Rate Equations and Mechanisms

A Level

The two steps in the gas phase reaction $\mathrm{X + 2\,Y \longrightarrow XY_2}$ are given below:

$$\mathrm{X + Y \xrightarrow{slow} XY}$$

$$\mathrm{XY + Y \xrightarrow{fast} XY_2}$$

What is the rate equation for the overall reaction?

- rate = $k[XY]^1[Y]^1$
- rate = $k[X]^0[Y]^2$
- rate = $k[X]^0[Y]^1$
- rate = $k[X]^1[Y]^1$
- rate = $k[X]^1[Y]^2$

Adapted with permission from UCLES, A Level, November 1989, Paper 3, Question 9

Acetone

A Level

In an acid medium, ketones react with iodine by the following equation:

$$\mathrm{RCOCH_3 + I_2 \longrightarrow RCOCH_2I + H^+ + I^-}$$

Experiments were run to determine the partial orders of this reaction with respect to $\mathrm{RCOCH_3}$, $\mathrm{I_2}$ and $\mathrm{H^+}$, using the isolation method. Two reagents were added in great excess to the third, so their concentrations stay approximately constant over the course of the reaction. Compare the different experiments to answer the questions below.

Experiment 1: Using $0.10\,\mathrm{mol\,dm^{-3}}$ ketone, $0.10\,\mathrm{mol\,dm^{-3}}$ acid and $1.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ iodine:

Time/ s	$[\mathrm{I_2}]/\mathrm{mol\,dm^{-3}}$
0	1.0×10^{-3}
5	7.5×10^{-4}
10	5.0×10^{-4}
15	2.5×10^{-4}

Experiment 2: Using $0.10\,\mathrm{mol\,dm^{-3}}$ ketone, $1.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ acid and $0.10\,\mathrm{mol\,dm^{-3}}$ iodine:

Time/ s	$[\mathrm{H^+}]/\mathrm{mol\,dm^{-3}}$
0	1.0×10^{-3}
100	9.5×10^{-4}
200	9.0×10^{-4}
400	8.2×10^{-4}
1000	6.1×10^{-4}

Experiment 3: Using $1.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ ketone, $0.10\,\mathrm{mol\,dm^{-3}}$ acid and $0.10\,\mathrm{mol\,dm^{-3}}$ iodine:

Time/ s	[ketone]/$\mathrm{mol\,dm^{-3}}$
0	1.0×10^{-3}
100	9.5×10^{-4}
300	8.6×10^{-4}
500	7.8×10^{-4}
700	7.0×10^{-4}

Part A Order of reaction

What are the reaction orders with respect to the ketone, iodine and acid? Give your answer in the form abc with no spaces.

Part B Apparent rate constant

What is the value of the apparent rate constant in experiment 2?

Part C Actual rate constant

What is the value of the actual rate constant?

Adapted with permission from UCLES, A Level Chemistry, June 1983, Special Paper, Question 1.

Essential Pre-Uni Chemistry M1.1

A Level

Equation 1:	$\mathrm{A} \longrightarrow \mathrm{B}$
Equation 2:	$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}$
Equation 3:	$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$
Equation 4:	$2\,\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$

Rate law 1:	rate = k
Rate law 2:	rate $= k[\mathrm{A}]$
Rate law 3:	rate $= k[\mathrm{A}]^2$
Rate law 4:	rate $= k[\mathrm{A}][\mathrm{B}]$
Rate law 5:	rate $= k[\mathrm{A}][\mathrm{B}]^2$
Rate law 6:	rate $= k[\mathrm{A}][\mathrm{B}][\mathrm{cat}]$

Part A Equation 1: order of reaction

A reaction described by equation 1 gets three times faster when the concentration of A is tripled. Give the order of reaction with respect to A.

Give the overall order of the reaction.

Part B Equation 2: rate law

If equation 2 proceeds as a single step, which rate law will it follow?

Part C Second order rate laws

Which rate law(s) is/are second order overall?

- 3 and 4
- 3 and 5
- 1 and 2
- 4 and 6

Part D Units of k

In which rate law(s) is/are the units of the rate constant, k, $\mathrm{mol\,dm^{-3}\,s^{-1}}$? If your answer includes more than one rate law, please list them as one number in ascending order: to answer rates laws 2, 4 and 6, type 246.

