \cdot 10^{-4}} R \approx +55.2 \text{ kJ mol}^{-1}$$

We leave the positive sign on  $E_a$  to signify that energy is consumed when the reaction is initiated. In fact we don't even need the rate constants to find out  $E_a$ , we only need a ratio of them at different temperatures. Suppose k tripled when the reaction temperature increased from 25 °C to 40 °C.

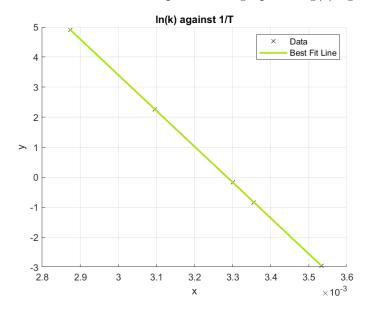
$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{1}{3}\right) = \frac{E_a}{R} \left(\frac{1}{40 + 273} - \frac{1}{25 + 273}\right)$$

$$\frac{E_a}{R} - 1.61 \cdot 10^{-4} = -1.10$$

$$E_a = +56.9 \text{ kJ mol}^{-1}$$

Alternatively, we can also find  $E_a$  when we are provided a graph of  $\log(k)$  against 1/T.



In the above plot,

$$m = -11900$$
 
$$\ln k = \ln A - \frac{E_a}{RT}$$

Our "x" variable is 1/T and our "y" variable is  $\ln(k)$ , so the slope of the line is  $-E_a/R$ .

$$-\frac{E_a}{R} = -11900 \Longrightarrow E_a = +99.0 \text{ kJ mol}^{-1}$$

# Checkpoint

1. The value of the rate constant of the reaction decreases from  $4.05\times10^{-2}$  to  $3.92\times10^{-4}$  when the temperature decreases from 470°C to 370°C . Calculate the activation energy of the reaction. (Gas constant, R = 8.31 J K–1 mol–1)

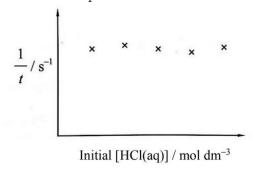
2. A student studied the following reaction:

$$\mathrm{Na_2S_2O_{3(aq)} + 2HCl}_{\mathrm{\;aq\;}} \rightarrow \mathrm{2NaCl}_{\mathrm{\;aq\;}} + \mathrm{SO_2}_{\mathrm{\;g\;}} + \mathrm{S}_{\mathrm{\;s\;}} + \mathrm{H_2O}_{\mathrm{\;1}}$$

To determine the order of reaction with respect to [HCl(aq)], five experiments were carried out in the set-up below by changing only the initial concentration of HCl(aq) while keeping other conditions constant to measure the time (t) required for certain equal amounts of sulphur formed.

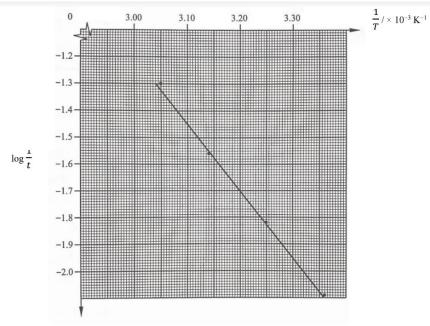
a. Explain why 1/t could be taken as the initial rate of the reaction.

- b. Suggest a controlled variable in the set-up to ensure that the certain amounts of sulphur formed for five experiments were equal by observation.
- c. The results obtained from the five experiments were shown in the graph below:



With reference to the above graph, deduce the order of reaction with respect to  $HCl_{(aq)}$ .

d. The student used the same set-up as (ii) to determine the activation energy of the reaction. The reaction proceeded under four different temperatures (T) and the time (t) required for the cross to disappear under different temperatures was measured. The initial reactant concentration is the same for all four trials. A graph of log (1/t) against 1/T was plotted below.

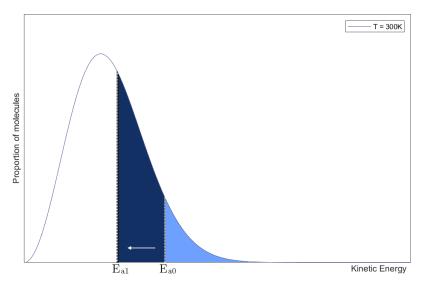


Find the activation energy  $(E_a)$  of the reaction.

# Catalysts

Catalysts can alter the reaction rate by providing an alternative reaction pathway. Here are a few basic properties of catalysts:

- They offer an alternative reaction pathway (typically with lower E<sub>a</sub>)
- They are required in small amounts
- Catalysts remain chemically unchanged after a reaction
- Catalysts are specific in action (they can only catalyse a small set of reactions)
- Catalyst can be poisoned by impurities, e.g. platinum in catalytic converters can be poisoned by lead.
- When acting on a reversible reaction, it increases the rate of the forward and backward reaction by equal extents, but it does not shift the equilibrium position.



