Reaction Kinetics Discussion Questions

1 The initial rate of the reaction **X** + **Z** $\longrightarrow$ **P** + **Q** was measured as a function of the concentration of each reactant. The following results were obtained:

Expt	[**X**] / mol dm^{-3}	[**Z**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.30	9.0×10^{-3}
2	0.20	0.40	12.0×10^{-3}
3	0.40	0.40	48.0×10^{-3}

(a) Determine the order of reaction with respect to **X**, **Y** and **Z**.

Comparing expt 1 and 2 where [X] and [Y] are the same.

When $\frac{[Z]_{expt2}}{[Z]_{expt1}} = \frac{0.40}{0.30} = \frac{4}{3}$, $\frac{Rate_2}{Rate_1} = \frac{12}{9} = \frac{4}{3}$

Hence 1st order wrt Z.

Comparing expt 2 and 3 where [Y] and [Z] are the same.

When $\frac{[X]_{expt3}}{[X]_{expt2}} = 2$, $\frac{Rate_3}{Rate_2} = 4$

$\Rightarrow$ Rate α $[X]^2$

Hence 2nd order wrt X

(b) Write the rate equation.

Rate = $k[X]^2[Z]$

2 The kinetics of the reaction between iodide and peroxodisulfate can be investigated by varying the volume of the reactants used. The two reactants are mixed in the presence of a known amount of $Na_2S_2O_3$ and a little starch. The time taken for an intense blue colour to be observed is then determined.

Experiment	Volume used/cm^3			t/s
	1.0 mol dm^{-3} KI	0.040 mol dm^{-3} $Na_2S_2O_8$	H_2O	
1	10.0	5.0	25.0	170
2	15.0	5.0	20.0	113
3	15.0	10.0	15.0	57
4	20.0	20.0	0.0	x

What is the value of x?

A 21 **B** 28 **C** 85 **D** 63

Rate $\propto \frac{1}{time\ taken}$

Expt	Volume used/cm^3			t/s	$\frac{1}{time\ taken}$
	1.0 mol dm^{-3} KI	0.040 mol dm^{-3} $Na_2S_2O_8$	H_2O		
1	10.0	5.0	25.0	170	$\frac{1}{170}$ = 0.00588
2	15.0	5.0	20.0	113	$\frac{1}{113}$ = 0.00885
3	15.0	10.0	15.0	57	$\frac{1}{57}$ = 0.01754
4	20.0	20.0	0.0	x	

Comparing expt 1 and 2 where [$Na_2S_2O_8$] is the same. When [KI] × 1.5, rate also × 1.5.

Hence it is 1st order wrt KI.

Comparing expt 2 and 3 where [KI] is the same. When [$Na_2S_2O_8$] × 2, rate also × 2.

Hence it is 1st order wrt $Na_2S_2O_8$

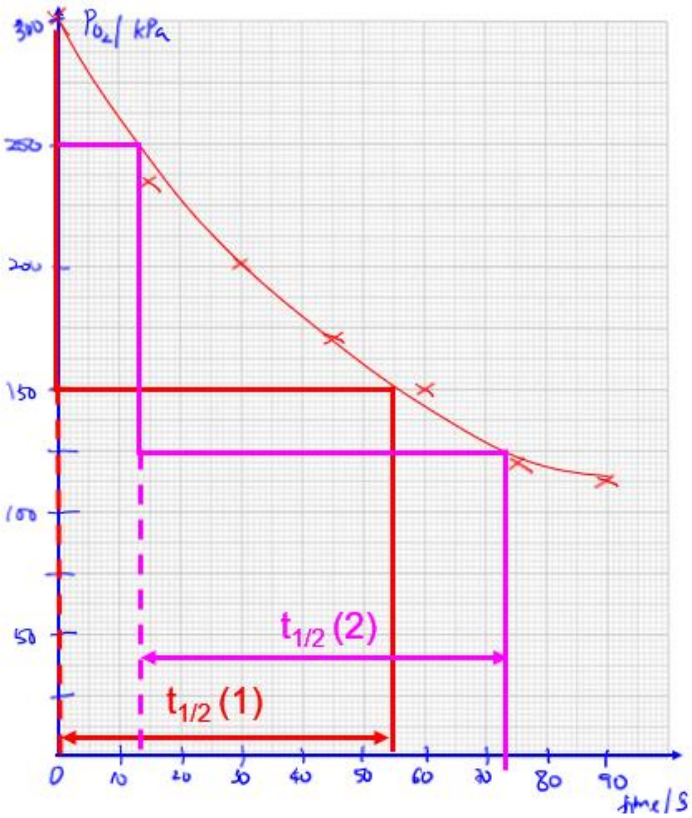
Rate = *k*[KI][$Na_2S_2O_8$]

