Chem Factsheet

www.curriculum-press.co.uk Number 160

How to Answer AS Questions on Kinetics

First test your basic knowledge and try deciding whether the following statements are true or false:

Statement	True	False
1 The activation energy depends on the temperature of the reaction.		
2 The peak of the Maxwell Boltzmann distribution is at the activation energy.		
3 The Maxwell Boltzmann distribution is a graph of rate of reaction against time.		
4 The higher the temperature the higher the peak of the Maxwell Boltzmann distribution.		
5 Both bond breaking and bond making can be exothermic.		
6 Exothermic reactions may go more slowly with increasing temperature.		
7 Using a catalyst lowers the energy of the transition state.		
8 A catalyst is always a biological enzyme		
9 The units for the rate of reaction may be different for each reaction.		

Only number 7 is true, the others are all false. If you are totally confused, as this Factsheet is an aid to using your knowledge in exams, read Factsheet 10 to revise first.

Reaction rate is defined as the change in concentration of a substance divided by the time taken for that change to take place. This actually gives the *average rate* over that time period – the rate at any particular point in time is given by the gradient of the tangent at that point. The unit of rate is **mol dm^{-3}s^{-1}** and this cannot vary. (However, if a reactant is being used up then the reaction rate will be defined as negative.)

Rates of Reaction and Temperature

All reactions go faster as the temperature is increased.

A common error is to confuse reaction rates with Le Chatelier's Principle which is used to predict effects of changes of conditions on equilibrium position – it plays no part in reaction rates! You may think that *exothermic* reactions go more slowly with increasing temperature, but this is always *in*correct. They *appear to go more slowly* when considering a *reversible* ***exothermic*** *reaction* because the rate of the backward reaction is increasing more rapidly than that of the forward reaction when the temperature is increased.

Activation Energy, E_a

Activation energy is the **minimum** energy required by colliding molecules in order for them to react.

Bond breaking must occur before new bonds can form and it always requires energy. Hence, a reaction cannot occur unless the reactants collide with at least the activation energy. Energy is provided by increasing the temperature or in some cases (e.g. photochlorination) by light energy which is absorbed by the molecule.

Collision Theory

Rate = number of collisions per unit time × fraction of collisions occurring with enough energy (E_a) to be successful.

The main idea here is that reactants must collide and do so with equal to or greater than the activation energy in order for bonds to break and a reaction to occur.

Diagrams

It is often a good idea to include a diagram to aid an explanation. However, these must be well drawn and correctly labelled. The examiner will not credit anything which is not clearly shown.

Extract from Examiners' Report: *"Students who chose not to include a diagram generally struggled to explain some of the points such as activation energy. Weaker students often lost marks through poorly drawn diagrams with inadequate or absent labelling."*

Symbols

It is a good idea to keep to those given in the question. If you have learnt different symbols (e.g. "EA" rather than E_a) and wish to use them, then you must be sure to explain this clearly with no ambiguity.

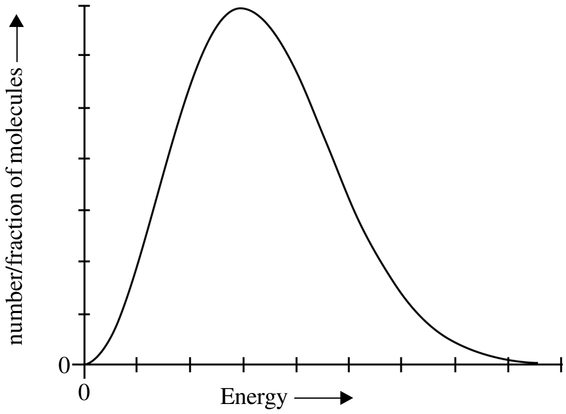
Extract from Examiners' Report: *"Some students failed to use the symbols given in the question, resulting in confusion."*

The Maxwell Boltzmann Distribution

Maxwell Boltzmann distribution is a graph of number (or fraction) of molecules with a given energy (y-axis) plotted against energy (x-axis).

