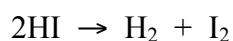


- At a certain temperature the following data were collected for the decomposition of HI.

Marks
4



Experiment	Initial [HI] (mol L ⁻¹)	Initial rate of reaction (mol L ⁻¹ s ⁻¹)
1	1.0×10^{-2}	4.0×10^{-6}
2	2.0×10^{-2}	1.6×10^{-5}
3	3.0×10^{-2}	3.6×10^{-5}

Determine the rate law for the reaction.

Between experiment (1) and (2), the concentration of HI is doubled. This leads to the rate increasing by a factor of 4.

Between experiment (1) and (3), the concentration of HI is trebled. This leads to the rate increasing by a factor 9.

The rate is proportional to [HI]²:

$$\text{rate} = k[\text{HI}]^2$$

What is the value of the rate constant for the decomposition of HI?

Using experiment (1), [HI] = 1.0×10^{-2} mol L⁻¹ and rate = 4.0×10^{-6} mol L⁻¹ s⁻¹:

$$\text{rate} = k[\text{HI}]^2$$

$$4.0 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} = (k) \times (1.0 \times 10^{-2} \text{ mol L}^{-1})^2$$

$$k = (4.0 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}) / (1.0 \times 10^{-2} \text{ mol L}^{-1})^2 = 4.0 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

Answer: $4.0 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$

- Four experiments were conducted to discover how the initial rate of consumption of BrO_3^- ions in the reaction below varied as the concentrations of the reactants were changed.



Experiment	Initial concentration (mol L^{-1})			Initial rate ($\text{mol L}^{-1} \text{s}^{-1}$)
	BrO_3^-	Br^-	H^+	
1	0.10	0.10	0.10	1.2×10^{-3}
2	0.20	0.10	0.10	2.4×10^{-3}
3	0.10	0.30	0.10	3.5×10^{-3}
4	0.20	0.10	0.15	5.4×10^{-3}

Use the experimental data in the table above to determine the order of the reaction with respect to *each* reactant.

Between experiments (1) and (3), $[\text{Br}^-]$ and $[\text{H}^+]$ are kept constant but $[\text{BrO}_3^-]$ is doubled. This doubles the rate: the rate is proportional to $[\text{BrO}_3^-]^1$ and so is first order with respect to BrO_3^- .

Between experiments (2) and (4), $[\text{BrO}_3^-]$ and $[\text{Br}^-]$ are kept constant but $[\text{H}^+]$ is increased by a factor of $(0.15/0.10) = 1.5$. This increases the rate by a factor of $(5.4 \times 10^{-3} / 2.4 \times 10^{-3}) = 2.25$: the rate is proportional to $[\text{H}^+]^2$ as $(1.5)^2 = 2.25$ and so is second order with respect to H^+ .

Between experiments (1) and (2), $[\text{BrO}_3^-]$ and $[\text{H}^+]$ are kept constant but $[\text{Br}^-]$ is increased by a factor of 3. This increases the rate by a factor of $(3.5 \times 10^{-3} / 1.2 \times 10^{-3}) = 2.9$: the rate is proportional to $[\text{Br}^-]^1$ and so is first order with respect to Br^- .

Overall,

$$\text{rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

What is the rate of formation of Br_2 when $[\text{BrO}_3^-] = [\text{Br}^-] = [\text{H}^+] = 0.10 \text{ M}$?

From the table, when $[\text{BrO}_3^-] = [\text{Br}^-] = [\text{H}^+] = 0.10 \text{ M}$, the rate of consumption of BrO_3^- is $1.2 \times 10^{-3} \text{ M s}^{-1}$. From the chemical equation, Br_2 is produced at three times this rate.

The rate of production of Br_2 is $3.6 \times 10^{-3} \text{ M s}^{-1}$.

Write the rate law for the reaction and determine the value of the rate constant, k .

From above, $\text{rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$. Using experiment (1):

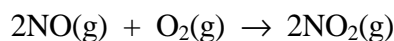
ANSWER CONTINUES ON THE NEXT PAGE

$$\begin{aligned}\text{rate} &= k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 \\ &= k(0.10 \text{ M})(0.10 \text{ M})(0.10 \text{ M})^2 = k(0.00010 \text{ M}^4) = 1.2 \times 10^{-3} \text{ M s}^{-1}\end{aligned}$$

So,

$$k = (1.2 \times 10^{-3} \text{ M s}^{-1}) / (0.00010 \text{ M}^4) = 12 \text{ M}^{-3} \text{ s}^{-1}$$

- Nitrogen monoxide, a noxious pollutant, reacts with oxygen to produce nitrogen dioxide, another toxic gas:



The following rate data were collected at 225 °C.