Part E Law 6: power of dm

In rate law 6, the rate constant, k, has units which include dm raised to which power?

Part F Law 5: reaction order of B

What is the order of reaction with respect to B in rate law 5?

Part G Constant half-life

Which rate law(s) describe a reaction in which reactant A always has constant half-life? If your answer includes more than one rate law, please list them as one number in ascending order: to answer rates laws 2, 4 and 6, type 246.

Part H Law 2: rate constant

In rate law 2, if $[\mathrm{A}] = 0.020\,\mathrm{mol\,dm^{-3}}$, and the $\mathrm{rate\ of\ reaction} = 1.2 \times 10^{-3}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$, find the value of k.

Part I Law 2: rate of reaction

In rate law 2, if k has a value of $150\,\mathrm{s^{-1}}$, find the rate of reaction when $[\mathrm{A}] = 0.80\,\mathrm{mol\,dm^{-3}}$.

Part J Law 3: $[\mathrm{A}]$

In rate law 3, find $[\mathrm{A}]$ at which the $\mathrm{reaction\ rate} = 0.025\,\mathrm{mol\,dm^{-3}\,s^{-1}}$ if $k = 0.0040\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$.

Essential Pre-Uni Chemistry M1.5

A Level

Use the data in the table below to find the order of reaction with respect to A, B and the catalyst, X, the overall order of reaction, and the value and units of the rate constant, k.

$[A]$ / $mol\,dm^{-3}$	$[B]$ / $mol\,dm^{-3}$	$[X]$ / $mol\,dm^{-3}$	Rate / $mol\,dm^{-3}\,s^{-1}$
0.50	0.080	0.0020	3.2×10^{-3}
0.50	0.080	0.0010	8.0×10^{-4}
0.75	0.080	0.0010	1.2×10^{-3}
0.75	0.040	0.0010	6.0×10^{-4}

Part A Order with respect to A

Order with respect to A:

Part B Order with respect to B

Order with respect to B:

Part C Order with respect to X

Order with respect to X:

Part D Overall order

Overall order:

Part E k

Value of k:

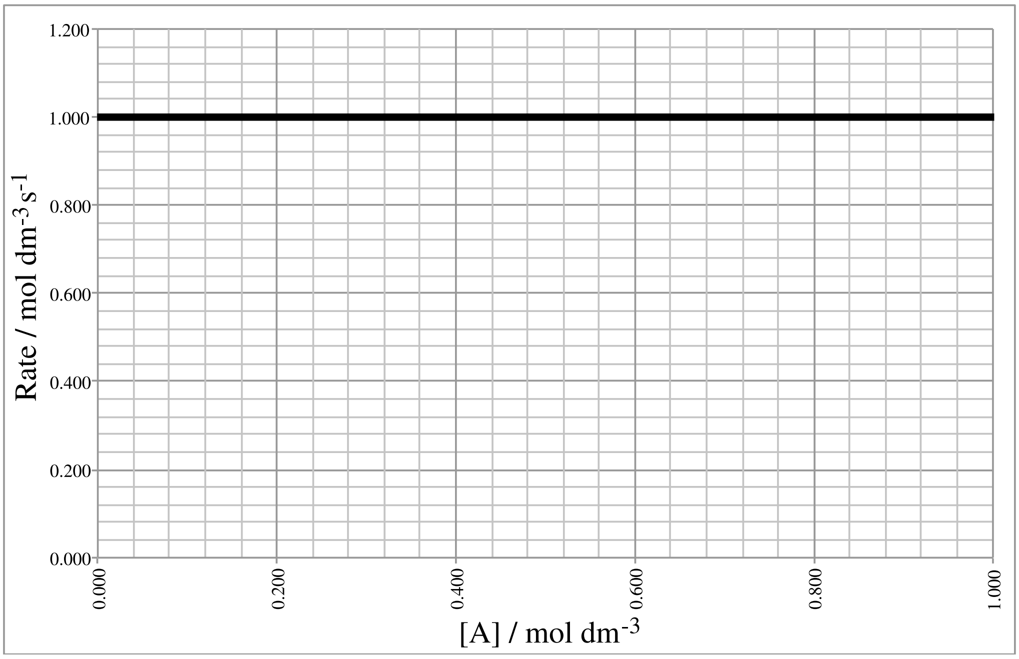
Essential Pre-Uni Chemistry M1.7

A Level

Equation 1:	$\mathrm{A} \longrightarrow \mathrm{B}$
Rate law 1:	rate = k
Rate law 2:	rate $= k[\mathrm{A}]$
Rate law 3:	rate $= k[\mathrm{A}]^2$
Rate law 4:	rate $= k[\mathrm{A}][\mathrm{B}]$
Rate law 5:	rate $= k[\mathrm{A}][\mathrm{B}]^2$
Rate law 6:	rate $= k[\mathrm{A}][\mathrm{B}][\mathrm{cat}]$