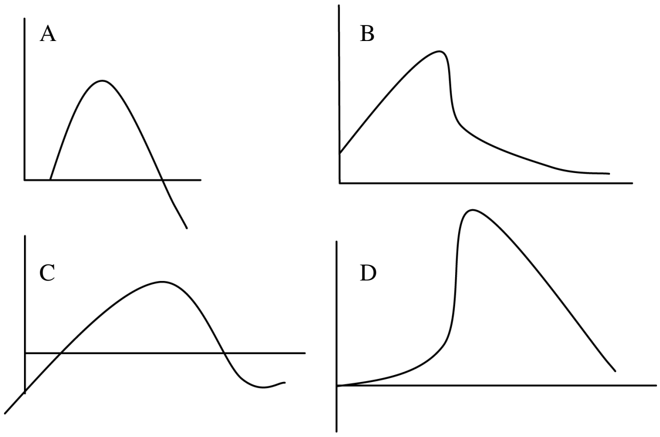
Drawing this Maxwell Boltzmann distribution is a question which examining boards often set and it is worth noting the following points:

1. The graph starts at the origin and ends asymptotically to the x-axis.
2. The activation energy is well to the right of the peak.
3. The curve is not symmetrical – it's skewed to the right.



Exercise

However, it can be difficult to draw accurately, so it is also a good idea to take note of common errors which lose marks. Look at the following and try to draw a ring around the features of each graph which probably would have lost a mark.



Answers

- None of the graphs have their axes labelled!
- Graph A clearly does not start at the origin (minus 1) and ends up crossing into negative number of molecules (minus 1).
- Graph B also does not begin at the origin (minus 1) and then goes straight down from the peak and shows a constant energy value while the number of molecules energy falls to less than half its peak value (minus 1)
- Graph C begins with a negative number of molecules having a negative energy (not possible = minus 1) and shows an increase in number of molecules with a very high energy at the end after the main peak (minus 1)
- Graph D begins too gradually with a slow asymptotical rise and then shows a constant energy while the number of molecules rises by two to three times (minus 1). From the peak it goes downwards in an almost straight line and would eventually cross the x-axis, rather than approaching it asymptotically as required (minus 1).

The Maxwell Boltzmann Distribution and Temperature Change and/or Addition of a Catalyst

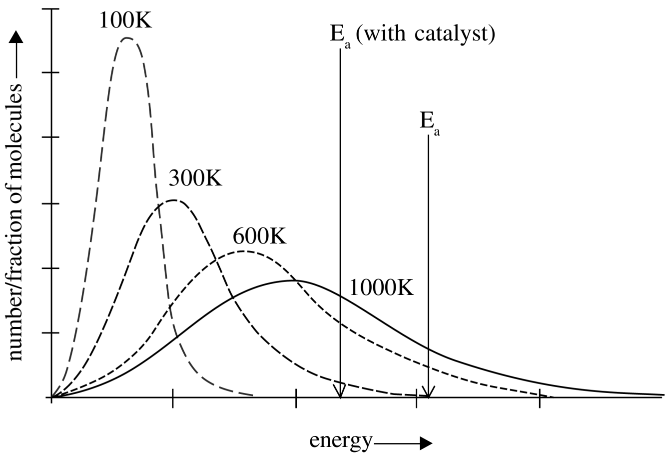
You may be asked to draw curves to compare temperatures and/or the effect of adding a catalyst and also to include the activation energy, so remember:

For *two different temperatures*, the *higher temperature curve* has the *peak to the right and lower*. It crosses the lower temperature curve only once. (Crossing it twice invariably results in loss of a mark.)

The *activation energy* will be the *same for both temperatures* and *well to the right of the peaks*.

The area under each curve should be approximately the same for each temperature since this area represents the total number of molecules in the system – hence, as the peak moves right it must get lower.

If a *catalyst* is used there will be *two activation energies*, *no catalyst* will be *further right*, and there will only be *one curve*. Be sure to mark which activation energy line is which.



The area under the curve to the right of the activation energy line represents the number of molecules which have the amount of energy (E_a) needed to react.

Heterogeneous and Homogeneous Catalysts

A catalyst increases a reaction rate without being altered chemically at the end of reaction. It does this by providing an alternative reaction route with lower activation energy.

