**Marks
2**

• Briefly explain how a catalyst works.

> **A catalyst provides an alternative reaction pathway that has a lower activation energy. This allows the reaction to proceed at lower temperatures or under milder conditions. The catalyst is not consumed during the reaction and does not affect the final position of equilibrium.**

				Marks
				3

• Given the following experimental data, find the rate law and the rate constant for the following reaction:

$$NO(g) + NO_2(g) + O_2(g) \rightarrow N_2O_5(g)$$

Run	[NO(g)] / M	[NO₂(g)] / M	[O₂(g)] / M	Rate / M s⁻¹
1	0.10	0.10	0.10	2.1×10^{-2}
2	0.20	0.10	0.10	4.2×10^{-2}
3	0.20	0.30	0.20	1.26×10^{-1}
4	0.10	0.10	0.20	2.1×10^{-2}

Between run (1) and (2), [NO(g)] is doubled but [NO$_2$(g)] and [O$_2$(g)] are kept constant. The doubling in [NO(g)] causes a doubling in the rate: the rate is proportional to [NO(g)]^1.

Between run (1) and (4), [O$_2$(g)] is doubled but [NO(g)] and [NO$_2$(g)] are kept constant. The doubling in [O$_2$(g)] causes no change in the rate: the rate is independent of [O$_2$(g)].

Between run (2) and (3), [NO$_2$(g)] is trebled but [NO(g)] is kept constant. Although [O$_2$(g)] is doubled, this has no effect on the rate (see directly above). The trebling in [NO$_2$(g)] causes the rate to treble: the rate is proportional to [NO$_2$(g)]^1

Overall:

rate = k[NO(g)][NO$_2$(g)]

Using run (1), rate = 2.1×10^{-2} M and [NO(g)] = [NO$_2$(g)] = 0.10 M. Hence:

k = rate / [NO(g)][NO$_2$(g)]
  = 2.1×10^{-2} M s^{-1} / (0.10 M)^2
  = 2.1 M^{-1} s^{-1}

Rate = k[NO(g)][NO₂(g)]	k = 2.1 M⁻¹ s⁻¹

ANSWER CONTINUES ON THE NEXT PAGE

- The rate constant for a reaction is 5.0×10^{-3} s^{-1} at 215 $^{\circ}$C and 1.2×10^{-1} s^{-1} at 452 $^{\circ}$C. What is the activation energy of the reaction in kJ mol^{-1}?

The rate constant varies with temperature according to the Arrhenius equation:

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

At $T_1 = (215 + 273)$ K = 488 K and $k_1 = 5.0 \times 10^{-3}$ s^{-1}. At $T_2 = (452 + 273)$ K = 725 K and $k_2 = 1.2 \times 10^{-1}$ s^{-1}. Hence:

$$\ln\left(\frac{1.2 \times 10^{-1}}{5.0 \times 10^{-3}}\right) = \frac{E_a}{8.314}\left(\frac{1}{488} - \frac{1}{725}\right)$$

$E_a = 39$ **kJ mol^{-1}**

Answer: **39 kJ mol^{-1}**

What is the rate constant for this reaction at 100 $^{\circ}$C?

Using $T_1 = 488$ K and $k_1 = 5.0 \times 10^{-3}$ s^{-1}, when $T_2 = (100 + 273)$ K = 373 K:

$$\ln\left(\frac{k_2}{5.0 \times 10^{-3}}\right) = \frac{39 \times 10^3}{8.314}\left(\frac{1}{488} - \frac{1}{373}\right)$$

$k_2 = 2.5 \times 10^{-4}$ s^{-1}

Answer: **2.5×10^{-4} s^{-1}**

Marks
5

- The following data were obtained for the iodide-catalysed decomposition of hydrogen peroxide, H_2O_2.

Experiment	$[I^-]$(M)	$[H_2O_2]$ (M)	Initial rate(M s^{-1})
1	0.375	0	0
2	0.375	0.235	0.000324
3	0.375	0.470	0.000657
4	0.375	0.705	0.001024
5	0.375	0.940	0.001487
6	0	0.948	0
7	0.050	0.948	0.00045
8	0.100	0.948	0.00095
9	0.150	0.948	0.00140
10	0.200	0.948	0.00193

Determine the rate law from these data.

The rate law is of the form, rate = $k[I^-]^x[H_2O_2]^y$.

