Marks 4

- The table below gives the concentrations of C_2H_4O as a function of time at 690 K for the following reaction:

$$C_2H_4O(g) \rightarrow CH_4(g) + CO(g)$$

$[C_2H_4O]$ (M)	time (mins)	$\frac{1}{t}(\ln[A]_0 - \ln[A])$
0.0860	0	
0.0465	50	**0.012298**
0.0355	72	**0.012289**
0.0274	93	**0.012299**
0.0174	130	**0.012291**

The reaction is first order with respect to C_2H_4O.

Use the above data to determine the rate constant and the half-life of the reaction.

For a first order reaction,

$$\ln[A] = \ln[A]_0 - kt \quad \text{or} \quad k = \frac{1}{t}(\ln[A]_0 - \ln[A]) \quad \text{and} \quad t_{1/2} = \frac{\ln 2}{k}$$

A plot of ln[A] *vs*. t has gradient k. Alternatively, the value of $\frac{1}{t}(\ln[A]_0 - \ln[A])$ is included in the table above for each measurement. To 3 significant figures:

$$k = 0.0123 \text{ min}^{-1} \quad \text{and hence} \quad t_{1/2} = \frac{\ln 2}{0.0123} = 56.4 \text{ min}$$

k = **0.0123 min^{-1}**	$t_{½}$ = **56.4 min**

How long does it take for 75% of the C_2H_4O to react?

Using $\ln[A] = \ln[A]_0 - kt$,

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

When 75% has reacted, $[A] = 0.25 \times [A]_0$:

$$\ln(1/0.25) = (0.0123 \text{ min}^{-1})t \quad \text{so } t = 113 \text{ min.}$$

Answer: **113 min**

- Sevoflurane is an anaesthetic with a half-life in the brain of 2.3 minutes. How long does it take for the concentration of sevoflurane in brain tissue to drop from 0.025 mM to one hundredth of this value? **3**

For the first order decay of sevoflurane (S),

$$\ln[S] = \ln[S]_0 - kt \quad \text{and} \quad t_{1/2} = \frac{\ln 2}{k}$$

Hence $k = \frac{\ln 2}{2.3 \text{ min}}$**. Using** $[S]_0 = 0.025$ **mM and** $[S] = 1/100 \times 0.025$ **mM:**

$$\ln(0.00025) = \ln(0.025) - \frac{\ln 2}{2.3 \text{ min}} \times t$$

so

$$t = 15 \text{ min}$$

Answer: **15 min**

Marks 4

- Phosgene is a toxic gas prepared by the reaction of carbon monoxide with chlorine.

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

The following data were obtained in a kinetics study of its formation at 150 °C.

Experiment	Initial [CO] (mol L^{-1})	Initial [Cl_2] (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
1	1.00	0.100	1.29×10^{-3}
2	0.100	0.100	1.33×10^{-4}
3	0.100	1.00	1.30×10^{-3}
4	0.100	0.0100	1.32×10^{-5}

Write the rate law for the formation of phosgene at 150 °C.

Between experiments (1) and (2), [Cl_2] is constant and [CO] is increased by a factor of ten. This leads to a tenfold increase in the rate. The reaction is first order with respect to [CO].

Between experiments (2) and (3), [CO] is constant and [Cl_2] is increased by a factor of ten. This leads to a tenfold increase in the rate. The reaction is also first order with respect to [Cl_2].

Hence, the rate law is,

$$\text{rate} = k[CO(g)][Cl_2(g)]$$

Calculate the value of the rate constant at 150 °C.

In experiment (1), rate = 1.29×10^{-3} mol L^{-1} s^{-1} when [CO] = 1.00 mol L^{-1} and [Cl_2] = 0.100 mol L^{-1}. Substituting into the rate law gives,

$$(1.29 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}) = k \times (1.00 \text{ mol L}^{-1}) \times (0.100 \text{ mol L}^{-1})$$

$$k = 1.29 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

The same method gives $k = 1.33 \times 10^{-2}$ mol^{-1} L s^{-1}, 1.30×10^{-2} mol^{-1} L s^{-1} and 1.32×10^{-2} mol^{-1} L s^{-1} for experiments (2), (3) and (4) respectively. The accuracy of the experiments suggests a value of 1.3×10^{-2} mol^{-1} L s^{-1}.

Answer: **1.3×10^{-2} mol^{-1} L s^{-1}**

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the rate of appearance of phosgene when $[CO] = [Cl_2] = 1.3$ M.