Comparing Expt 1 and 4,
When [KI] × 2, and [$Na_2S_2O_8$] × 4, rate is 2×4 = 8 times of expt 1.
Rate of expt 4 = 8 × 0.00588 = 0.0470

$\frac{1}{x}$ = 0.0470, x = 21.3 s
Answer is A

3 The following reaction is monitored by measuring the changes in total pressure during the reaction, with initial pressure of O_2 at 300 kPa.

$$3O_2(g) \rightarrow 2O_3\ (g)$$



Determine the order of reaction with respect to oxygen

As shown in the graph,

$t_{1/2}$ (1) is 55s (from 300 kPa to 150 kPa)

$t_{1/2}$ (2) is 59s (from 250 kPa @ t =14 to 125 kPa @ t=73)

As the reaction proceeds, P_{O2} decreases and hence $[O_2]$ decreases.

It is observed that the rate of reaction decreases with a <u>constant half-life of 57s.</u>

Hence it is first order w.r.t O_2.

4 Explain, using collision theory, how the following changes can affect the initial reaction rate of a gaseous system.

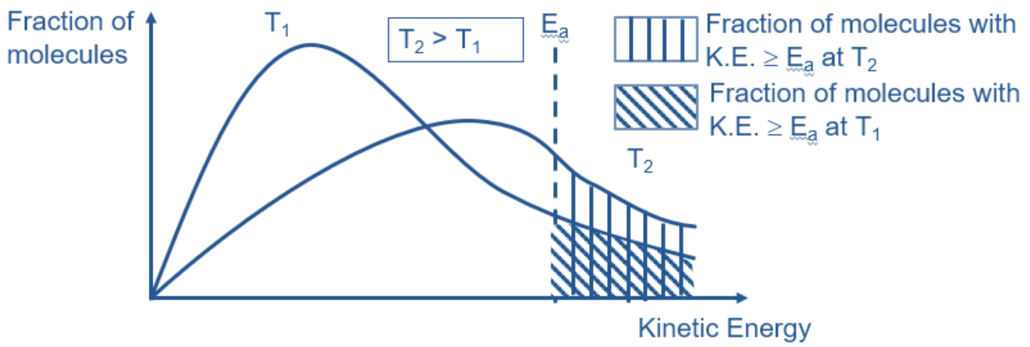
Illustrate your answer with the Boltzmann distribution curve for parts **(ii)** and **(iii)**.

(i) increasing the pressure

There is greater no of particle per unit volume leading to <u>greater collision frequency</u> therefore <u>frequency of effective collision increases</u> leading to <u>increase in rate</u>.

Note: Assumption made that increase in total pressure comes from smaller volume.

