

1. A researcher follows the progress of a reaction and tabulates the concentration of the reactant with respect to time of the reaction. How could the scientist prove that the reaction follows first order kinetics and find the rate constant,  $k$ ? Please select all that apply.

- ✓ Plot a graph of [reactant] against time, and find half-life

$$(t_{1/2}).$$

✓ **Correct**

If a plot of concentration against time is constructed, for a first order reaction, the half-life of the reactant is independent of its initial concentration. Thus, the half-life will not change and as long as the reaction has been followed for enough time to allow at least three half-lives this will become apparent. Rearranging the equation  $t_{1/2} = \frac{\ln 2}{k}$ , it is possible to find the rate constant,  $k$ . If a reaction follows first order kinetics, a graph of  $\ln[\text{reactant}]$  against time will give a straight-line graph where the gradient  $= -k$ .

- ✓ Plot a graph of  $\ln [\text{reactant}]$  against time.

✓ **Correct**

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2. A first order rate constant,  $k = 3.75 \times 10^{-2} \text{ s}^{-1}$ . What is the reaction's half-life,  $t_{1/2}$ ?

☐  $0.01875 \text{ s}^{-1}$

☐  $53.33 \text{ s}$

☐  $26.67 \text{ s}$

☒  $18.48 \text{ s}$



**Correct**

The half-life of a first order reaction is  $t_{1/2} = \frac{\ln 2}{k}$ . Thus,  $t_{1/2} = \frac{\ln 2}{3.75 \times 10^{-2} \text{ s}^{-1}} = 18.48 \text{ s}$ .

3. The rate of reaction depends on the concentration of reactant A only. Determine the order of the reaction from the data below.

Initial Concentration $[A]_0/10^{-3} \text{ mol dm}^{-3}$	0.025	0.05
Initial Rate/ $\times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$	0.4250	1.700

- ☐ Zero order
- ☐ First order
- ☒ Second order
- ☐ Third order

✓ **Correct**

The data given comes from the initial rates method where a series of experiments are done where the concentration of the reactant is changed and the initial rate of reaction is measured. If the rate changes then it is clear that reactant A changes the rate of reaction. The next step is to chart the effect of increasing the concentration of A to the increase or decrease of the rate of reaction. Here, when the reactant concentration is doubled, the rate of reaction quadruples, this means that the reactant order is 2 and overall the reaction order is second order.

4. Match the following brief description with the term used to describe a reaction mechanism and its reaction steps.

(a) The step in a reaction mechanism that determines the rate of reaction

(b) A reaction step that involves two molecules

(c) The rate of change of concentration of a reactive species, in a sequence of reactions is approximately zero

(d) A highly unstable species

(i) = steady state approximation

(ii) = reactive intermediate

(iii) = rate-determining step

(iv) = bimolecular

(a) rate-determining step

The step in a reaction mechanism that determines the rate of reaction

(b) bimolecular

A reaction step that involves two molecules

(c) steady state approximation

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(d) reactive intermediate

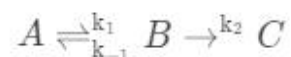
A highly unstable species

✓ **Correct**

A complex reaction is made up by a series of elementary steps, these make up the mechanism of the reaction. All of these steps will have individual rate constants, and often one step is slower than others in the mechanism, this is the rate-determining step. Usually, an elementary step involves one or two molecules and this is signified as a unimolecular or bimolecular reaction. In the steady-state approximation the concentration of the highly reactive intermediates is deemed to be constant.



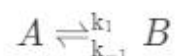
5. In the following reaction sequence the first step is reversible.



and  $k_2$  is small relative to  $k_1$  and  $k_{-1}$ .

Please select all that apply.

- ☐ The rate-determining step is step one:



- ☒ The rate of reaction =  $-\frac{d[A]}{dt}$ .

✓ **Correct**

The conversion of B to C takes place slowly as  $k_2$  is smaller than  $k_1$  or  $k_{-1}$ , thus it is the rate-determining step.

Since, the rate-determining step, is step two, this determines the rate equation for the overall reaction.

This, the rate of reaction =  $k_2[B]$  and since  $[B] = k_c[A] = k_2 \frac{k_1}{k_{-1}} [A]$

Also, the rate of reaction =  $-\frac{d[A]}{dt}$

since  $-\frac{d[A]}{dt} = \frac{d[C]}{dt}$

So, the rate of consumption of A equals the rate of formation of C.

✓ The rate of reaction =  $k_2 \frac{k_1}{k_{-1}} [A]$ .