Using the rate law derived above.

$$\textbf{rate} = (1.3 \times 10^{-2}\ \text{mol}^{-1}\ \text{L s}^{-1}) \times [CO] \times [Cl_2]$$
$$= (1.3 \times 10^{-2}\ \text{mol}^{-1}\ \text{L s}^{-1}) \times (1.3\ \text{mol L}^{-1}) \times (1.3\ \text{mol L}^{-1})$$
$$= 2.2 \times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Answer: **2.2×10^{-2} mol L^{-1} s^{-1}**

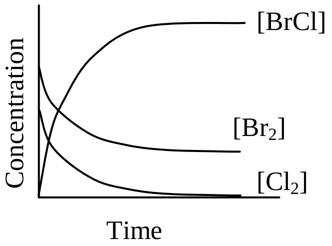
Marks
4

- In the reaction of Cl_2 with Br_2 in CCl_4 solution, BrCl forms according to the equation:

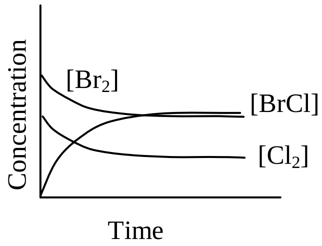
$$Br_2 + Cl_2 \rightarrow 2BrCl \qquad K_c = 2$$

With initial concentrations of $[Br_2]$ = 0.6 M, $[Cl_2]$ = 0.4 M and [BrCl] = 0.0 M, which of the following concentration versus time graphs represents this reaction? Explain why you rejected each of the other three graphs.

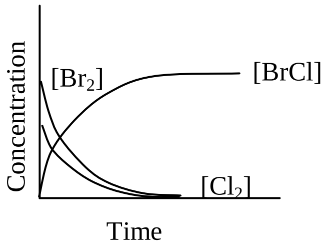
(a)



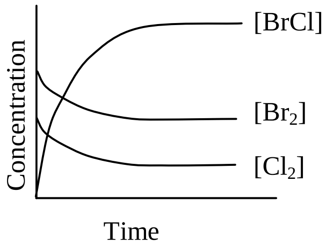
(b)



(c)



(d)



Graph B is correct.

Graph A has $[Cl_2]$ tending to zero and graph C has both $[Cl_2]$ and $[Br_2]$ tending to zero. As K_c = 2, the reaction does not go anywhere near to completion.

In Graph C, the rates of change of $[Br_2]$ and $[Cl_2]$ are different. The chemical reaction shows that these react with a 1 : 1 stoichiometry and so their concentrations should decrease at the same rate.

As the initial concentration of $[Cl_2]$ > $[Br_2]$ and these react with a 1 : 1 stoichiometry, $[Cl_2]$ is the limiting reagent. The maximum value of [BrCl] is limited by the initial $[Cl_2]$. As $[Cl_2]_{initial}$ = 0.4 M and the chemical equation shows that 2BrCl are made from each Cl_2, $[BrCl]_{final}$ = 0.8 M. In graph D, [BrCl] is larger than 2 × $[Cl_2]_{initial}$ so this graph can also be ruled out.

Marks
2

- The radioactive isotope ^{99m}Tc has a half life of 6.0 hours. How much time after production of the ^{99m}Tc isotope do radiologists have to examine a patient if at least 25 % of the original activity is required to get useful exposures?

As the half life is 6.0 hours, the activity will be reduced to 50 % of its original value after 6.0 hours.

After a further 6.0 hours, it will be reduced by another 50 % and so will be 25% of its original value. Therefore 2 half lives are required: 12 hours.

Alternatively, the activity decreases with time according to the equation:

$$\ln\left(\frac{A_0}{A_t}\right) = kt.$$

If the activity has decreased to 25 %, $\frac{A_0}{A_t} = \frac{100}{25} = 4$**. As** $t_{1/2}$ **= 6.0 hours, the activity coefficient = ln2 /** $t_{1/2}$**. Therefore:**

$$\ln 4 = \left(\frac{\ln 2}{6.0 \text{ hours}}\right) \times t \text{ so } t = 12 \text{ hours}$$

Answer: **12 hours**

Marks
3

- Briefly explain the two factors necessary for a collision between two molecules to result in a reaction.

The molecules need to be orientated correctly and they need to have energy ≥ the activation energy, E_a for a reaction to occur.

Briefly describe the relationship between the rate of a reaction and the activation energy for the reaction.

The relationships between the activation energy, E_a, the temperature, T, and the rate constant, k, are summarised by the Arrhenius equation, $k = Ae^{-E_a/RT}$.

This shows that the higher the activation energy, the lower the rate constant and the lower the reaction rate.

	Marks
• The radioactive isotope ^{99m}Tc has a half life of 6.0 hours. How much time after production of the ^{99m}Tc isotope do radiologists have to examine a patient if at least 35 % of the original activity is required to get useful exposures?	**2**

If the half life is 6.0 hours, the activity coefficient, λ, is:

$$\lambda = \ln 2 / t_{1/2} = \ln 2 / (6.0 \text{ hours}) = 0.116 \text{ hours}^{-1}$$

As the activity is proportional to the number of nuclei present, the activity at a time *t* is related to the original activity by:

$$\ln(A_0 / A_t) = \lambda t$$

If $A_t = 0.35 \times A_0$ then:

$$\ln(1/0.35) = (0.116 \text{ hours}^{-1})t$$

$$t = 9.1 \text{ hours}$$

Answer: **9.1 hours**