Kinetics

Review

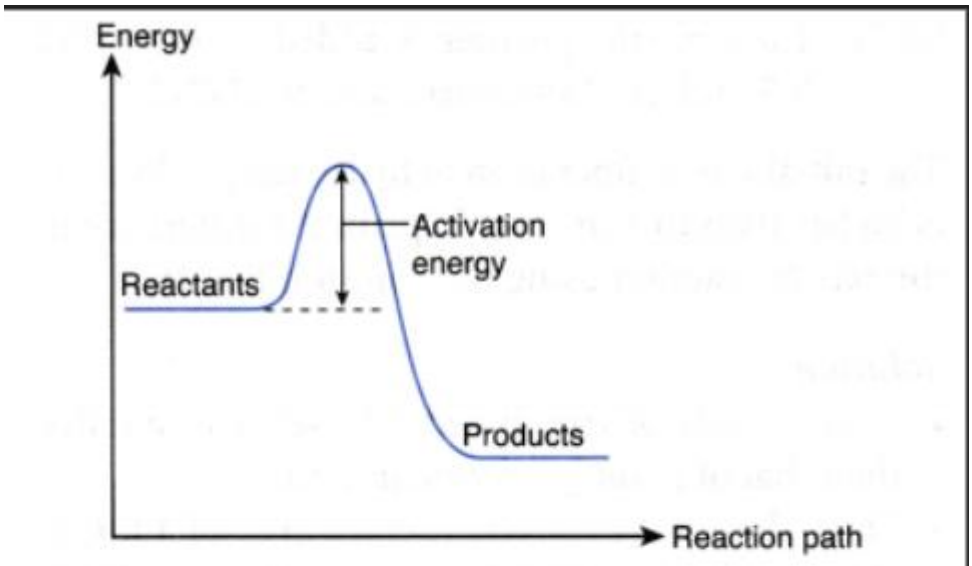


Figure *Energy profile diagram for exothermic reaction*

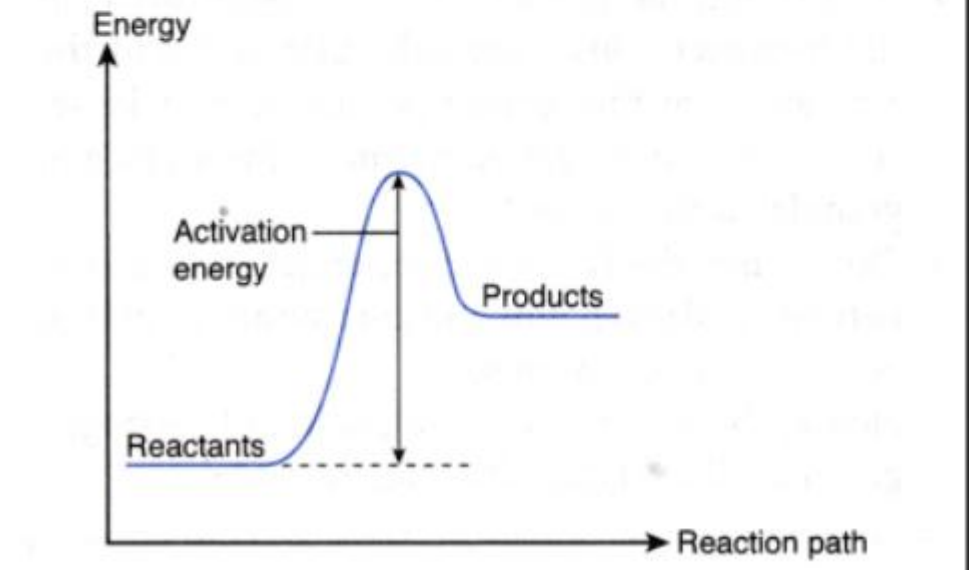


Figure *Energy profile diagram for endothermic reaction*

1.Rate of reaction

When we talk about the rate of a chemical reaction, what we mean is the rate at which reactants are used up, or equivalently the rate at which products are formed. The rate therefore has units of concentration per unit time, mol dm^{-3} s^{-1}

To measure a reaction rate, we simply need to monitor the concentration of one of the reactants or products as a function of time.

$$\text{rate} = \frac{\text{change in amount of reactants or products}}{\text{time}}$$

The factors affecting the rate of reaction between aqueous sodium thiosulfate and hydrochloric acid can be investigated. The ionic equation for the reaction is shown.

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

Which of the following can be used to investigate the rate of this reaction?

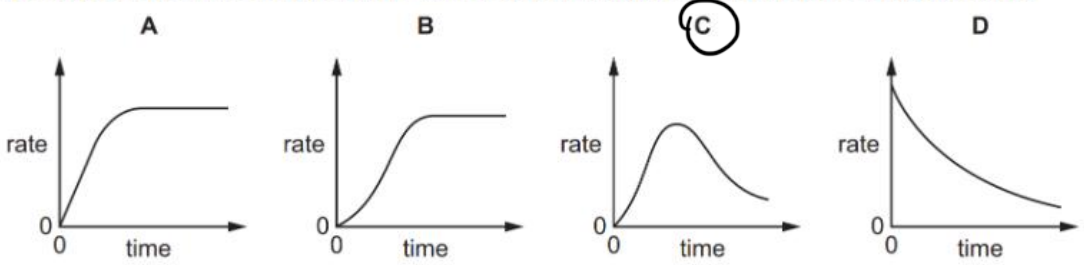
1 change of mass ∈ no change!