Part A   Rate vs [A]

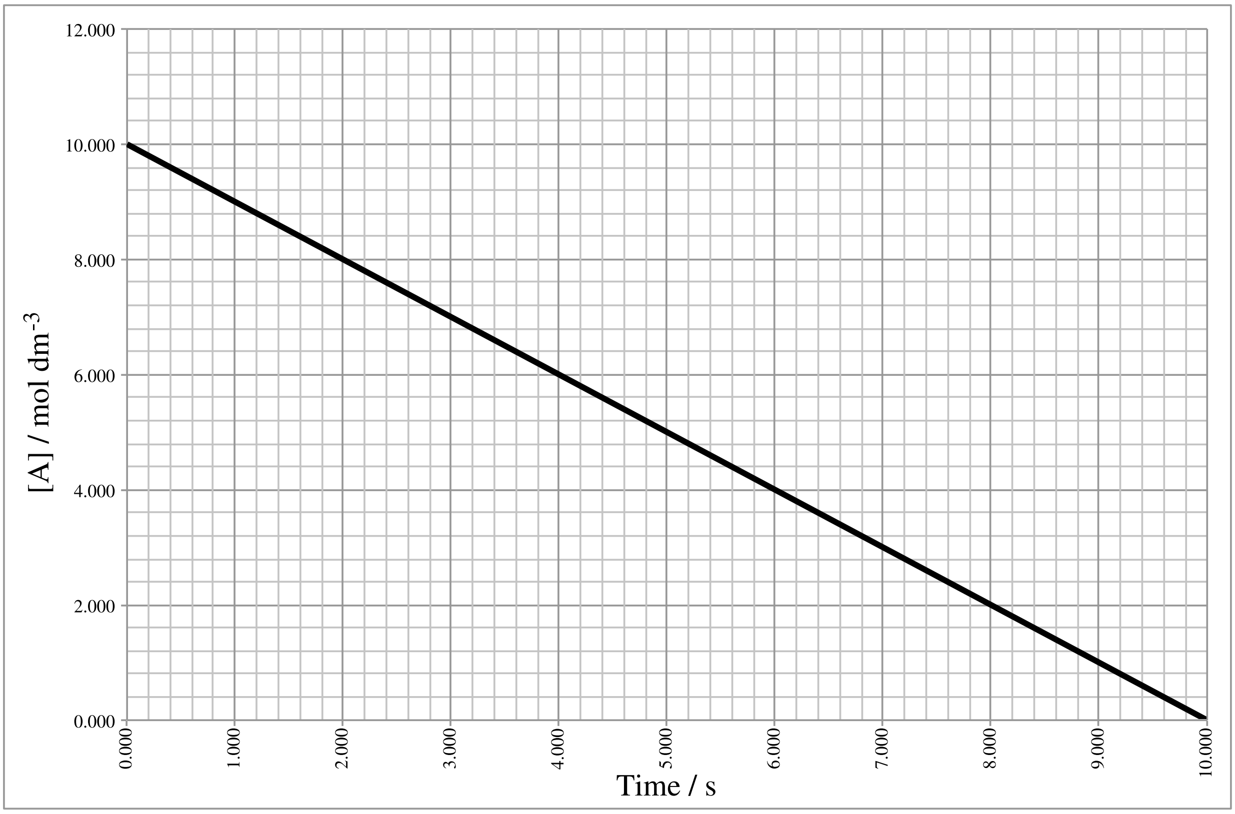
A reaction described by equation 1 shows the behaviour of the graph in **Figure 1**.



Which rate law does it follow?

Part B [A] vs time

A reaction described by equation 1 shows the behaviour of the graph in **Figure 2**.



Which rate law does it follow?