(ii) decreasing the temperature

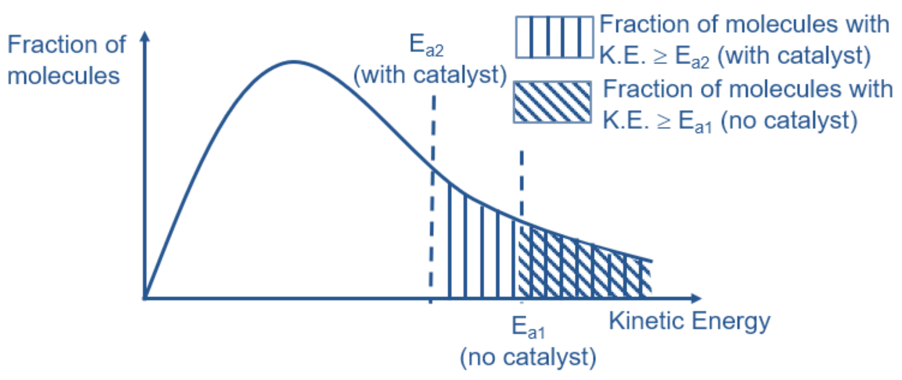


As the temperature decreases, the average kinetic energy of the particles decreases.

There are less particles with kinetic energy equal or greater than the activation energy as shown in the Boltzmann distribution.

This result in lower frequency of effective collisions. Hence rate of reaction decreases.

(iii) addition of a catalyst



In the presence of catalyst, the reaction proceeds with an alternative reaction pathway of lower activation energy(E_a').

There are more particles with kinetic energy equal or greater than the lowered activation energy as shown in the Boltzmann distribution curve.

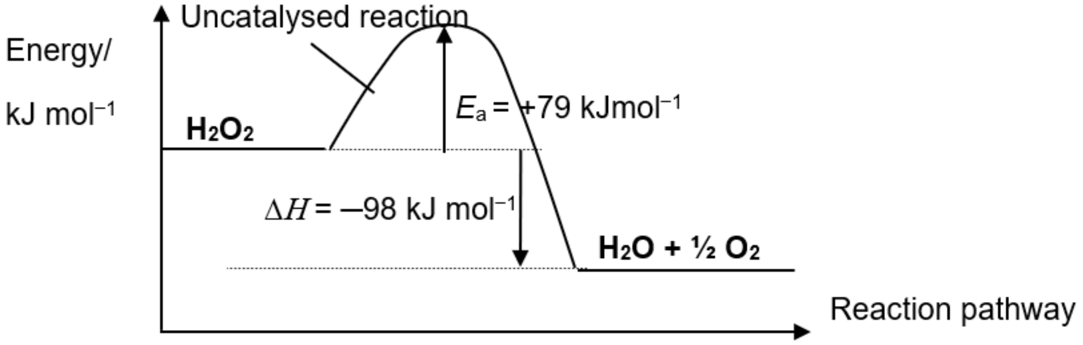
This result in greater frequency of effective collisions. Hence rate of reaction increases.

5 The decomposition of hydrogen peroxide is a first order reaction.

$$H_2O_2 \longrightarrow H_2O + ½\ O_2 \qquad \Delta H = -98\ \text{kJ mol}^{-1}$$

The uncatalysed reaction has an activation energy of 79 kJ mol^{-1}.

(a) Use the data provided to construct a reaction pathway diagram for this uncatalysed reaction.



(b) Explain what is meant by the term *activation energy*.
Activation energy (E_a) is **the minimum amount of energy that reactants must possess before a reaction can occur**.

(c) The enzyme catalase act as catalysts, and speed up the reaction.

What effect will the presence of the catalyst have on the rate constant for this reaction? Explain your answer.
A catalyst **provides an alternative reaction path of lower activation energy** than that of the uncatalysed reaction, rate constant increases and rate increases

Multiple Choice Questions

6 Lead is the final product formed by a series of changes in which the rate-determining stage is the radioactive decay of uranium-238. This radioactive decay is a first order reaction with a half-life of 4.5×10^9 years.

What would be the age of the rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1:7?

Time	**Amt of Uranium left**	**Amt of Lead formed**	**Mole ratio of U : Pb**
0, Inital	1	0	1 : 0
One $t_{1/2}$	0.5	0.5	1 :1
Two $t_{1/2}$	0.25	0.75	1 : 3
Three $t_{1/2}$	0.125	0.875	1 : 7

Mole ratio of **U : Pb** = 1:7 → 3 half lives
Half-life = 4.5×10^9 years
Age of rock = $3 \times 4.5 \times 10^9$ years = 13.5×10^9 years

7 The decomposition

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is first order with respect to N_2O_5.