2 change of appearance caused by formation of a precipitate

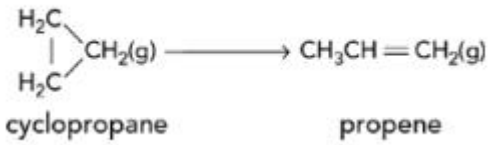
3 change of electrical conductivity

An autocatalytic reaction is a reaction in which one of the products catalyses the reaction.

Which curve would be obtained if the rate of an autocatalytic reaction is plotted against time?



2.Calculating rate of reaction graphically



cyclopropane propene

Figure 9.5 shows how the concentration of propene changes with time.

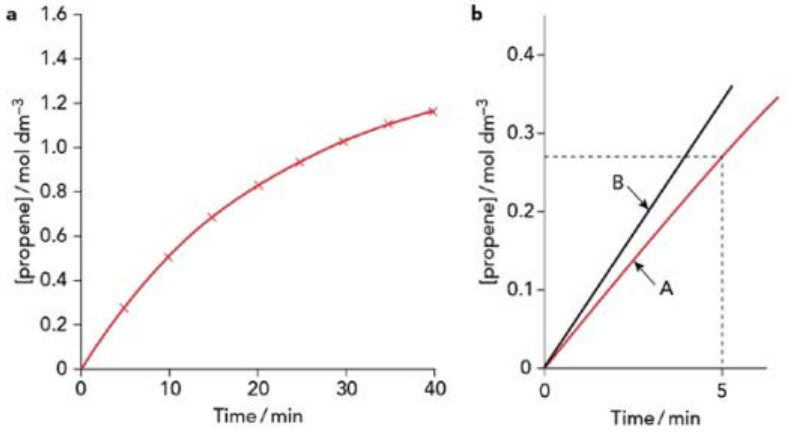
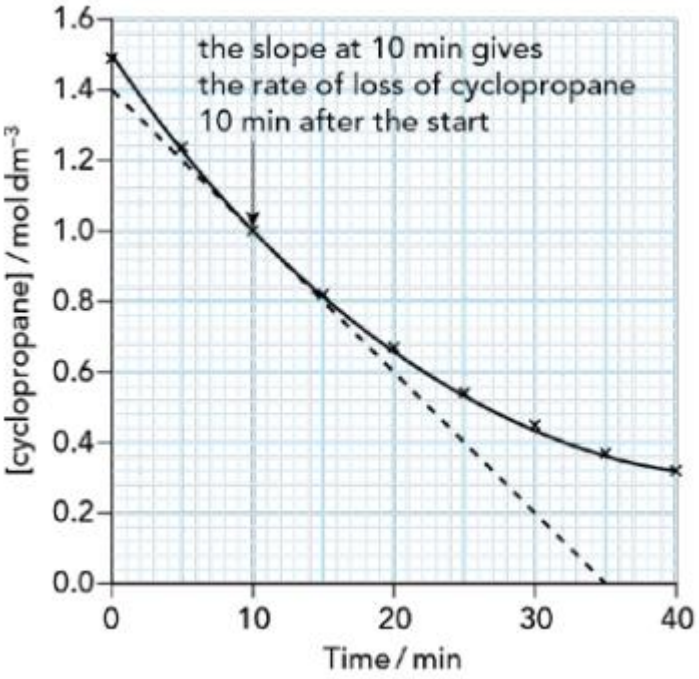
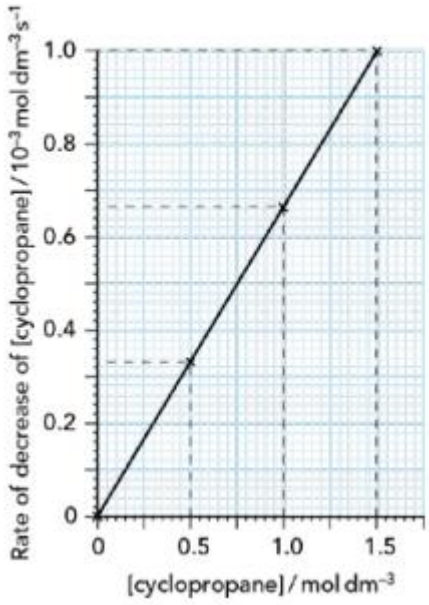


Figure 9.5: How the concentration of propene changes with time in the reaction cyclopropane → propene. **a** the whole curve. **b** The first part of the curve magnified. Line A shows the average rate over the first 5 minutes. Line B shows the actual initial rate found by drawing a tangent at the start of the curve.