Between experiments 2 and 3, $[I^-]$ is unchanged. The increase in rate is due to the increase in $[H_2O_2]$:

$$\frac{\text{rate (3)}}{\text{rate (2)}} = \frac{k(0.375)^x(0.470)^y}{k(0.375)^x(0.235)^y} = \frac{(0.470)^y}{(0.235)^y} = \frac{0.000657}{0.000324} \qquad \textbf{so } y = 1$$

Between experiments 7 and 8, $[H_2O_2]$ is unchanged. The increase in rate is due to the increase in $[I^-]$:

$$\frac{\text{rate (8)}}{\text{rate (7)}} = \frac{k(0.100)^x(0.948)^y}{k(0.050)^x(0.948)^y} = \frac{(0.100)^y}{(0.050)^y} = \frac{0.00095}{0.00045} \qquad \textbf{so } x = 1$$

Hence,

    rate = $k[I^-][H_2O_2]$

Use the data from Experiment 10 to calculate the rate constant for this reaction.

In experiment 10, $[I^-]$ = 0.200 M, $[H_2O_2]$ = 0.948 M and rate = 0.00193 M s^{-1}. Hence:

    k = rate / $[I^-][H_2O_2]$ = (0.00193 M s^{-1}) / (0.200 M × 0.948 M)

      = 0.0102 M^{-1} s^{-1}

k = 0.0102 M^{-1} s^{-1}

**ANSWER CONTINUES ON THE NEXT PAGE**

Iodide ion is used as a catalyst in this reaction. What is the role of a catalyst in a chemical reaction?

A catalyst provides a reaction pathway of lower activation energy and hence increases the rate of the reaction. It is unchanged at the end of the reaction and does not change the equilibrium position.

	Marks
	2

• When irradiated with visible light, CdS can catalyse the production of H_2 from water.

$$H_2O \; + \; light \; \underrightarrow{CdS} \; H_2 \; + \; \tfrac{1}{2}O_2$$

The rate of H_2 production from 80 mL of water at constant illumination varies with the amount of catalyst present (*i.e.* CdS loading) as shown below.
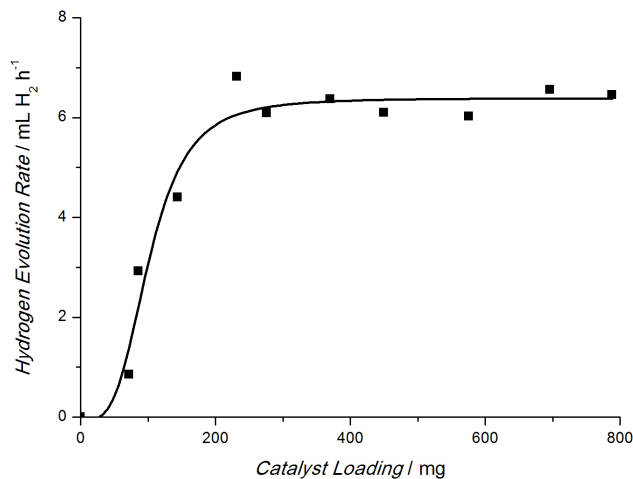
Why does the rate of H_2 production as a function of catalyst loading plateau?

Energy from light causes the water to split. The energy input is constant and this determines the maximum rate of reaction. (Essentially, light is the limiting reagent.)

Increasing the amount of catalyst increases the amount of light captured (0 - 200 catalyst loading), but cannot increase it above the amount being provided (plateau region).

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

				Marks
				3

• Consider the reaction $A(g) + B(g) + C(g) \rightarrow D(g)$ for which the following data were obtained at 25 °C.

Experiment	Initial [A] (mol L^{-1})	Initial [B] (mol L^{-1})	Initial [C] (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
1	0.0500	0.0500	0.1000	6.25×10^{-3}
2	0.1000	0.0500	0.1000	1.25×10^{-2}
3	0.1000	0.1000	0.1000	5.00×10^{-2}
4	0.0500	0.0500	0.2000	6.25×10^{-3}

Write the rate law and calculate the value of the rate constant.

The general form of the rate equation for this reaction is:

rate $= k[A]^a[B]^b[C]^c$

Between experiments 1 and 2, [B] and [C] are constant. [A] is doubled. This leads to a doubling of the rate: the rate depends on $[A]^1$ so $a = 1$.

Between experiments 2 and 3, [A] and [C] are constant. [B] is doubled. This leads to the rate increasing by a factor of four: the rate depends on $[B]^2$ so $b = 2$.

Between experiments 1 and 4, [A] and [B] are constant. [C] is doubled but there is no change in the rate: the rate is independent of [C] so $c = 0$.