In an experiment, 0.10 mol of pure N_2O_5 was put into an evacuated flask. It was found that there was 0.025 mol of N_2O_5 left 34 minutes later.

Which statement is true?

A It took 17 minutes for the amount of NO_2 to rise from 0 mol to 0.10 mol

B There was 0.0625 mol of N_2O_5 left after 17 minutes.

C There was 0.0125 mol of N_2O_5 left after 68 minutes.

D The amount of NO_2 in the flask went up by four times in the first 34 minutes.

Since it is a first order reaction, half lives are constant.

Time	0		1^{st} $t_{1/2}$		2^{nd} $t_{1/2}$		3^{rd} $t_{1/2}$		4^{th} $t_{1/2}$
Amount of N_2O_5 /mol (reactant)	0.1	→	0.05	→	0.025	→	0.0125	→	0.00625
Amount of NO_2 /mol (product)	0	→	$2 \times (0.05) = 0.10$	→	$2 \times 0.075 = 0.15$				

Since there are 0.025 mol of N_2O_5 left after 34 min, we know that two half-lives = 34 min
Hence, $t_{1/2}$ = 17 min

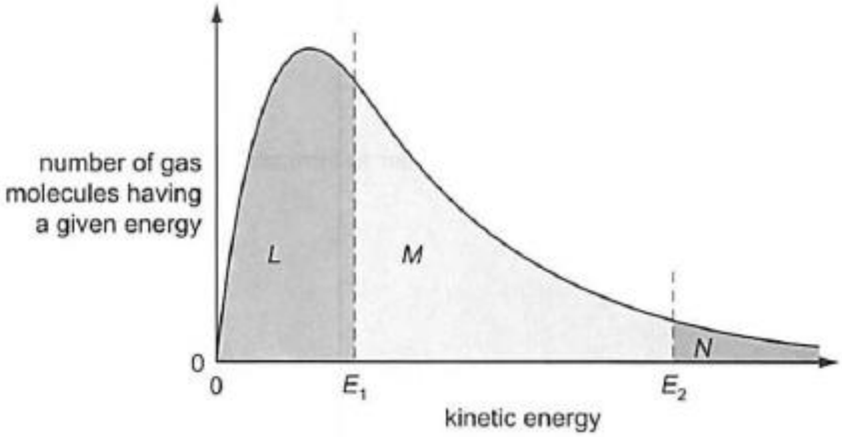
After 17min, amount of N_2O_5 reacted = 0.05 mol
After 17min, amount of NO_2 formed = **2**(0.05) = 0.10 mol
Option A is true.

After 17 min, there was 0.05 mol of N_2O_5 left.
After 68 min (after four $t_{1/2}$), there was 0.00625 mol ($0.1 \times ½ \times ½ \times ½ \times ½$) of N_2O_5 left.
Option B & C are false.

After 34 min, amount of NO_2 formed = **2**(0.10–0.025) = 0.15 mol
Therefore the amount of NO_2 went up from 0 to 0.15 mol.
Option D is false.

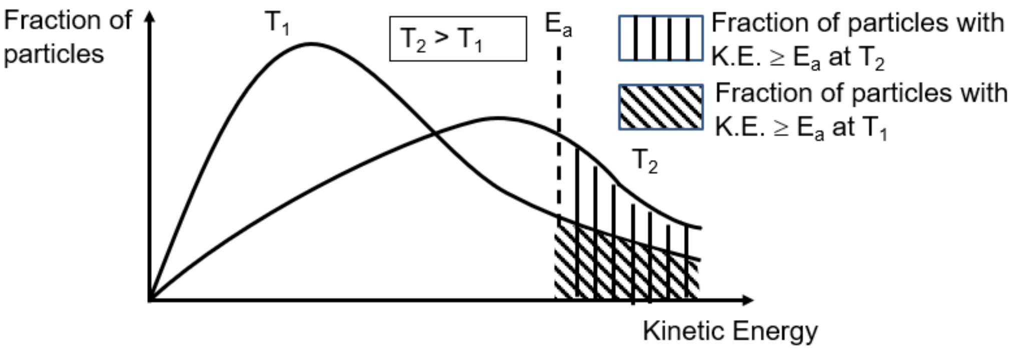
8 The Boltzmann distribution shows the number of gas molecules having a particular kinetic energy at constant temperature.