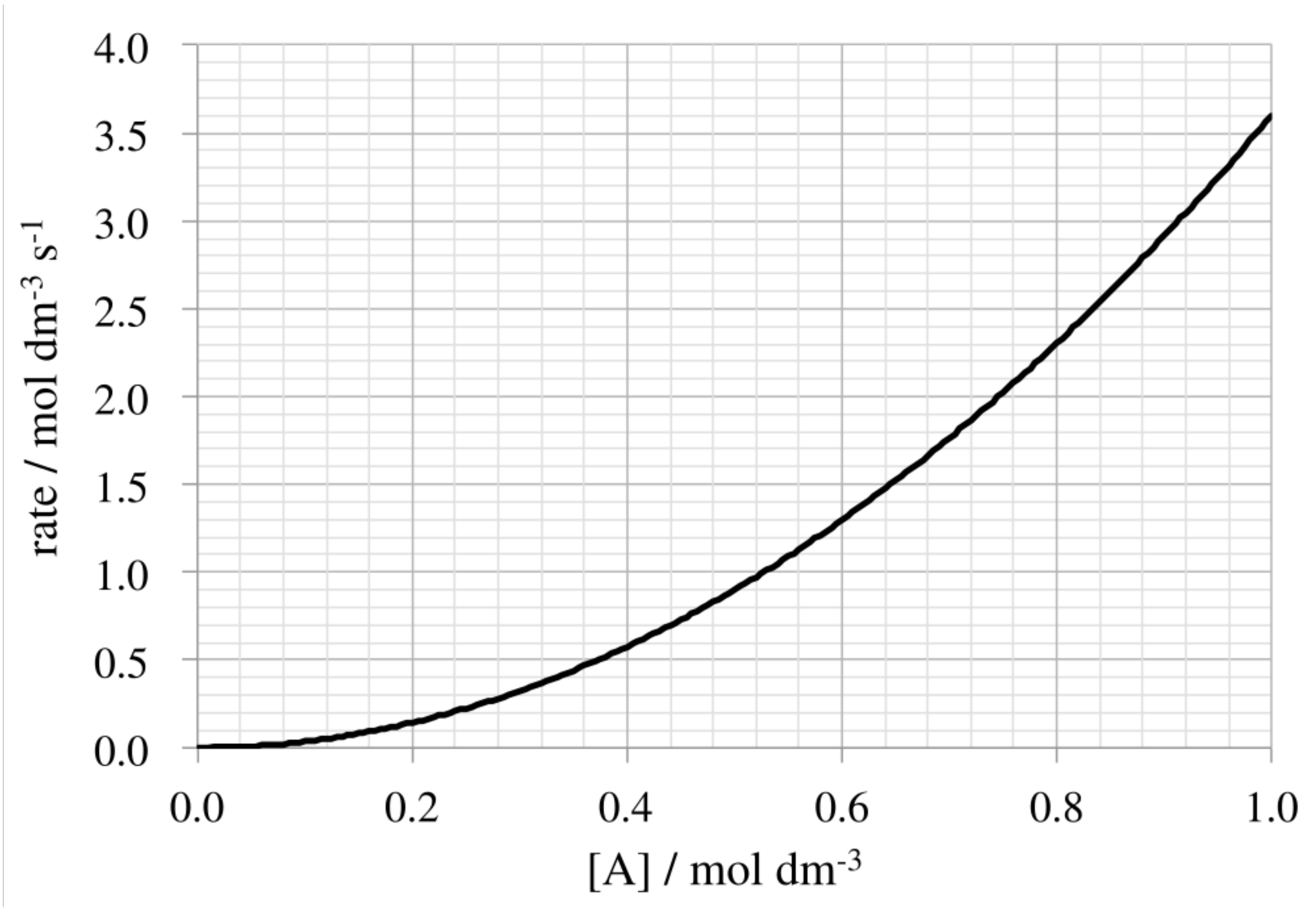
Essential Pre-Uni Chemistry M1.9

A Level

Equation 1: $\mathrm{A} \longrightarrow \mathrm{B}$

Rate law 3: rate $= k[\mathrm{A}]^2$

A reaction described by equation 1 and following rate law 3 is investigated and the following graph is produced from the data obtained:



Estimate the rate constant, k. Give your answer to 2 significant figures.

Physics. You work it out.