A catalyst provides an alternative reaction pathway with lower activation energy. (see  $E_{a1} < E_{a0}$ ) Thus, more molecules now have kinetic energy equal to or greater than the activation energy requirement and can undergo effective collisions. This is signified in the graph by the increase in area under the curve when  $E_a$  decreases from  $E_{a0}$  to  $E_{a1}$ . This increases the frequency of effective collisions, thus increasing the rate of reaction.

Mini-Checkpoint: In the space below, try to illustrate the effect of a catalyst on the activation energy using an energy profile of the reaction.

# Checkpoint

Consider the following reaction:

$$S_2O_{8(aq)}^{2-} + 2I_{~aq}^- \ \rightarrow 2SO_{4~aq}^{2-} \ + I_{2~aq}$$

- a. Explain why the above reaction has high activation energy
- b. Describe how you can show experimentally  $Fe^{2+}(aq)$  is a positive catalyst of reaction (1) by using iodine clock reaction. The following reagents and apparatus are provided: KI(s), 1.0 M  $FeSO_4(aq)$ , 0.5M  $Na_2S_2O_3(aq)$ , 0.2 M  $Na_2S_2O_8(aq)$ , starch indicator, beakers Given:  $S_2O_3$  is an oxidizing agent which can react with iodide ions.

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$

c. With the aid of a maxwell Boltzmann distribution diagram, illustrate how the reaction is catalysed by  $Fe^{2+}$ 

d. Comment on the following statement.

'If 0.20M FeSO4(aq) catalyses reaction (1) **faster** than 0.10 M FeSO4(aq), the rate equation should include [Fe<sup>2+</sup>] and the order of reaction with respect to [Fe<sup>2+</sup>] should be greater than zero.'

#### Industrial processes

#### **Haber Process**

The Haber Process converts nitrogen and hydrogen into ammonia, which is further used to synthesize other compounds. In particular, ammonia is commonly used to make fertilizers since it is high in nitrogen content. The Haber Process has allowed humans to cheaply and efficiently create large amounts of fertilizers, which then further increased humans' food production and allowed the world population to skyrocket in the 20<sup>th</sup> century.

$$N_{2(g)} + 3H_{2(g)} \buildrel \over Finely divided Fe} \buildrel 2NH_{3(g)} \begin{subarray}{l} $\Delta H < 0$ \\ \hline \\ $Finely divided Fe \end{subarray}$$

Haber process chemical equation with conditions

At a temperature lower than 450°C, the rate of reaction is lower because less particles possess energy greater than or equal to the activation energy. At a temperature higher than 450°C, the production is lowered because the forward reaction is exothermic, equilibrium position shift to the reactant side at higher temperatures, lowering the yield.

At low pressures, since the number of moles of gases on the reactant side is less than that on the product side, the equilibrium position will shift to the reactant side, resulting in a low yield. At high pressures, even though the equilibrium position shifts to the product side and increase the yield, the cost for maintaining reaction chambers that can withstand the high pressure becomes expensive, thus making the process uneconomical.

The feedstocks, reactants used for this process are nitrogen gas and hydrogen gas. Nitrogen gas can be obtained through fractional distillation of liquefied air, while hydrogen gas can be obtained through the steam-methane reforming process.

Steam-methane reforming process chemical equation with conditions

The steam-methane reforming process also produces carbon monoxide (CO) as a side product, the mixture of  $H_2$  and CO gas is called *syngas*.

#### Ostwald process

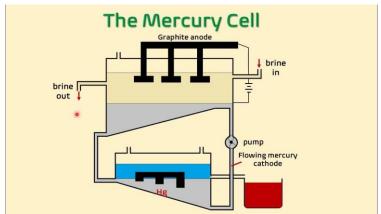
Ammonia produced from the above equation is then treated with the Ostwald process to create nitric acid.

$$\begin{split} 4 \mathrm{NH_{3(g)}} + 5 \mathrm{O_{2(g)}} &\rightarrow 4 \mathrm{NO_{\ g}} \ + 6 \mathrm{H_2O_{\ l}} \\ 2 \mathrm{NO_{\ g}} \ + \mathrm{O_{2(g)}} &\rightarrow 2 \mathrm{NO_{2(g)}} \\ 4 \mathrm{NO_{2(g)}} + \mathrm{O_{2\ g}} \ + 2 \mathrm{H_2O_{\ l}} &\rightarrow 4 \mathrm{HNO_{3(aq)}} \end{split}$$

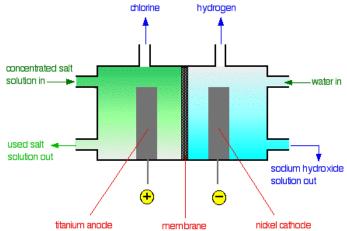
Nitric acid can then react with ammonia to create ammonium nitrate, which is a common fertilizer.

$$HNO_{3 \text{ aq}} + NH_{3 \text{ aq}} \rightarrow NH_4NO_{3(\text{aq})}$$

# Chloroalkali processes



A flowing mercury cell turns its feedstock, brine – concentrated sodium chloride solution into various products by electrolysis. Brine can be obtained from seawater, hence, it is common for chloroalkali plants to be located near the sea as it reduces the transportation cost of the feedstock. Note that the anode is made of graphite instead of platinum since chlorine gas produced will attack and corrode platinum.