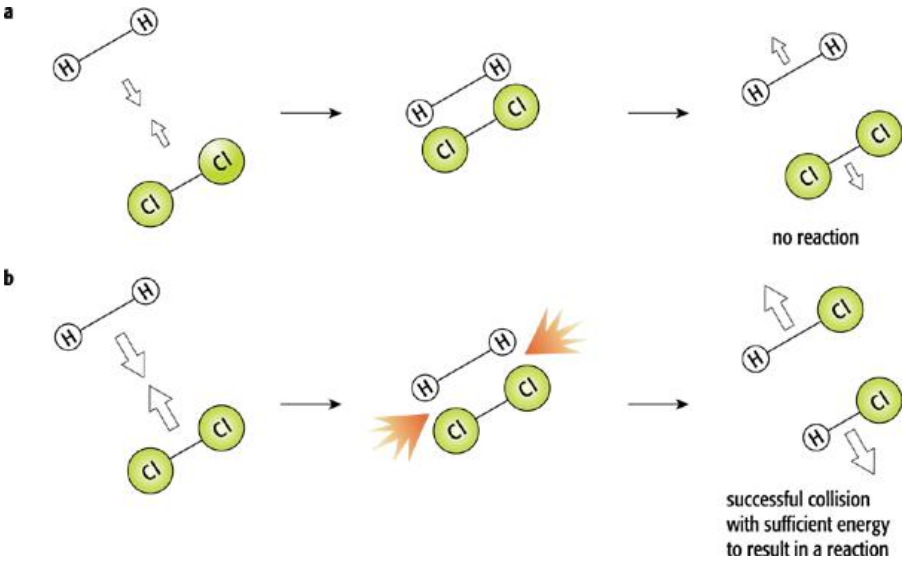


the rate is directly proportional to the concentration of cyclopropane.

3.Collision theory

Collision theory states that in order to react with each other, particles must collide in the correct orientation and with sufficient energy. The particles might be atoms, ions or molecules.

effective collision



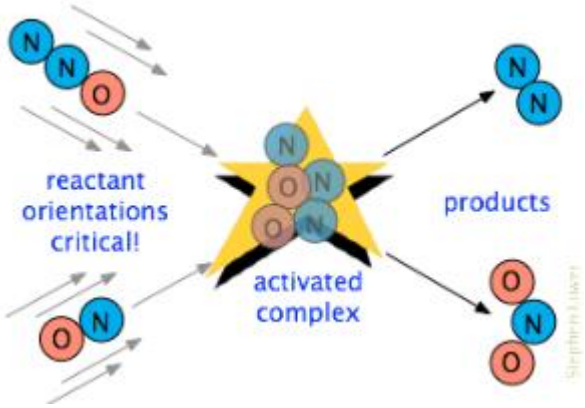
According to the collision theory, a reaction will speed up if:

speed (energy)
direction
Collision

UNSUCCESSFUL COLLISION AS PARTICLES DID NOT COLLIDE WITH ENOUGH ENERGY

SUCCESSFUL COLLISION AS PRODUCT MOLECULES WERE FORMED INDICATING THE ENERGY WITH WHICH THE PARTICLES COLLIDED WAS GREATER THAN THE ACTIVATION ENERGY

Not all Collisions are Equal

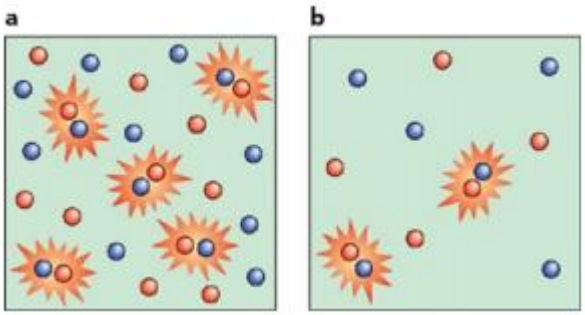


There is often one additional requirement. In many reactions, especially those involving more complex molecules, the reacting species must be oriented in a manner that is appropriate for the particular process. For example, in the gas-phase reaction of dinitrogen oxide with nitric oxide, the oxygen end of N2O must hit the nitrogen end of NO; altering the orientation of either molecule prevents the reaction. Owing to the extensive randomization of molecular motions in a gas or liquid, there are always enough correctly-oriented molecules for some of the molecules to

react. However, the more critical this orientational requirement is, the fewer collisions will be effective.

Conditions for generating effective or successful collision

The effect of concentration on rate of reaction



A chemical company used a catalyst in a chemical process. The company has now decided not to use the catalyst but to increase the temperature so that the rate of the reaction is the same as it was when the catalyst was used.