Hence, the rate law is:

rate $= k[A][B]^2$

The rate constant, k, can be calculated using the results of any of the experiments. Using experiement 1:

rate $= k[0.0500$ mol L$^{-1}][0.0500$ mol L$^{-1}]^2 = 6.25 \times 10^{-3}$ mol L^{-1} s^{-1}

so

$k = 50.0$ L^2 mol^{-2} s^{-1}

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

**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 qualitatively why you rejected each of the other three graphs.
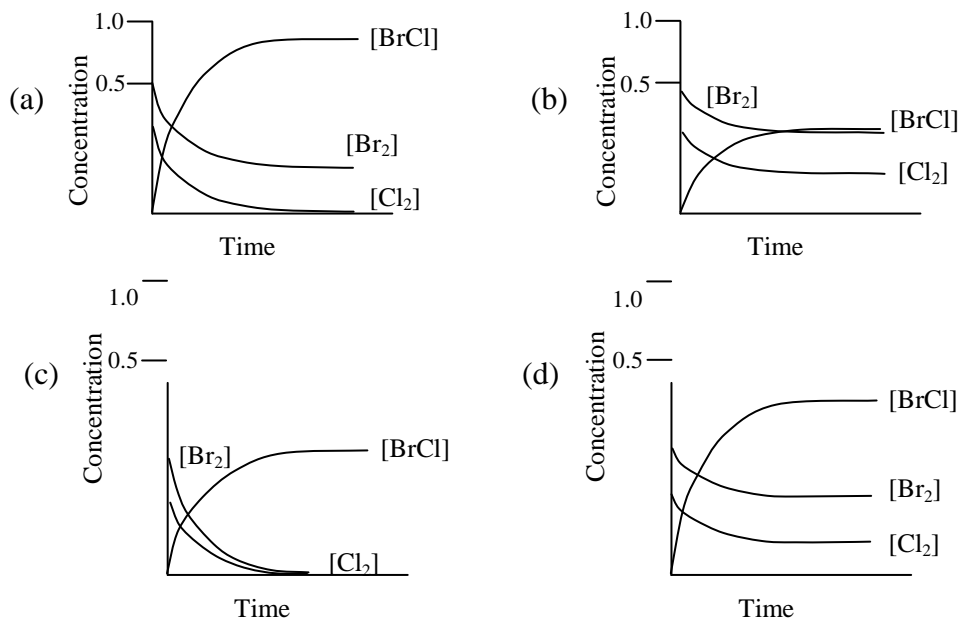

Graph B is correct.

Graphs A and C: As $K_c = 2$, the reaction does not go anywhere near to completion. At equilibrium, the concentrations of reactants and products are both significant. Graphs A and C can therefore be rejected because at least one reagent in both these graphs has dropped to 0. Also, in Graph C, the rates of change of $[Br_2]$ and $[Cl_2]$ are different, at variance with the stoichiometry of the reaction.

Graph D: Cl_2 is the limiting reagent, so the maximum $[BrCl]$ that can form is twice the initial $[Cl_2]$. But as only half the Cl_2 has been used, the maximum $[BrCl]$ that can form is $0.2 \times 2 = 0.4$ M.

	Marks
	3

- Hydrogenation of NO to N_2 and water is a potential means of reducing smog-forming NO_x gases:
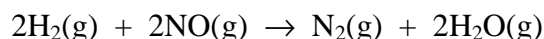
$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures (P_0).

Experiment	P_0 H$_2$ (kPa)	P_0 NO (kPa)	Rate (kPa s^{-1})
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

What is the order of the reaction? Show all working.

The rate law is in the form:

rate $= k(P(H_2))^n(P(NO))^m$

The order of the reaction is equal to $n + m$.

Between experiments (1) and (2), $P(H_2)$ is constant. $P(NO)$ is decreased from 40.0 kPa to 20.3 kPa. It is almost halved. This causes the rate to drop from 0.137 kPa s^{-1} to 0.033 kPa s^{-1}. It is decreases by (0.033 / 0.137) % = 24.1 %

As halving the amount of NO reduces the rate by a factor of 4, $m = 2$.

Between experiments (3) and (4), $P(NO)$ is constant. $P(H_2)$ is decreased from 38.5 kPa to 19.6 kPa. It is almost halved. This causes the rate to drop from 0.213 kPa s^{-1} to 0.105 kPa s^{-1}. It is decreases by (0.105 / 0.213) % = 49.2 %

As halving the amount of NO reduces the rate by a factor of 2, $n = 1$.