When answering exam questions, the ideas that it does this by providing an alternative route with lower energy for the reaction/ lowering the activation energy needed, or it adsorbs/ forms temporary bonds with reagents can gain credit. This means that more molecules/particles at a given temperature will have collisions with sufficient energy to result in a reaction. However, "provides surface" or "extra surface area" are *not* acceptable here.

Extract from Examiners' Report: *"Many long, detailed accounts of how catalysts work gained no credit because the candidates omitted to state their effect on reaction rate! A significant number of candidates believed that all catalysts are biological enzymes."*

A heterogeneous catalyst is not in the same phase/state as the reactants.

An example of this is **solid** platinum in catalytic converters, catalysing the reaction which removes toxic **gases** from exhaust fumes. e.g. $NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$

A homogeneous catalyst is in the same phase/state as the reactants.

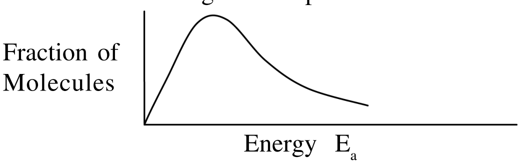
An example of this is the **gaseous** chlorine free radical, $Cl^{\bullet}$, in the stratosphere catalysing the breakdown of **gaseous** ozone to **gaseous** oxygen. i.e. $2O_3 \rightarrow 3O_2$.

Measuring Rates of Reaction

The stoichiometry of the reaction (that is how much of each reactant and product is involved) must first be known. Then a method must be devised for measuring the amount of product formed (or reactant used up) as the reaction proceeds. If a coloured product or reactant is involved then spectrophotometry may be used. This measures the amount of light of a particular wavelength that can pass through a sample. If a gas is being produced then the pressure or volume produced with time can be monitored. A change in acidity or basicity can be monitored by sampling, freezing and carrying out suitable titrations as the reaction proceeds.

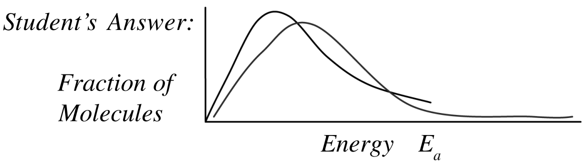
Sample Student Worked Question

(a) The diagram below shows the energy distribution of reactant molecules at a given temperature.



(i) Draw a second curve on the diagram to show the energy distribution of the same number of molecules at a higher temperature. (2 marks)

Student's Answer:



Comments: The curve starts almost at (0,0) and does have its' maximum at a lower value than the given curve so gains one mark (assuming that the deviation from the origin at the starting point is allowed). The maximum is to the right of the given curve, but the curve crosses the given curve twice and so the second mark is not given. If it had come down from the peak much less sharply and carried on above the given line, then the second mark would have been given. (This would also have ensured that more molecules had energies greater than the activation energy, at the higher temperature.)

(ii) Use your diagram to explain how increasing the temperature can cause the reaction rate to increase. (2 marks)

Student's answer. There are more molecules to the left of E_a and so there is more of a reaction.

Comments: This answer gains no marks, partly due to the candidate trying to fit the answer to an incorrect graph. If there are problems explaining the curve you have drawn, then probably the curve is wrong! The answer should be that there is a larger area to the right of E_a meaning there are more molecules with an energy greater than the activation energy (1 mark) [Note: If you have drawn a poor graph why not try 'There **should be** a larger area to the right of E_a meaning there are more molecules with an energy greater than the activation energy] and so there are more successful/effective_collisions per second (1 mark). The statement 'more of a reaction' is far too vague to gain any credit, as is 'more collisions'.

(iii) Explain the effect of adding a catalyst. (2 marks)

Student's answer. More molecules will have enough energy and react.

Comments: The student's statement is true but is not an explanation and 'enough energy' is too vague. The activation energy is lowered by providing an alternative reaction route with lower activation energy. This could be shown on the graph as $E_{a(cat)}$ to the left of E_a (1 mark). This means that more of the molecules have greater than the activation energy, so there will be more successful collisions per second. (1 mark)

(b) When hydrogen reacts with oxygen, the rate of reaction depends on the pressure as well as the temperature.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\quad \Delta H = -285\ kJmol^{-1}$

(i) Explain the effect of increasing the pressure on the rate of this reaction. (2 marks)

Student's answer. The concentration of the molecules is greater and so the reaction rate is greater as the pressure is increased.