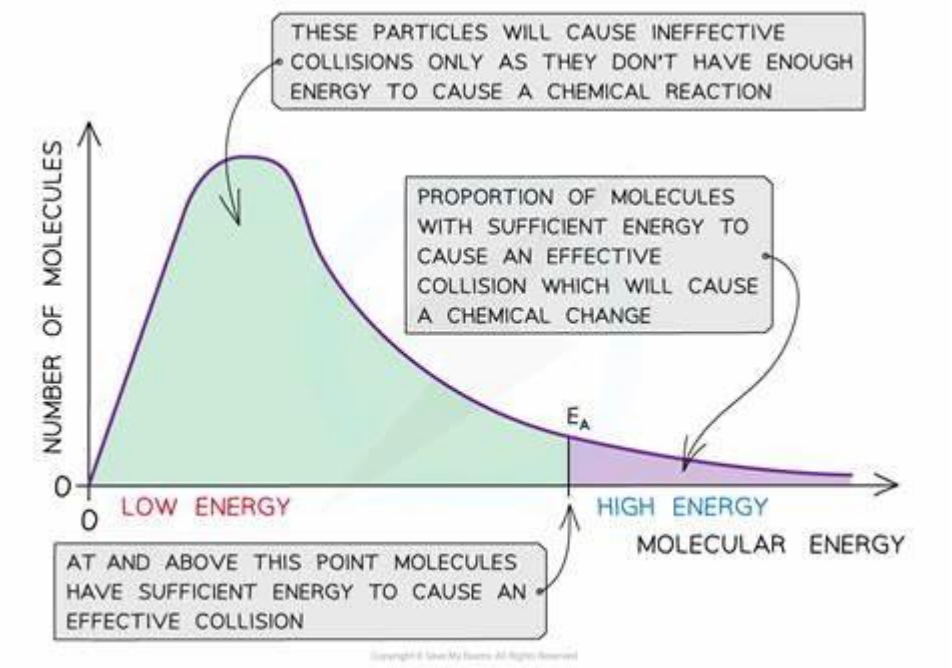
Which statement about the new conditions compared to the original conditions is correct?

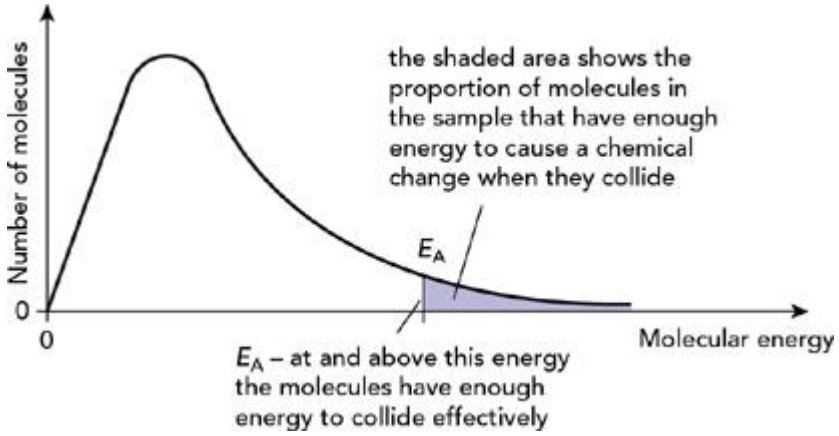
A. The activation energy has been decreased.
B. The activation energy has been increased.
C. There are fewer successful collisions per unit time.
D. There are more successful collisions per unit time.

The effect of temperature on rate of reaction

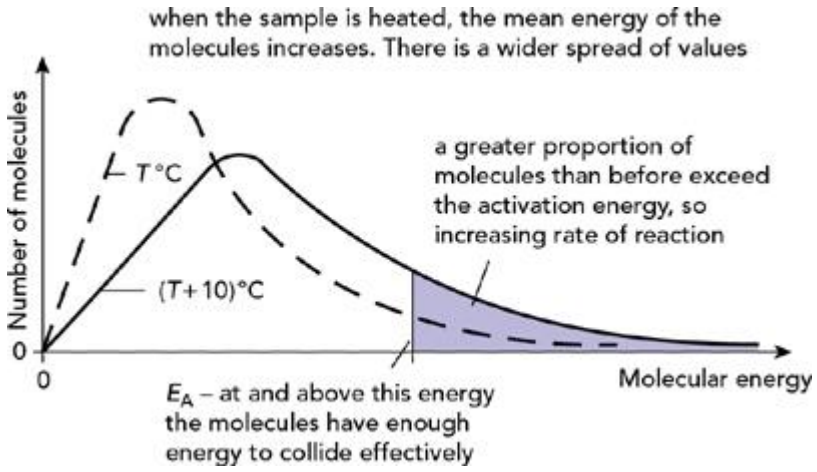
In a sample of any substance, at a given temperature, the particles will not all possess the same amount of energy as each other. A few particles will have a relatively small amount of energy. A few particles will have a relatively large amount of energy. Most particles will have an amount of energy somewhere in between.

The distribution of energies at a given temperature can be shown on a graph (see Figure 9.15). This is called the Boltzmann distribution.





We have seen that the activation energy is defined as the minimum energy required for colliding particles to react. When we raise the temperature of a reaction mixture, the average kinetic (movement) energy of the particles increases. Particles in solution and in gases will move around more quickly at a higher temperature, resulting in more frequent collisions.