Marks
7

Experiment	[NO] ₀ (M)	[O ₂] ₀ (M)	Initial rate, -d[O ₂]/dt, (M s ⁻¹)
1	1.3 × 10 ⁻²	1.1 × 10 ⁻²	1.6 × 10 ⁻³
2	1.3 × 10 ⁻²	2.2 × 10 ⁻²	3.2 × 10 ⁻³
3	2.6 × 10 ⁻²	1.1 × 10 ⁻²	6.4 × 10 ⁻³

Determine the rate law for the reaction.

Between experiments 1 and 2, [NO] is held constant and [O₂] doubles. This leads to a doubling of the rate: the reaction is 1st order with respect to O₂.

Between experiments 1 and 3, [O₂] is held constant and [NO] doubles. This leads to the rate increasing by a factor of 4: the rate is 2nd order with respect to NO.

The rate law is therefore:

$$-\text{d}[\text{O}_2]/\text{d}t = k[\text{NO}]^2[\text{O}_2]$$

Calculate the value of the rate constant at 225 °C.

In experiment 1, [NO] = 1.3 × 10⁻² M, [O₂] = 1.1 × 10⁻² M and rate = 1.6 × 10⁻³ M s⁻¹. Substituting these values into the rate law gives:

$$(1.6 \times 10^{-3} \text{ M s}^{-1}) = k \times (1.3 \times 10^{-2} \text{ M})^2 \times (1.1 \times 10^{-2} \text{ M})$$

Hence:

$$k = 860 \text{ M}^{-2} \text{ s}^{-1}$$

Answer: **860 M⁻² s⁻¹**

Calculate the rate of appearance of NO₂ when [NO] = [O₂] = 6.5 × 10⁻³ M.

Substituting the values into the rate law gives:

$$\begin{aligned} -\text{d}[\text{O}_2]/\text{d}t &= k[\text{NO}]^2[\text{O}_2] \\ &= (860 \text{ M}^{-2} \text{ s}^{-1}) \times (6.5 \times 10^{-3} \text{ M})^2 \times (6.5 \times 10^{-3} \text{ M}) = 2.35 \times 10^{-4} \text{ M s}^{-1} \end{aligned}$$

From the chemical equation, the rate of appearance of NO₂ is twice the rate of loss of O₂:

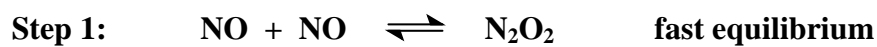
$$\text{d}[\text{NO}_2]/\text{d}t = 2 \times -\text{d}[\text{O}_2]/\text{d}t = (2 \times 2.35 \times 10^{-4} \text{ M s}^{-1}) = 4.7 \times 10^{-4} \text{ M s}^{-1}$$

Answer: **4.7 × 10⁻⁴ M s⁻¹**

ANSWER CONTINUES ON THE NEXT PAGE

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

A possible mechanism is:



If the first step is at equilibrium with equilibrium constant K_1 :

$$K_1 = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \Rightarrow [\text{N}_2\text{O}_2] = K_1[\text{NO}]^2$$

The rate of step 2 is therefore

$$\begin{aligned} \text{rate} &= k_2[\text{N}_2\text{O}_2][\text{O}_2] \\ &= k_2K_1[\text{NO}]^2[\text{O}_2] \end{aligned}$$

This is consistent with the experiment rate law with $k = k_1K$.

Marks
5

- 2-Bromo-2-methylpropane reacts with hydroxide ions to give 2-methyl-2-propanol.



The following rate data were collected at 55 °C.

Experiment	$[(\text{CH}_3)_3\text{CBr}]_0$ (M)	$[\text{OH}^-]_0$ (M)	Initial rate ($d[(\text{CH}_3)_3\text{COH}]/dt$, M s^{-1})
1	0.050	0.10	5.0×10^{-4}
2	0.20	0.10	2.0×10^{-3}
3	0.20	0.30	2.0×10^{-3}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[\text{OH}^-]_0$ is constant. $[(\text{CH}_3)_3\text{CBr}]_0$ is increased by a factor of 4 and this leads to the rate increasing by a factor of 4: rate \propto $[(\text{CH}_3)_3\text{CBr}]$.

Between experiments (2) and (3), $[(\text{CH}_3)_3\text{CBr}]_0$ is constant. $[\text{OH}^-]_0$ is increased by a factor of 3 and this leads to no change in the rate. The rate is independent of $[\text{OH}^-]_0$.

Overall, rate $= k[(\text{CH}_3)_3\text{CBr}]$.

Calculate the value of the rate constant at 55 °C.

From the rate law, $k = \text{rate} / [(\text{CH}_3)_3\text{CBr}]$.