Comments: The student has correctly stated that the reaction rate increases with pressure and so gains one mark. For the second mark the idea that the molecules are closer together as the pressure increases is needed.

(ii) This reaction involves a sudden rapid increase in the rate of a reaction causing an explosion to occur. Why are highly exothermic reactions such as this one more likely to explode than other reactions? (2 marks)

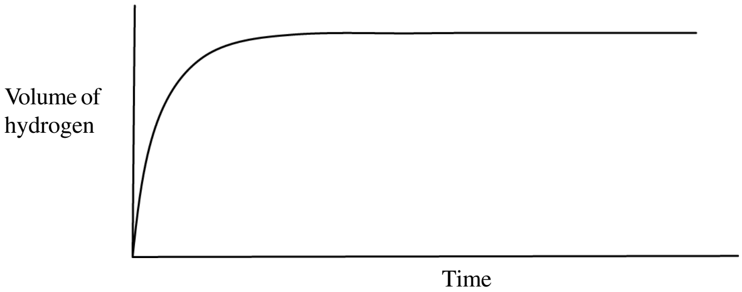
Student's answer. The molecules have a lot more energy than the activation energy, so a lot more react at the same time.

Comments: This answer gains no marks. The ideas needed are that after the reaction has started the energy given out in the exothermic reaction causes the temperature/energy/speed of the molecules to increase (1 mark) and the idea that many more molecules then have $E>E_a$ which causes the reaction to speed up (1 mark).

Practice Questions

1. State and explain the effect on the rate of reaction of the following factors:
   (a) pressure/concentration
   (b) surface area
   (c) temperature
   (d) catalyst.
   Maximum 10 marks

2. The rate of reaction between magnesium and hydrochloric acid was found by measuring the volume of hydrogen formed as the reaction progressed.



   Add a line to the graph to show the effect of a lower temperature. (2 marks)

3. Refer to the Maxwell Boltzmann distribution to explain the effect on the rate of reaction of the following:
   (a) temperature increase (3 marks)
   (b) a catalyst (3 marks)
   [Here a diagram is an excellent idea, providing it is accurate and labelled.]

Answers

The following points are creditworthy:

1. (a) Increase of pressure/concentration causes more particles to collide per second (1 mark), because particles are closer together (1 mark). This means there are also more successful collisions per second (1 mark).

   (b) Increased surface area gives more particle collisions (1 mark) so there will be more successful collisions and the rate will increase (1 mark).

   (c) Increase in temperature means that particles have more energy, greater kinetic energy or greater velocity (1 mark), rate increases as temperature increases (1 mark), the increase in rate with temperature is exponential or rapid (1 mark), small increase in temperature causes a large increase in the number of molecules with $E > E_a$ (1 mark), more successful collisions (1 mark).

   (d) A catalyst provides and alternative route (1 mark) of lower activation energy (1 mark) and so there are more molecules with $E > E_{a\,(cat)}$ (1 mark).

2. The line should: begin at (0,0) and have a lower gradient, reaching its maximum after a longer time (1 mark), and level off at the same value on the y axis as the graph given (1 mark).

3. Note: an answer which does not refer to the Maxwell Boltzmann distribution will gain little or no credit.

   (a) The increase in temperature causes the rate of reaction to increase. (1 mark)

   The peak of the Maxwell Boltzmann Distribution is shifted to the right, i.e. to higher energy. (1 mark) There is more area under the curve to the right of the activation energy and this means that there are more molecules which have the activation energy necessary for the reaction to occur, and thus more collisions per second are successful. (1 mark)

   (b) The catalyst increases the rate of reaction. (1 mark)

   The activation energy is lowered (as a result of the catalyst causing the reaction to follow a different reaction route). That is, it is moved to the left on the x-axis (energy) of the Maxwell Boltzmann distribution. (1 mark) This means that there is more area under the curve to the right of the catalysed activation energy, thus more molecules have the activation energy needed and more collisions per second occur with the activation energy and are successful. (1 mark)

Acknowledgements: *This Factsheet was researched and written by Christine Collier.*
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ISSN 1351-5136