A large excess of marble chips is reacted with 25 cm^3 of 1.0 mol dm^{-3} hydrochloric acid at 40 °C.

How is the result different when the reaction is repeated with 60 cm^3 of 0.5 mol dm^{-3} hydrochloric acid at 40 °C?

A. The reaction is faster and more of the products are made when the reaction is complete.

B. The reaction is faster and less of the products are made when the reaction is complete.

C. The reaction is slower and more of the products are made when the reaction is complete.

D. The reaction is slower and less of the products are made when the reaction is complete.

Ammonia is made by the Haber process. The reactants are nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H \text{ is negative}$$

What will increase the rate of the forward reaction?

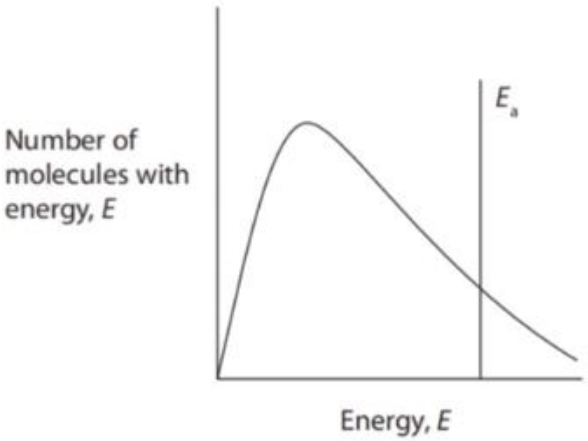
A. adding argon to the mixture but keeping the total volume constant
B. decreasing the temperature
C. increasing the total pressure by reducing the total volume at constant temperature
D. removing ammonia as it is made but keeping the total volume of the mixture the same

Which factors can lead to an increase in the rate of a reaction?

1. a lower activation energy
2. an increase in temperature
3. an increase in the concentration of a reactant

A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

The diagram below is a Maxwell-Boltzmann distribution of molecular energies.



(a) If the temperature was raised, what would be the effect on the shape of the curve?

- ☒ **A** The peak would shift to the left and be higher.
- ☒ **B** The peak would shift to the left and be lower.
- ☒ **C** The peak would shift to the right and be higher.
- ☒ **D** The peak would shift to the right and be lower.

The height of the peak of the curve in a Boltzmann distribution represents the number of molecules that have the most probable energy.

A sample of gas has its temperature decreased without changing the number of molecules present.

Which statement correctly describes a feature of the Boltzmann distribution for the gas when the temperature decreases?

A. The value of the most probable energy would stay the same.
B. The number of molecules with the most probable energy would increase.
C. The area under the molecular energy distribution curve would decrease.
D. The number of molecules at the very high energy end of the distribution would stay the same.

Methanol, CH_3OH, can be produced industrially by reacting CO with H_2.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -91 \text{ kJ mol}^{-1}$$

The process can be carried out at 4×10^3 kPa and 1150K.

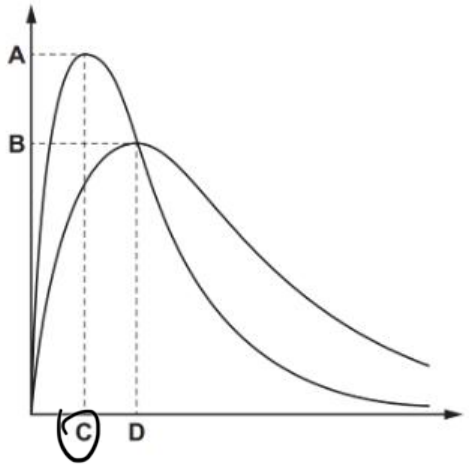
Which statements about this reaction are correct?

1. Increasing the temperature will increase the rate of reaction because more effective collisions will occur.
2. Lowering the temperature will reduce the rate of reaction because the forward reaction is exothermic.
3. Increasing the pressure will reduce the rate of reaction because there are a larger number of moles on the left-hand side of the equation.

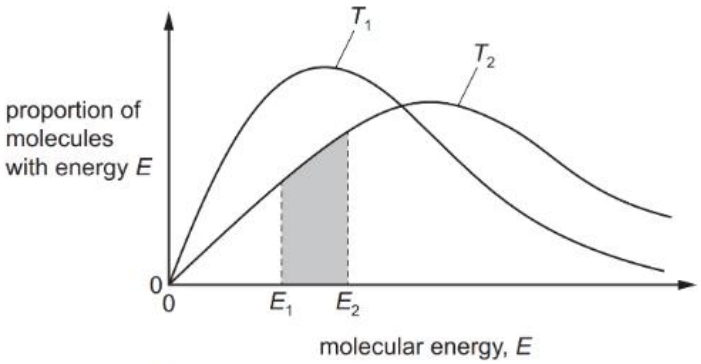
A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

The diagram shows the Boltzmann energy distribution curves for molecules of a sample of a gas at two different temperatures.

Which letter on the axes represents the most probable energy for molecules of the same sample of gas at the **lower** temperature?