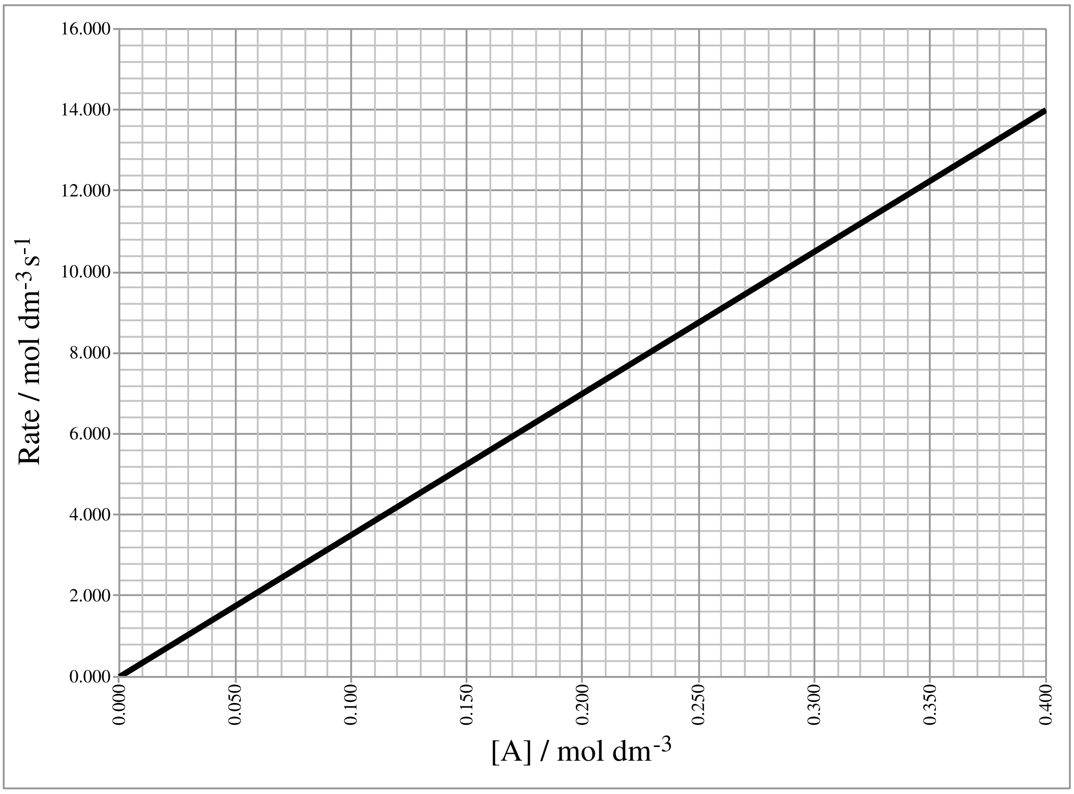
Essential Pre-Uni Chemistry M1.10

A Level

Equation 2: $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}$

Rate law 4: rate $= k[\mathrm{A}][\mathrm{B}]$

A reaction described by equation 2 and obeying rate law 4 gave the following initial rates for different initial concentrations of A without varying the initial concentration of B:



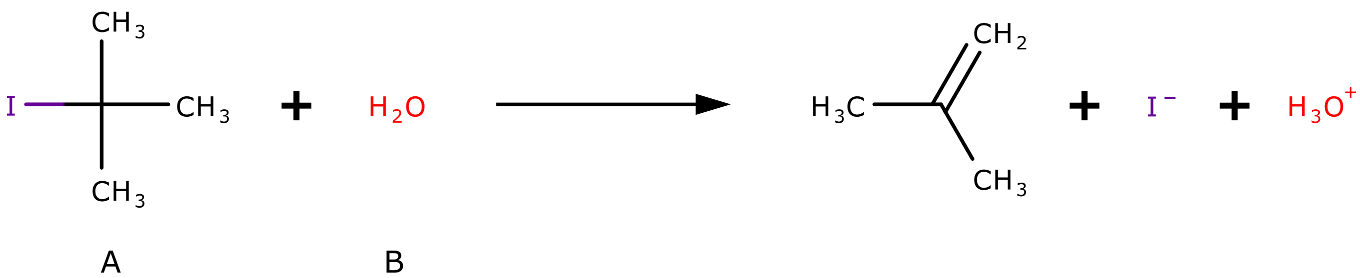
Estimate the initial concentration of B if the rate constant is $140\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. Give your answer to 2 significant figures.