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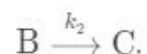
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So, the rate of consumption of A equals the rate of formation of C.

✓ The rate-determining step is step two:



✓ **Correct**

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6. A plot of  $\ln k$  against  $\frac{1}{T}$  has a slope of  $-3257 \text{ K}$  and an intercept of 25. What is the activation energy ( $E_a$ ) ( $\text{kJ mol}^{-1}$ ) of the reaction?

☐ 25

☒ 27

☐ 329

☐  $-3257$



**Correct**

The gradient of a plot of  $\ln k$  against  $\frac{1}{T}$  is  $-\frac{E_a}{R}$ . Thus, rearranging

$$E_a = 3257 \text{ K} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$E_a = 27079 \text{ J mol}^{-1} = 27 \text{ kJ mol}^{-1}$$

7. A plot of  $\ln k$  against  $\frac{1}{T}$  has a slope of  $-2575 \text{ K}$  and an intercept of  $31.5$ . What is the pre-exponential factor  $A(\text{s}^{-1})$  of this first order reaction?

- ☐  $-2575$
- ☒  $4.8 \times 10^{13}$
- ☐  $31.5$
- ☐  $21409$



**Correct**

The intercept of the plot of  $\ln k$  against  $\frac{1}{T}$  is  $\ln A$ . Hence, since  $\ln A = 31.5$  and  $A = e^{31.5} = 4.8 \times 10^{13} \text{ s}^{-1}$ .

8. The activation energy ( $E_a$ ) of a first order reaction is

$70 \text{ kJ mol}^{-1}$ . The rate constant ( $k_1$ ) at  $25^\circ\text{C}$  is  $2.25 \times 10^{-5} \text{ s}^{-1}$ . What is the rate constant ( $k_2$ ) ( $\text{s}^{-1}$ ) at  $70^\circ\text{C}$ ?

☐  $2.25 \times 10^{-5}$

☐  $2.26 \times 10^{-5}$

☐  $2.39 \times 10^{89}$

☒  $9.13 \times 10^{-4}$

 **Correct**

If the rate constant,  $k_1$  at a temperature,  $T_1$ , the

Arrhenius equation can be used to calculate the value of the rate

constant,  $k_2$ , at another temperature,  $T_2$ , within the

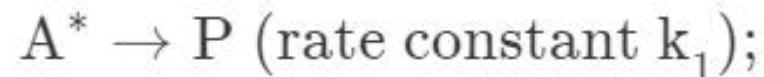
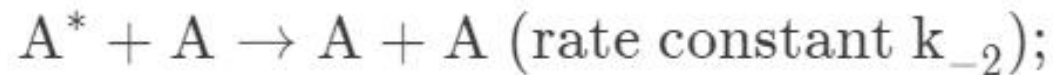
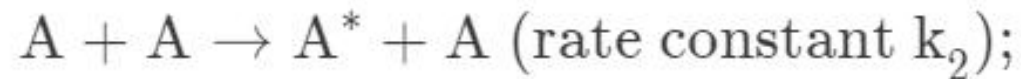
limits of experimental observation. The ratio of two rate constants is

given by the following relation:

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

9. A reaction  $A \rightarrow P$  shows complex behaviour

with the following elementary steps:



with a rate of reaction given by

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_1 + k_{-2} [A]}$$

Which of the following statements are correct?

- ✓ At atmospheric pressure the reaction is first order.

✓ **Correct**

At atmospheric pressure  $k_2 \gg k_1$  and therefore the

equation simplifies to  $\frac{d[P]}{dt} = \frac{k_1 k_2 [A]}{k_{-2}}$

which is first order. At low pressure  $k_{-2}[A] \ll k_1$  and therefore the equation simplifies to

$\frac{d[P]}{dt} = k_2 [A]^2$  which second order.

- ✓ At low pressure the reaction is second order.

✓ **Correct**

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10. Adding a catalyst to a reaction reduces the activation energy from 94 to 70 kJ mol<sup>-1</sup> by what factor is the reaction rate increased at 25°C.

☐ 1.4 × 10<sup>50</sup>

☐ 6.2 × 10<sup>-5</sup>

☒ 16105



**Correct**

The rate of reaction is given by the Arrhenius expression and the relative rate is given by dividing two such terms:

$$\frac{k_1}{k_2} = e^{\frac{E_a^1 - E_a^2}{RT}}$$

Inserting the two activation energies

given with the absolute temperature,  $T = 298$  K, and  $R = 8.314$  J mol<sup>-1</sup> K<sup>-1</sup> gives a relative reaction rate 16105.

☐ 9.69