The order of the reaction is equal to $n + m$ so is 3.

Answer: **3**

What is the value of the rate constant?

From above, the rate law is:

rate $= k(P(H_2))(P(NO))^2$

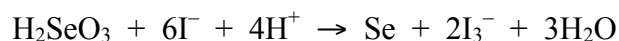**From experiment (1), rate = 0.137 kPa s^{-1} when $P(H_2)$ = 53.3 kPa and $P(NO)$ = 40.0 kPa. Hence:**

k = rate / [$(P(H_2))(P(NO))^2$]

= (0.137 kPa s^{-1}) / (53.3 kPa)(40.0 kPa)^2

= 1.61×10^{-6} kPa^{-2} s^{-1}

(Note that the units can be derived from the equation and would be required to gain the marks in this question.)

Answer: **1.61×10^{-6} kPa^{-2} s^{-1}**

- The following reaction is run from 4 different starting positions.

$$H_2SeO_3 + 6I^- + 4H^+ \rightarrow Se + 2I_3^- + 3H_2O$$

Experiment Number	Initial $[H_2SeO_3]$ (mol L^{-1})	Initial $[I^-]$ (mol L^{-1})	Initial $[H^+]$ (mol L^{-1})	Initial rate of increase of $[I_3^-]$ (mol L^{-1} s^{-1})
1	0.100	0.100	0.100	1.000
2	0.100	0.075	0.100	0.422
3	0.075	0.100	0.100	0.750
4	0.100	0.075	0.075	0.237

Determine the rate law for the reaction.

The rate law has the form:

$$\text{rate} = k[H_2SeO_3]^x[I^-]^y[H^+]^z$$

Between experiments (1) and (2), only $[I^-]$ is varied:

$$\frac{\text{rate}_{(1)}}{\text{rate}_{(2)}} = \frac{\left([I^-]_{(1)}\right)^y}{\left([I^-]_{(2)}\right)^y} \qquad \text{so} \qquad \frac{1.000}{0.422} = \left(\frac{0.100}{0.075}\right)^y$$

Solving this gives $y = 3$.

Between experiments (1) and (3), only $[H_2SeO_3]$ is varied:

$$\frac{\text{rate}_{(1)}}{\text{rate}_{(3)}} = \frac{\left([H_2SeO_3]_{(1)}\right)^x}{\left([H_2SeO_3]_{(3)}\right)^x} \qquad \text{so} \qquad \frac{1.000}{0.750} = \left(\frac{0.100}{0.075}\right)^x$$

Solving this gives $x = 1$.

Between experiments (2) and (4), only $[H^+]$ is varied:

$$\frac{\text{rate}_{(2)}}{\text{rate}_{(4)}} = \frac{\left([H^+]_{(2)}\right)^z}{\left([H^+]_{(4)}\right)^z} \qquad \text{so} \qquad \frac{0.422}{0.237} = \left(\frac{0.100}{0.075}\right)^z$$

Solving this gives $z = 2$.

Rate law: **rate $= k[H_2SeO_3][I^-]^3[H^+]^2$**

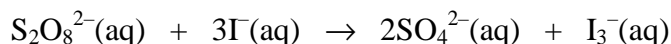Calculate the value of the rate constant.

Using experiment (1):

$(1.000 \text{ mol L}^{-1} \text{ s}^{-1}) = k \times (0.100 \text{ mol L}^{-1}) \times (0.100 \text{ mol L}^{-1})^3 \times (0.100 \text{ mol L}^{-1})^2$

$k = 1.00 \times 10^6 \text{ mol}^{-5} \text{ L}^5 \text{ s}^{-1}$

Answer: $k = 1.00 \times 10^6 \text{ mol}^{-5} \text{ L}^5 \text{ s}^{-1}$

**Marks
3**

- Peroxydisulfate and iodide ions react according to the following equation.

$$S_2O_8{}^{2-}(aq) + 3I^-(aq) \rightarrow 2SO_4{}^{2-}(aq) + I_3{}^-(aq)$$

The following rate data were collected at room temperature.

Experiment	$[S_2O_8{}^{2-}(aq)]_0$ (M)	$[I^-(aq)]_0$ (M)	Initial rate (mol L^{-1} s^{-1})
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.160	0.017	2.2×10^{-4}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[S_2O_8{}^{2-}(aq)]_0$ is constant and $[I^-(aq)]_0$ is halved from 0.034 M to 0.017 M. This halves the initial rate. The rate is directly proportional to $[I^-(aq)]$: the reaction is first order with respect to $[I^-(aq)]$.