The diagram shows the Boltzmann distribution of molecular energies in one mole of a gas at two temperatures, T_1 and T_2.



Which statements are correct?

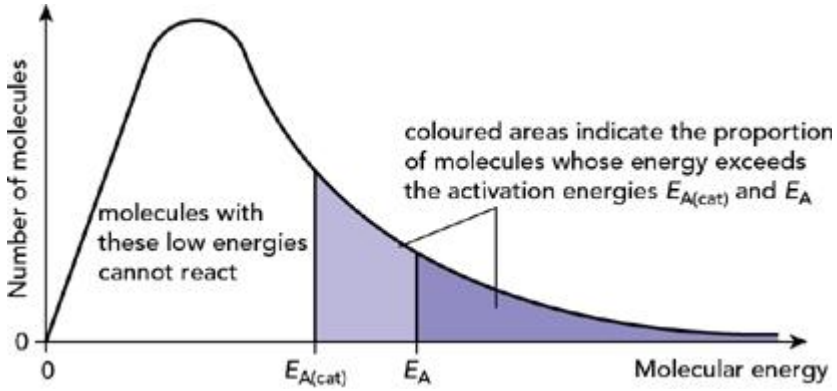
1. The shaded area represents the proportion of molecules with energies between E_1 and E_2 at temperature T_2.
2. No particles have zero energy at either temperature.
3. T_2 is a higher temperature than T_1.

A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

Catalysts increase the rate because they make the reaction go by a different reaction pathway (mechanism) that has a lower activation energy than the uncatalysed reaction.

The presence of a catalyst does not affect the shape of the Boltzmann distribution.

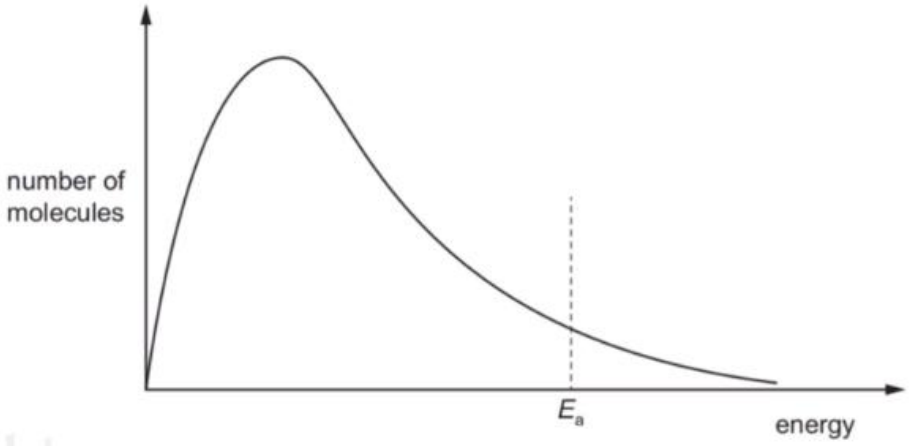
Therefore, the rate at which effective collisions occur, and so the rate of the catalysed reaction, is greatly increased compared with the rate of the uncatalysed reaction.



The Haber process involves a reaction between nitrogen and hydrogen at a temperature of 450 °C and a pressure of 20 000 kPa. At a higher reaction temperature, the rate of production of ammonia would be greater.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3 \qquad \Delta H = -92\,kJ\,mol^{-1}$$

The Boltzmann distribution curve shows the distribution of energies in a mixture of nitrogen and hydrogen at 450 °C.



(i) Sketch a second line onto the axes above to show the distribution of energies in the same mixture of gases at a higher temperature. [2]

(ii) With reference to the two curves, explain why the rate of production of ammonia would be greater at a higher temperature.

.....

.....

..... [2]

(iii) Add a suitable label to the horizontal axis above and use it to explain why a catalyst is used in the Haber process.

.....

.....

..... [2]

Disaccharides are hydrolysed in slightly acidic solutions. This reaction is very slow.

A biological catalyst is added to a slightly acidic mixture of three disaccharides, sucrose, maltose and lactose. The hydrolysis reaction remains slow for sucrose and maltose but is now much faster for lactose.

Which statements about the catalyst are correct?

1. The catalyst increases the activation energy of all three hydrolysis reactions.
2. The catalyst shows specificity.
3. The hydrolysis of lactose using a catalyst has a different mechanism to the hydrolysis of lactose without a catalyst.

A. **1**, **2** and **3** are correct
B. **1** and **2** only are correct
C. **2** and **3** only are correct
D. **1** only is correct

Hydrogen chloride gas is formed by the reaction shown.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

What will change the average kinetic energy of the reacting gas particles?