Another type of cell used in the chloroalkali industry is the membrane cell. The membrane in the middle only allows cations to pass through but not the chloride anions. The membrane also separates the solution of the two sides and prevents them from mixing together. Compared to the flowing mercury cell, this cell does not require the use of mercury, which is toxic. Moreover, the cell can also operate at a lower voltage, hence consuming less electricity.

Since the concentration of Cl<sup>-</sup> in brine is high, the following reactions occur at both electrodes for the two cells:

	Cathode	Anode
Flowing mercury cell	$\mathrm{Na}_{\mathrm{aq}}^{+} + \mathrm{Hg}_{1} + \mathrm{e}^{-} \rightarrow \mathrm{Na}/\mathrm{Hg}_{1}$	
	Na/Hg <sub>(1)</sub> : Sodium amalgam	$2\text{Cl}_{\text{aq}}^- \to \text{Cl}_{2(g)} + 2\text{e}^-$
$Membrane\ cell$	$2\mathrm{H}^+_{\mathrm{aq}}\ + 2\mathrm{e}^- \to \mathrm{H}_{2(\mathrm{g})}$	

### Production of NaOH

One of the major products of the processes is NaOH, which is a commonly used alkali in industry.

In the flowing mercury cell, Na<sup>+</sup> ions are preferentially discharged to form Na/Hg<sub>(l)</sub> at the cathode, Na/Hg<sub>(l)</sub> then reacts with water to produce NaOH<sub>(aq)</sub>. Sodium hydroxide produced from this process has high purity and concentration.

$$2\mathrm{Na}/\mathrm{Hg_{(1)}} + 2\mathrm{H_2O} \rightarrow 2\mathrm{NaOH}_{\mathrm{\ aq\ }} + 2\mathrm{Hg}_{\mathrm{\ 1}} \, + \mathrm{H_{2(g)}}$$

In the membrane cell,  $H^+$  is preferentially discharged to form  $H_{2(g)}$  at the cathode, so  $OH^-_{(aq)}$  becomes in excess. Na<sup>+</sup> travel through the membrane to reach the cathode compartment of the cell, so NaOH<sub>(aq)</sub> is formed.

### Products of electrolysis of brine

Product	Production method	Use
$ m H_2$	Reduction at cathode of membrane cell	Fuel for rockets, fuel for
	$2\mathrm{H_{aq}^+} + 2\mathrm{e^-} \rightarrow \mathrm{H_{2(g)}}$	hydrogen-oxygen fuel cells
$\mathrm{Cl}_2$	Oxidation at anode of both cells	Sterilizing swimming pools
	$2\text{Cl}_{\text{aq}}^- \to \text{Cl}_{2(g)} + 2\text{e}^-$	
NaOH	See Production of NaOH	Producing caustic soda, drain
		cleaner, etc.
NaOCl	$\mathrm{Cl}_{2~\mathrm{g}}~+2\mathrm{NaOH}_{\mathrm{aq}}$	Bleach/ Bleaching agent
	$ ightarrow$ NaCl $_{ m aq}$ + NaOCl $_{ m aq}$ + H $_{ m 2}$ O $_{ m 1}$	

#### Production of methanol

Methanol is particularly important as it is a one-carbon compounds, which means it is used in organic synthesis commonly to create other compounds or as a solvent. Methanol is also used as a fuel. It is a very clean fuel as its carbon content is very low. Moreover, compared to other low carbon content fuels like methane, methanol is a liquid at room temperature instead of a gas, so it is much easier to store and transport.

Methanol is formed from carbon dioxide and hydrogen, or *syngas*. As mentioned in <u>Haber Process</u>, these two can be obtained from the steam methane reforming process.

After that, methanol can be directly formed by reacting the syngas under the correct conditions.

$$\begin{array}{c} {\rm Cu/ZnO/Al_2O_3} \\ {\rm CO}_{\rm g} \ + 2{\rm H}_{\rm 2(g)} & \rightleftharpoons \quad {\rm CH_3OH}_{\rm g} \\ 250^{\rm o}{\rm C}, 50-100 \ {\rm atm} \end{array}$$

After creating the methanol from the process, it may be mixed with a small amount of water, the methanol can be purified or extracted by simple distillation.