Between experiments (2) and (3), $[I^-(aq)]_0$ is constant and $[S_2O_8{}^{2-}(aq)]_0$ is doubled from 0.080 M to 0.160 M. This doubles the initial rate. The rate is directly proportional to $[S_2O_8{}^{2-}(aq)]$: the reaction is first order with respect to $[S_2O_8{}^{2-}(aq)]$.

Hence:

rate = $k[S_2O_8{}^{2-}(aq)][I^-(aq)]$

Calculate the value of the rate constant at room temperature.

From experiment (1), the rate = 2.2×10^{-4} M s^{-1} when $[S_2O_8{}^{2-}(aq)]$ = 0.080 M and $[I^-(aq)]$ = 0.034 M. Hence:

2.2×10^{-4} M s^{-1} = k(0.080 M)(0.034 M)

k = 0.081 M^{-1} s^{-1}

(Note that the units are worked out by requiring that the units on the two sides of the rate law are the same.)

Answer: **0.081 M^{-1} s^{-1}**

**Marks
5**

- Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation.

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$
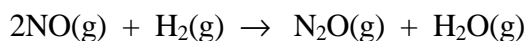
The following rate data were collected at 225 ^{o}C.

Experiment	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial rate (d[NO]/dt, M s^{-1})
1	6.4×10^{-3}	2.2×10^{-3}	2.6×10^{-5}
2	1.3×10^{-2}	2.2×10^{-3}	1.0×10^{-4}
3	6.4×10^{-3}	4.4×10^{-3}	5.1×10^{-5}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[H_2]_0$ is constant whilst $[NO]_0$ doubles. This causes the rate to increase by a factor of $(1.0 \times 10^{-4} / 2.6 \times 10^{-5}) = 3.8 \sim 4$. The reaction is second order with respect to NO.

Between experiments (1) and (3), $[NO]_0$ is constant whilst $[H_2]_0$ doubles. This causes the rate to increase by a factor of $(5.1 \times 10^{-5} / 2.6 \times 10^{-5}) = 2.0$. The reaction is first order with respect to H_2.

Thus, overall, rate $= k[NO]^2[H_2]$

Calculate the value of the rate constant at 225 ^{o}C.

Using experiment (1), the rate – 2.6×10^{-5} M s^{-1} when $[NO]_0 = 6.4 \times 10^{-3}$ M and $[H_2]_0 = 2.2 \times 10^{-3}$ M. Hence, inserting these values into the rate equation gives

$(2.6 \times 10^{-5}$ M s$^{-1}) = k \times (6.4 \times 10^{-3}$ M$)^2 \times (2.2 \times 10^{-3}$ M$)$ so $k = 290$ M^{-2} s^{-1}

The units of k are obtained by ensuring that the units on the left and right-hand side of the equation balance.

Answer: **290 M^{-2} s^{-1}**

Calculate the rate of appearance of N_2O when $[NO] = [H_2] = 6.6 \times 10^{-3}$ M.
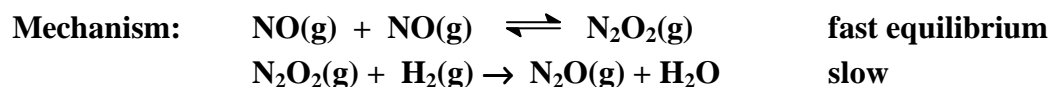
From the chemical equation, *one* N_2O is made by the reaction of *two* NO. The rate of appearance of N_2O is one half of the rate of disappearance of NO:

rate $= 0.5 \times k[NO]^2[H_2] = 0.5 \times (290$ M^{-2} s$^{-1}) \times (6.6 \times 10^{-3}$ M$)^2 \times (6.6 \times 10^{-3}$ M$)$

$= 4.2 \times 10^{-5}$ M s^{-1}

Answer: **4.2×10^{-5} M s^{-1}**

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

As collisions of three molecules is *very* unlikely, a possible reaction mechanism involves a fast equilibrium follow by the rate determining step:

Mechanism: $NO(g) + NO(g) \rightleftharpoons N_2O_2(g)$ **fast equilibrium**

$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O$ **slow**

The second step is the slowest and is rate determining. It involves the reaction of one N_2O_2 molecule with one H_2 molecule so its rate law is first order with respect to each:

rate of reaction = rate of step 2 = $k_2[N_2O_2(g)][H_2(g)]$

However, the rate law as written contains $[N_2O_2(g)]$. The concentration of this highly reactive reaction intermediate cannot be controlled or measured. To test the rate law experimentally, it should contain only species whose concentrations can be changed. N_2O_2 molecules are generated by the first step.