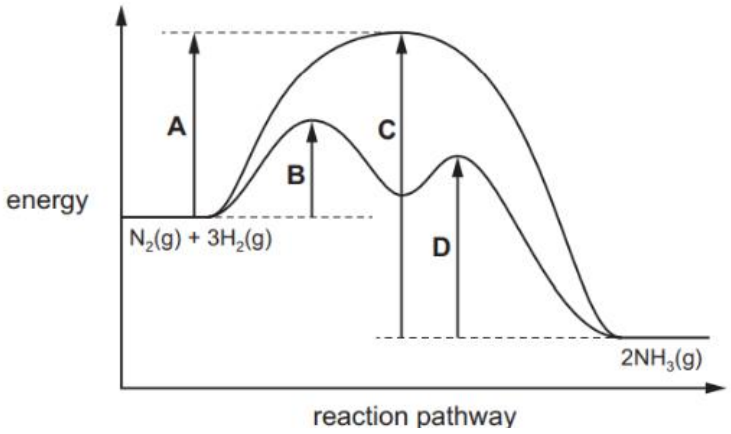
1. increasing the temperature and increasing the concentration of hydrogen
2. cooling the reaction mixture and adding a catalyst
3. adding a catalyst and increasing the concentration of chlorine

A. **1**, **2** and **3** are correct
B. **1** and **2** only are correct
C. **2** and **3** only are correct
D. **1** only is correct

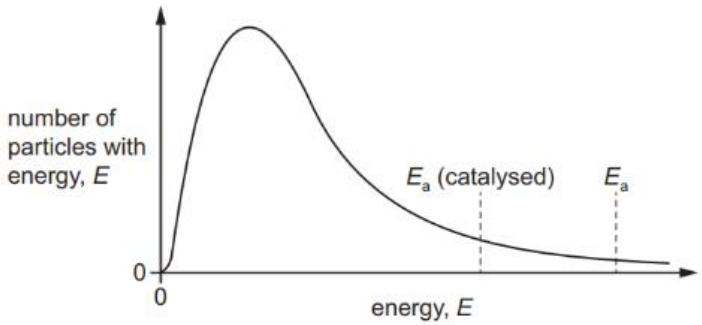
The reaction pathway diagram for the catalysed reaction and the uncatalysed reaction between N_2 and H_2 is shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Which letter represents the activation energy for the first step in the decomposition of NH_3 in the presence of a catalyst?



The Boltzmann distribution curve for a gaseous mixture of ethene and hydrogen is shown. Nickel is an effective catalyst for the reaction that occurs.



How does the diagram appear if the same reaction mixture is at a higher temperature?

A. The curve is unchanged.

B. The values of both E_a (catalysed) and E_a decrease.

C. The values of both E_a (catalysed) and E_a increase.

D. The values of both E_a (catalysed) and E_a remain the same.

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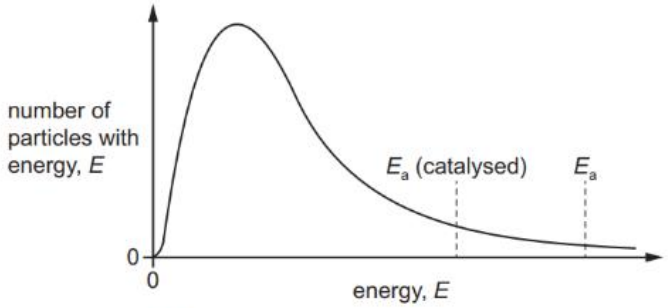

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D. The values of both E_a (catalysed) and E_a remain the same.

Vanadium and pepsin can both act as catalysts. Vanadium is a metal. Pepsin is an enzyme.

Which statements are correct for **both** vanadium and pepsin?

1. They will speed up any chemical reaction.
2. They can lower the activation energy for a reaction.
3. They are not used up when they act as catalysts.

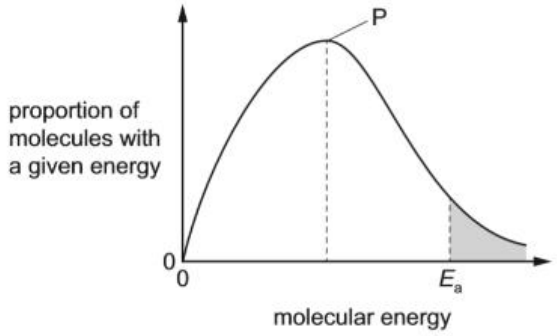
A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

The temperature of a sample of an inert gas is increased.

What effect does this have on the number of molecules with the most probable energy and on the number of molecules with high energy?

	number of molecules with the most probable energy	number of molecules with high energy
A	decreases	decreases
B	decreases	increases
C	increases	decreases
D	increases	increases

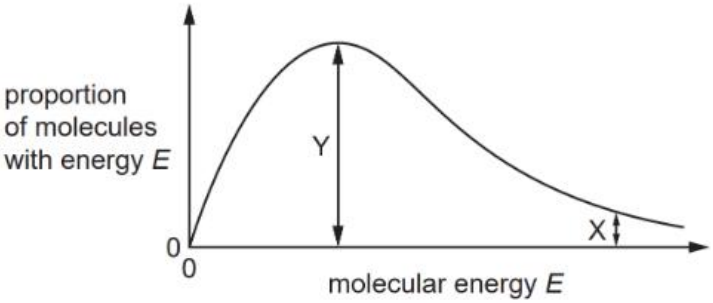
The diagram shows the Boltzmann distribution of energies in a gas. The gas can take part in reaction with an activation energy, E_a. The gas is maintained at a constant temperature.