For experiment 1, rate $= 5 \times 10^{-4} \text{ M s}^{-1}$ and $[(\text{CH}_3)_3\text{CBr}] = 0.050 \text{ M}$ and so

$$k = (5 \times 10^{-4} \text{ M s}^{-1}) / (0.050 \text{ M}) = 1.0 \times 10^{-2} \text{ s}^{-1}$$

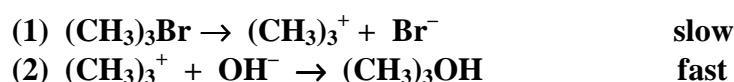
Answer: $k = 1.0 \times 10^{-2} \text{ s}^{-1}$

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

The rate is independent of $[\text{OH}^-]$ suggesting that it is involved in a step after the rate determining step.

The rate is directly proportional to $[(\text{CH}_3)_3\text{CBr}]$ suggesting that a rate determining step which is unimolecular in $(\text{CH}_3)_3\text{CBr}$.

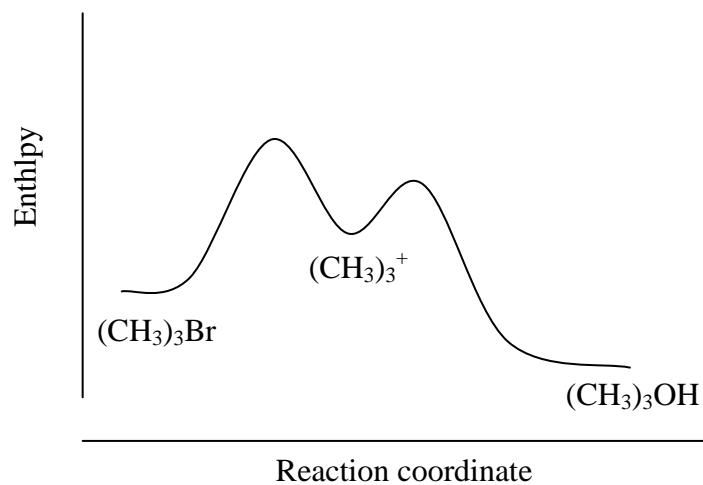
A possible mechanism is:



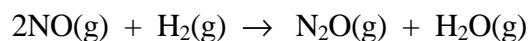
The reaction is exothermic. Draw the potential energy vs reaction coordinate diagram for this mechanism, labelling all species that can be isolated.

Marks
2

From 2008-N-6, the mechanism involves two steps: a slow first step and a fast second step. As the first step is rate determining, it has a higher activation energy. As the reaction is exothermic overall, the products have lower enthalpy than the reactants.



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



The following rate data were collected at 225 °C.

Marks
5

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), [H₂]₀ is constant and [NO]₀ doubles. As the rate increases by a factor of $\frac{1.0 \times 10^{-4}}{2.6 \times 10^{-5}} = 3.8 \sim 4$, the rate is second order with respect to [NO]₀.

Between experiments (1) and (3), [H₂]₀ doubles and [NO]₀ is constant. As the rate increases by a factor of $\frac{5.1 \times 10^{-5}}{2.6 \times 10^{-5}} = 2.0$, the rate is first order with respect to [NO]₀.

Overall,

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

Calculate the value of the rate constant at 225 °C.

Using experiment (1),

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

$$k = 2.9 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$$

$$\text{Answer: } k = 2.9 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$$

Calculate the rate of appearance of N₂O when [NO] = [H₂] = 6.6 × 10⁻³ M.

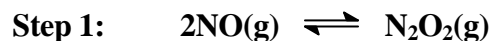
$$\begin{aligned} \text{rate of disappearance of NO} &= k[\text{NO}]^2[\text{H}_2] \\ &= (2.9 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}) \times (6.6 \times 10^{-3} \text{ M})^2 \times (6.6 \times 10^{-3} \text{ M}) \\ &= 8.3 \times 10^{-5} \text{ M s}^{-1} \end{aligned}$$

The rate of appearance of N₂O is *half* this value as, from the chemical equation, NO is disappearing at twice the rate than N₂O is appearing.

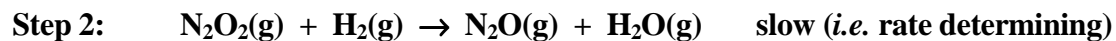
$$\text{Answer: } 4.1 \times 10^{-5} \text{ M s}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE

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



This is a fast equilibrium and so $K = \frac{[\text{N}_2\text{O}_2(\text{g})]}{[\text{NO}(\text{g})]^2}$ **or** $[\text{N}_2\text{O}_2(\text{g})] = K[\text{NO}(\text{g})]^2$



As this is rate determining,

$$\text{rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

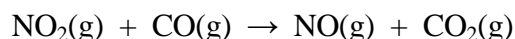
As $[\text{N}_2\text{O}_2(\text{g})] = K[\text{NO}(\text{g})]^2$, **this can be rewritten as,**

$$\text{rate} = kK[\text{NO}]^2[\text{H}_2]$$

This is consistent with the experimentally determined rate law with $k_{\text{exp}} = k_2K$.