If the first step is in equilibrium,

$$K_{eq} = \frac{[N_2O_2(g)]}{[NO(g)]^2}$$ **or $[N_2O_2(g)] = K_{eq}[NO(g)]^2$**

Putting this expression into the rate law for the rate determining step (step 2) gives:

rate = $k_2[N_2O_2(g)][H_2(g)] = k_2 K_{eq}[NO(g)]^2 [H_2(g)] = k[NO(g)][H_2(g)]$

This mechanism gives the same rate law as found experimentally. It is thus a *possible* mechanism.

**Marks
2**

- The following data were obtained for the reaction between gaseous nitric oxide and chlorine at –10 °C:

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$
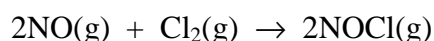
Experiment Number	Initial P_{NO} (atm)	Initial P_{Cl_2} (atm)	Initial Reaction Rate (atm s^{-1})
1	2.16	2.16	0.065
2	2.16	4.32	0.130
3	4.32	4.32	0.518

Derive an expression for the rate law for this reaction and calculate the value of the rate constant.

Between experiments (1) and (2), the partial pressure of NO is kept constant and the partial pressure of Cl₂ is doubled. This leads to a doubling of the rate so the reaction is first order with respect to Cl₂.

Between experiments (2) and (3), the partial pressure of Cl₂ is kept constant and the partial pressure of NO is doubled. This leads to the rate quadrupling. The reaction is second order with respect to NO.

Overall,

rate $= kP_{NO}{}^2 P_{Cl_2}$ or rate $= k'[NO(g)]^2[Cl_2(g)]$

As the partial pressure is proportional to the concentration. Either form is acceptable.

Using experiment (1), rate = 0.065 atm s^{-1} when P_{NO} = 2.16 atm and P_{Cl_2} = 2.16 atm. Hence,

0.065 atm s^{-1} $= k \times$ (2.16 atm)$^2 \times$ (2.16 atm)

k = 0.0064 atm^{-2} s^{-1}

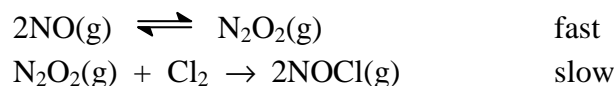**The units of k are obtained by ensuring that those in the equation balance:**

atm s^{-1} = (units of k) $\times$ (atm)$^2 \times$ (atm)   so k has units of atm^{-2} s^{-1}.

Rate law: **rate $= kP_{NO}{}^2 P_{Cl_2}$ or rate $= k'[NO(g)]^2[Cl_2(g)]$**

Rate constant: k = **0.0064 atm^{-2} s^{-1}**

**Marks
4**

The mechanism for this reaction has been postulated to be that below.

$$2NO(g) \rightleftharpoons N_2O_2(g) \qquad\qquad \text{fast}$$
$$N_2O_2(g) + Cl_2 \rightarrow 2NOCl(g) \qquad \text{slow}$$

Work out the rate law expected for this mechanism and hence show that it is consistent with the experimental rate law and the chemical equation.

The rate determining step is the slow, second step. As this is an elementary step, its rate law can be written down from its stoichiometry:

$$\text{rate} = k_2[N_2O_2(g)][Cl_2(g)]$$

where k_2 is the rate constant for this step.

This rate law involves the reactive intermediate N_2O_2. The concentration of this cannot be controlled so this rate law cannot be experimentally tested.

The first reaction is a fast equilibrium. The rate laws for the forward and backward elementary reactions are:

$$\text{rate of forward reaction} = k_1[NO(g)]^2$$
$$\text{rate of backward reaction} = k_{-1}[N_2O_2(g)]$$

where k_1 and k_{-1} are the rate constants for the forward and backward reactions, respectively.

At equilibrium, the rate of the forward and backward reactions are equal so

$$k_1[NO(g)]^2 = k_{-1}[N_2O_2(g)]$$

$$[N_2O_2(g)] = \frac{k_1}{k_{-1}}[NO(g)]^2 \qquad \text{and} \qquad \frac{[N_2O_2(g)]}{[NO(g)]^2} = \frac{k_1}{k_{-1}} = K_c$$

Substituting this value into the rate law for the second step gives,

$$\text{rate} = k_2[N_2O_2(g)][Cl_2(g)]$$
$$= k_2\frac{k_1}{k_{-1}}[NO(g)]^2[Cl_2(g)] = k'[NO(g)]^2[Cl_2(g)] \quad \text{with } k' = k_2\frac{k_1}{k_{-1}} = k_2K_c$$

This rate law is second order with respect to NO and first order with respect to Cl_2, just as in the experimentally determined rate law in 2008-N-8. The proposed mechanism is thus consistent with the experiment.