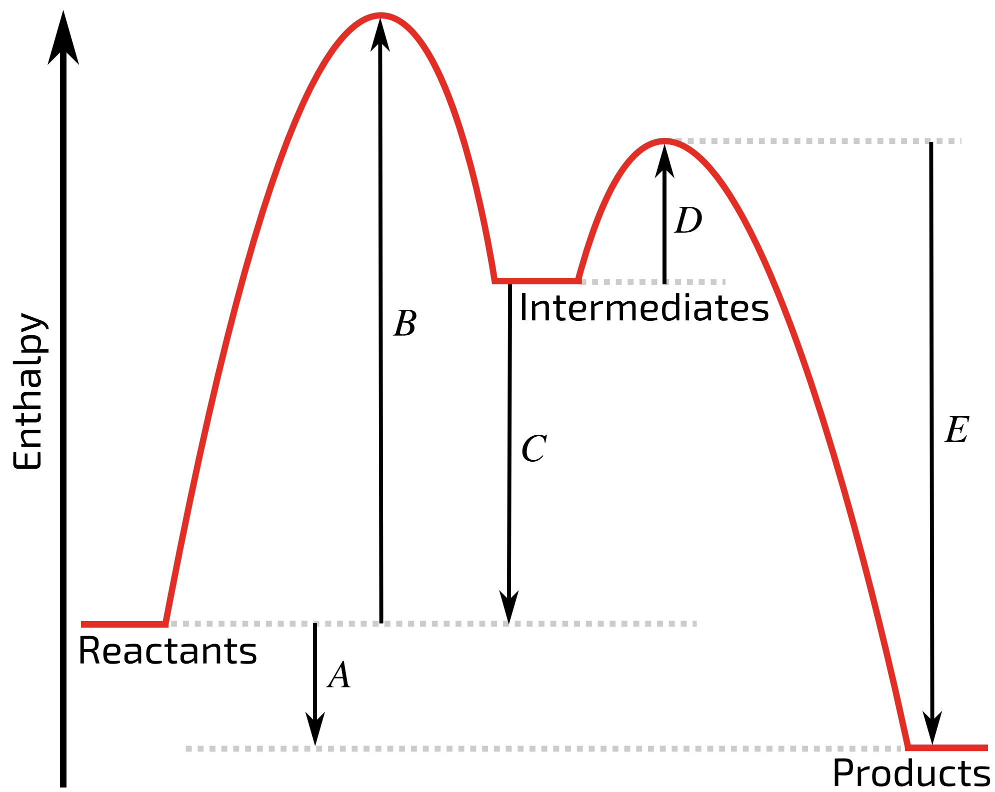
Home Gameboard Chemistry Physical Energetics Reaction Profiling

Reaction Profiling

A Level

An energy profile and an overall reaction equation for a reaction is shown below. This is called an E1 reaction, and is similar to the S_N1 substitution, but it is an elimination reaction.





E1 reaction profile

Part A Rate determining step

Which reactants participate in the rate determining step?

- None of them
- A and B
- Any other combination
- A
- B

Part B Intermediate

What is the shape of the intermediate?

- Linear
- Trigonal planar
- Trigonal Bipyramidal
- Octahedral
- Bent Linear
- Tetrahedral

Part C Activation energy

On the reaction profile what is the apparent activation energy of the reaction?

- $-A - C$
- $-E$
- B
- $E - C + D$
- $B + E - A$
- $D - C$

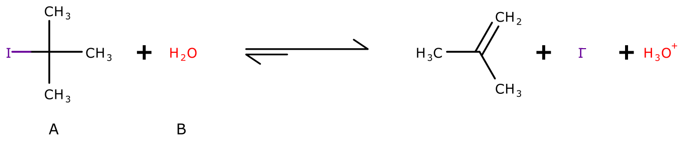
Part D Enthalpy change

What is the overall enthalpy change of the reaction?

- $-C$
- $E + D$
- A
- $E - C + D$
- $D - C$

Part E Reaction yield

Now consider the reaction as a reversible reaction. What would happen to the yield of the reaction if the temperature at which it occurs was raised?



- Decrease
- Stay the same
- Increase
- Something Else

Part F Yield change

Why does the yield change in the way it does?