E_1 and E_2 are fixed energy values.



If the temperature is decreased, what happens to the size of the areas labelled *L*, *M* and *N*?

	L	*M*	*N*
A	decreases	decreases	decreases
B	decreases	increases	decreases
C	increases	decreases	decreases
D	increases	decreases	increases

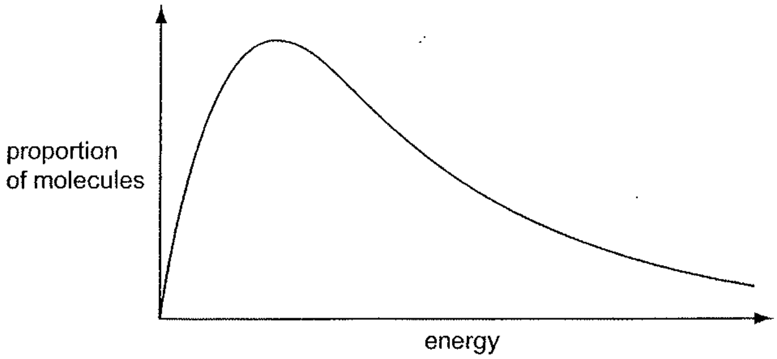


When temperature **de**creases from T_2 to T_1, maximum of the curve is displaced to the Left.

Area L increase, M decreases, N decreases

Ans : C

9 The diagram represents the Boltzmann distribution of molecular energies at a given temperature.



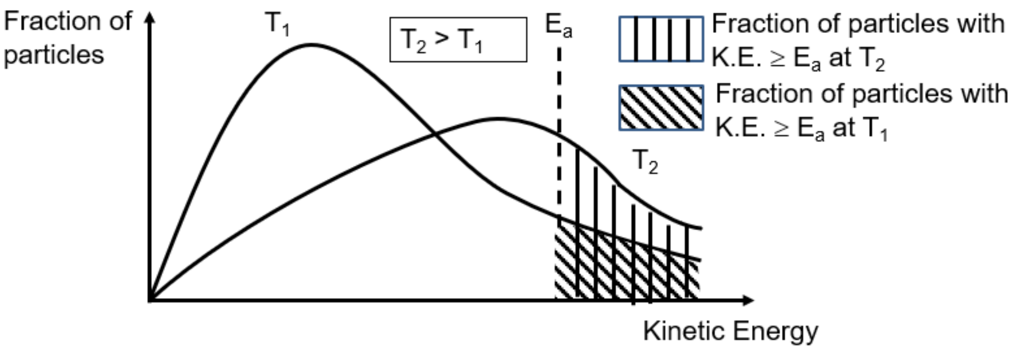
As temperature increases, which statements are correct?

1 The maximum of the curve is displaced to the right.

2 The proportion of molecules with energies **above** any given value increases.

3 The proportion of molecules **with** any given energy increases.

A	B	C	D
1, **2** & **3** are correct	**1** & **2** only are correct	**2** & **3** only are correct	**1** only are correct



When temperature increases from T_1 to T_2, maximum of the curve is displaced to the right. **Option 1 is correct.**

The number of molecules with energy above any given value increases, E.g. K.E. ≥ E_a .(as can be seen from the greater shaded area in the diagram above). **Option 2 is correct**.

However, the proportion of molecules with lower energy decreases. **Option 3 is incorrect**.

Answer: **(B)**