ANSWER CONTINUES ON THE NEXT PAGE

The reaction is exothermic. Draw the potential energy *vs* reaction coordinate diagram for this mechanism, labelling all species that can be isolated.

The second step is the rate determining step so it has the larger activation energy. The reaction is exothermic so the products have lower enthalpy than the reactants.
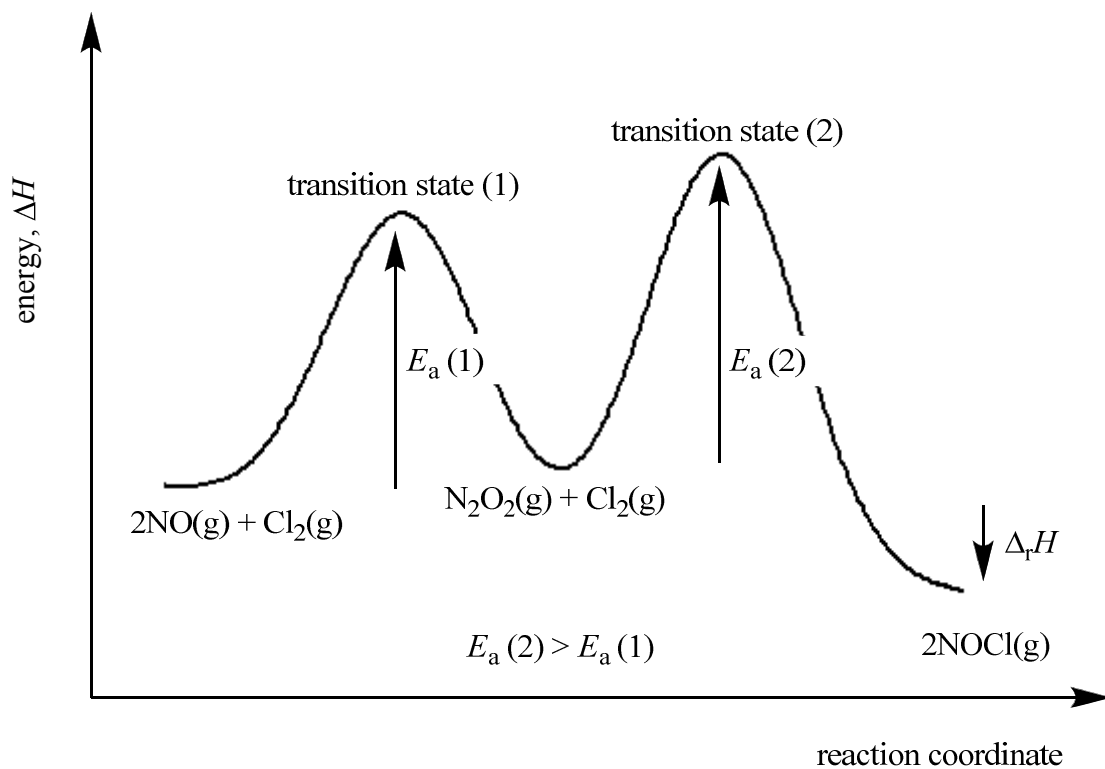
Marks
4

- The following data were obtained for the reaction between gaseous nitric oxide and chlorine at –10 °C.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$
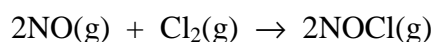
Experiment Number	Initial [NO] (mol L^{-1})	Initial [Cl$_2$] (mol L^{-1})	Initial Reaction Rate (mol L^{-1} min^{-1})
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.44

Deduce the rate law for this reaction and calculate the value of the rate constant.