Which statement is correct?

A. If a catalyst is added, peak P will be lower and E_a will move to the left.
B. If a catalyst is added, peak P will be lower and E_a will move to the right.
C. If a catalyst is added, peak P will be the same and E_a will move to the left.
D. If a catalyst is added, peak P will be the same and E_a will move to the right.

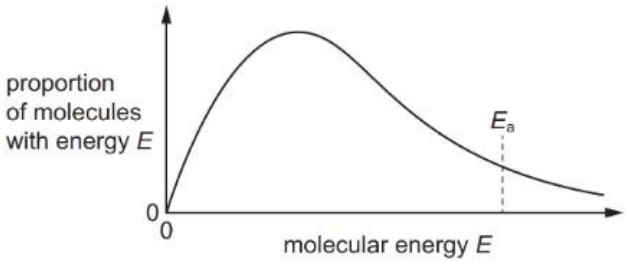
The diagram shows the Boltzmann distribution of the energy of gaseous molecules at a particular temperature.



Which statement is correct?

A. If the temperature of the gas is raised, the height of the maximum of the curve increases.
B. If the temperature of the gas is raised, the maximum of the curve moves to the right.
C. The length of the line labelled X shows the activation energy for the reaction.
D. The length of the line labelled Y shows the enthalpy change of the reaction.

The Boltzmann distribution for the hydrogenation of an alkene at a particular temperature in the absence of a catalyst is shown.



Which row correctly describes the effects of adding nickel to the reaction vessel?

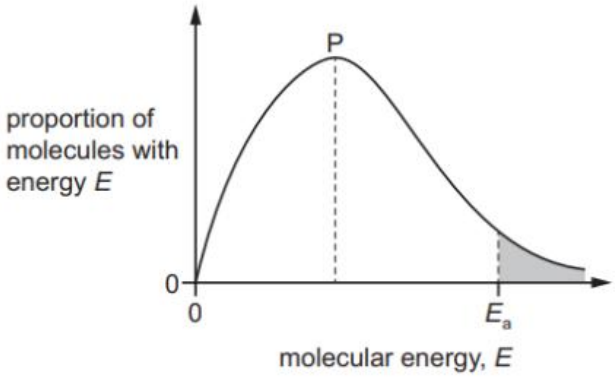
	the shape of the Boltzmann distribution	activation energy, E_a
A	changes	decreases
B	changes	increases
C	does not change	decreases
D	does not change	increases

In a chemical system the particles involved have a range of energies. This can be shown on a graph called the Boltzmann distribution.

Which statement correctly explains the effect of a catalyst on the particles in a chemical system?

A. A catalyst enables particles with a lower energy to collide successfully.
B. A catalyst increases the number of particles with higher energies.
C. A catalyst increases the number of particles with the most probable energy value.
D. A catalyst increases the value of the most probable particle energy.

The diagram shows the Boltzmann distribution of energies in a gas. The gas undergoes a reaction with an activation energy, E_a. The peak of the distribution is labelled P.



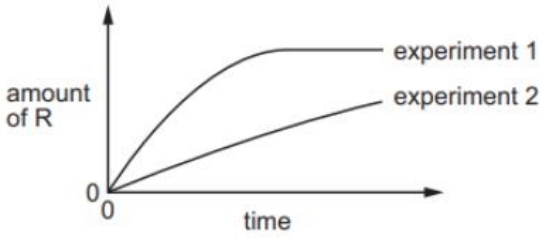
If the same reaction is carried out in the presence of a catalyst, which statement is correct?

A. The peak P is at a lower height and the position of E_a moves to the left.
B. The peak P is at a lower height and the position of E_a moves to the right.
C. The peak P remains at the same height and the position of E_a moves to the left.
D. The peak P remains at the same height and the position of E_a moves to the right.

The stoichiometry of a catalysed reaction is shown by the equation below.

$$P(g) + Q(g) \rightleftharpoons R(g) + S(l)$$

Two experiments are carried out in which the amount of R is measured. The results are shown in the diagram.



Which changes in the conditions could explain the results shown?

1. A lower pressure was used in experiment 2.
2. A different catalyst was used in experiment 2.
3. Product S was continuously removed from the reaction vessel in experiment 2.

A. **1, 2** and **3** are correct
B. **1** and **2** only are correct
C. **2** and **3** only are correct
D. **1** only is correct

4. Homogeneous and heterogeneous catalysts

Reactions that are facilitated by catalysts can be divided into two major classes: homogeneous catalysis and heterogeneous catalysis.

A homogeneous catalyst is present in the same phase as the reactants.

A heterogeneous catalyst is present in a different phase from the reactants.

Catalytic converter

$$2NO + 2CO \xrightarrow{Ni} 2CO_2 + N_2$$

5. Summary