- Le Chatelier's Principle
- Hess' Law
- Snell's Law
- Markovnikov's Rule
- Avogadro's Law

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Physics. You work it out.

General Rate Constant

A Level

Part A General expression for rate constant

Think about what a generalised expression for the rate constant, k, of a reaction with two reactants would look like.

Perhaps consider the following general equation to help with your expression.

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

The lower case letters denote the stoichiometric coefficients.

Part B Units of the rate constant

Hence, or otherwise, determine the generalised form of the units of the rate constant.

- $\mathrm{mol^{1-(a+b)}\ dm^{3(a+b)-3}\ s^{-1}}$
- $\mathrm{mol^{1+(a+b)}\ dm^{-3(a+b)+3}\ s^{-1}}$
- $\mathrm{mol^{1-(a+b)}\ dm^{3(ab)}\ s^{-1}}$
- $\mathrm{mol^{1-(ab)}\ dm^{-3+(ab)}\ s^{-1}}$
- $\mathrm{mol^{1-a+b}\ dm^{a+b-3}\ s^{-1}}$
- $\mathrm{mol^{-(a+b)}\ dm^{(a+b)}\ s^{-1}}$

Part C Special case

In which special case are the units of the rate constant simply $\mathrm{s^{-1}}$? Write down the equation which must be satisfied for this to occur (it should include a and b).

The following symbols may be useful: `a`, `b`

Part D Zeroth order

If both $a = 0$ and $b = 0$, what are the units of the rate constant?

- $\mathrm{mol\,dm^{-3}\,s^{-1}}$
- $\mathrm{mol^2\,dm^{-6}\,s^{-1}}$
- $\mathrm{s^{-1}}$
- $\mathrm{mol\,dm^{-3}}$
- $\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$
- $\mathrm{mol^0\,dm^0\,s^0}$

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Mushroom Kinetics

A Level

Vitamin D is essential for healthy bone structure. Mushrooms are a rich source of ergosterol, a precursor of vitamin D_2. Cultivated mushrooms grown in the dark have little vitamin D_2, but when exposed to UV light, ergosterol is converted into vitamin D_2.

In a kinetics experiment, different mushroom varieties were irradiated with UV light for varying periods of time and then analysed for their concentrations of ergosterol and vitamin D_2.

The kinetics of production of vitamin D_2 from ergosterol were expected to be of the form:

$$\text{rate of production of vitamin } D_2 = k[\text{ergosterol}]^a$$

where k is the rate constant for the particular mushroom, $[\text{ergosterol}]$ is the concentration of the reactant ergosterol, and a is the order of reaction with respect to the concentration of ergosterol.

The following data shows the quantity of D_2 produced over $40\,\text{minutes}$ of irradiation, measured in micrograms per gram of dry mushroom.

Time / min	**Oyster mushroom D_2 /** $\mu\text{g per g of dry mushroom}$	**Button mushroom D_2 /** $\mu\text{g per g of dry mushroom}$
0	7	3
5	12	4
10	17	5
15	21	7
20	25	8
25	29	9
30	33	11
35	37	12
40	42	14

Part A Determining the order

By examining this data, what is the value of a, the observed order of reaction with respect to $[\mathrm{ergosterol}]$? If you are struggling, graph the data.

Part B Determining the rate constant

Using the data, determine the rate constant for the production of vitamin D_2 from oyster mushrooms in units of $(\mu\mathrm{g\ per\ g\ dry\ mushroom\ s^{-1}})$ to 2 significant figures.

Part C Mass of D_2

Estimate the mass of vitamin D_2 in $10\,\mathrm{g}$ of dried button mushrooms that have been irradiated for $1\,\mathrm{hour}$.

Part D Effect of temperature

The rate constant for the production of vitamin D_2 is found to vary with temperature according to the Arrhenius equation:

$$k = A \times e^{\frac{-E_a}{RT}}$$

where k is the rate constant at temperature T;

A is an unknown constant, called the pre-exponential factor;

E_a is the activation energy for the reaction;

T is the temperature in K;

R is the gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$).

Given that the rate constant for the production of vitamin D_2 from shiitake mushrooms at $35\,^{\circ}\mathrm{C}$ is twice that at $25\,^{\circ}\mathrm{C}$, calculate the activation energy for the reaction.

Adapted from RSC, Chemistry Olympiad, 2008, Question 2