RATE LAW

Between experiments (1) and (2), [NO] is constant and [Cl$_2$] is doubled. This doubles the rate:

   rate α [Cl$_2$]

Between experiments (2) and (3), [Cl$_2$] is constant and [NO] is doubled. The rate increases by a factor of 4:

   rate α [NO]^2

Overall,

   rate α [Cl$_2$][NO]^2 = k[Cl$_2$][NO]^2

RATE CONSTANT

Using any of the three experiments,

$$k = \frac{rate}{[Cl_2][NO]^2}$$

For experiment 1:

$$k = \frac{0.18}{(0.10)(0.10)^2} = 180$$

For experiment 2:

$$k = \frac{0.36}{(0.20)(0.10)^2} = 180$$

For experiment 3:

$$k = \frac{1.44}{(0.20)(0.20)^2} = 180$$

The units of k are given by:

$$units\,of\,k = \frac{units\,of\,rate}{(concentration\,units)^3}$$

$$= \frac{(mol\,L^{-1}\,min^{-1})}{(mol\,L^{-1})^3}$$

$$= mol^{-2}L^2\,min^{-1}$$

Answer: **rate = k[Cl$_2$][NO]^2**

Answer: **180 mol^{-2} L^2 min^{-1}**

**Marks
3**

- Hydrogenation of nitric oxide to nitrogen and water is a potential means of reducing smog-forming NO_x gases:
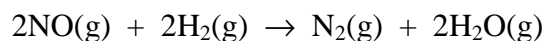
$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures (P_0).

Run	P_0 (H_2) / kPa	P_0 (NO) / kPa	Rate / kPa s^{-1}
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

Derive an expression for the rate law for this reaction.

Between Run 1 and 2, P_0 (H_2) is constant and P_0 (NO) is halved. This causes the rate to be reduced by a factor of four. The rate is second order with respect to NO.

Between Run 3 and 4, P_0 (H_2) is halved and P_0 (NO) is constant. This causes the rate to be reduced by a factor of two. The rate is first order with respect to H_2.

Overall,

$$\textbf{rate} = \boldsymbol{k \times P(H_2) \times P^2(NO)}$$

Answer: **rate $= k \times P(H_2) \times P^2(NO)$**

Calculate the value of the rate constant.

Using Run 1, rate = 0.137 kPa s^{-1} when $P(H_2)$ = 53.3 kPa and $P(NO)$ = 40.0 kPa:

0.137 kPa s^{-1} $= k \times$ 53.3 kPa $\times$ (40.0 kPa)^2

$k = 1.61 \times 10^{-6}$ kPa^{-2} s^{-1}

Answer: $\boldsymbol{k = 1.61 \times 10^{-6}}$ **kPa^{-2} s^{-1}**

What is the order of the reaction?   **1 (H_2) + 2 (NO) = 3 (third order)**

- Briefly describe two factors that determine whether a collision between two molecules will lead to a chemical reaction.

1

   For a collision to lead to a chemical reaction:

- **the molecules must collide with sufficient energy to overcome the activation energy for the reaction, and**

- **the molecules need to be orientated in the correct way for the reaction to occur.**

Marks
4

- The following initial rate data have been obtained for the gas phase reaction of nitrogen dioxide, $NO_2(g)$, and ozone, $O_3(g)$, at 300 K.

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g)$$
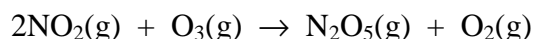
$[NO_2(g)]$ M	$[O_3(g)]$ M	Rate M s^{-1}
0.65	0.80	2.61×10^4
1.10	0.80	4.40×10^4
1.10	1.60	8.80×10^4

What is the order of this reaction with respect to each reagent?

Between the first and second experiments, $[O_3(g)]$ is kept constant and $[NO_2(g)]$ increases by about 1.7. This leads to the rate also increasing by about 1.7. The reaction is therefore first order with respect to $[NO_2(g)]$.

Between the second and third experiments, $[NO_2(g)]$ is kept constant and $[O_3(g)]$ is doubled. This also leads to a doubling of the rate. The reaction is therefore also first order with respect to $[O_3(g)]$.

rate = k$[NO_2(g)][O_3(g)]$

What is the rate constant of the reaction?

Using the rate law rate = k$[NO_2(g)][O_3(g)]$, k can be worked out using any of the three experiments. For example, using the first experiment:

rate = 2.61×10^4 = k$[NO_2(g)][O_3(g)]$ = k × (0.65) × (0.80)

Hence k = $\dfrac{2.61 \times 10^4}{(0.65)(0.80)} = 5.0 \times 10^4$

The units of k are obtained by balancing those in the rate law: the rate has units of M s^{-1} and the concentrations both have units of M. Hence:

Units of k = $\dfrac{M\ s^{-1}}{(M)(M)} = M^{-1} s^{-1}$

Answer: **$5.0 \times 10^4\ M^{-1}\ s^{-1}$**