Marks
7

- The major pollutants NO(g), CO(g), NO₂(g) and CO₂(g) are emitted by cars and can react according to the following equation.



The following rate data were collected at 225 °C.

Experiment	[NO ₂] ₀ (M)	[CO] ₀ (M)	Initial rate (d[NO ₂]/dt, M s ⁻¹)
1	0.263	0.826	1.44 × 10 ⁻⁵
2	0.263	0.413	1.44 × 10 ⁻⁵
3	0.526	0.413	5.76 × 10 ⁻⁵

Determine the rate law for the reaction.

Between experiments (1) and (2), [NO₂]₀ is constant and [CO]₀ is halved. The rate does not change. The rate is independent of [CO]: zero order with respect to [CO].

Between experiments (2) and (3), [CO]₀ is kept constant and [NO₂]₀ is doubled. The rate increases by a factor of four: the rate is second order with respect to [NO₂].

Overall,

$$\text{rate} \propto [\text{NO}_2]^2 = k[\text{NO}_2]^2$$

Calculate the value of the rate constant at 225 °C.

In experiment (1), rate = 1.44 × 10⁻⁵ M s⁻¹ when [NO₂] = 0.263 M. Using the rate law:

$$1.44 \times 10^{-5} = k \times (0.263)^2 \quad \text{so } k = 2.08 \times 10^{-4}$$

The units of k can be deduced from the rate law:

$$\text{rate} = k[\text{NO}_2]^2$$

$$\text{M s}^{-1} = (\text{units of } k) \times (\text{M})^2 \quad \text{so } k \text{ must have units of "M}^{-1} \text{s}^{-1}\text{"}$$

Answer: $2.08 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the rate of appearance of CO₂ when [NO₂] = [CO] = 0.500 M.

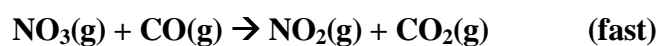
$$\text{When } [\text{NO}_2] = 0.500 \text{ M, rate} = \frac{d[\text{NO}_2]}{dt} = (2.08 \times 10^{-4}) \times (0.500)^2 = 5.20 \times 10^{-5} \text{ M s}^{-1}$$

From the chemical equation, one mole of CO₂ is produced for every mole of NO₂ that is removed. Thus, rate of appearance of CO₂ = rate of loss of NO₂.

Answer: $5.20 \times 10^{-5} \text{ M s}^{-1}$

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

A possible mechanism is:



The first step is slow and is rate determining. For this step, rate $\propto [\text{NO}_2]^2$, as observed. The second step is fast and does not contribute to the overall rate of the reaction and so the rate is independent of [CO(g)].

- 2-Propanol can be oxidised to acetone using $\text{Cr}_2\text{O}_7^{2-}$ in acidic solution as indicated in the reaction below. The rate of decrease of the $\text{Cr}_2\text{O}_7^{2-}$ ion under a certain set of conditions is $3.0 \text{ mol L}^{-1} \text{ s}^{-1}$.



What is the rate of increase in the concentration of Cr^{3+} ?

6.0 mol L⁻¹ s⁻¹

What is the rate of decrease in the concentration of 2-propanol?

9.0 mol L⁻¹ s⁻¹

The rate law for this reaction is: $\text{Rate} = k [\text{Cr}_2\text{O}_7^{2-}][\text{CH}_3\text{CH}(\text{OH})\text{CH}_3][\text{H}^+]^2$

Complete the following table by writing *increase*, *decrease* or *no change* in the box to indicate how the rate of the reaction is affected by each of the following changes.

Increase in $[\text{CH}_3\text{CH}(\text{OH})\text{CH}_3]$	increase
Increase in $[\text{CH}_3\text{COCH}_3]$	no change
Increase in pH	decrease
Increase in temperature	increase

- Complete the following table.

Formula	Systematic name	Oxidation state of transition metal	Number of <i>d</i> -electrons
$\text{K}_2[\text{Pt}(\text{CN})_4]$	potassium tetracyanidoplatinate(II)	+2	8
$[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$	hexaaquacobalt(II) chloride	+2	7

Marks
4

4

- Explain in terms of their electronic configurations and ionisation energies why the alkali metals (Group 1) are powerful *reducing* agents.

Marks
2

Ionisation energies increase across a period in the periodic table because the increasing nuclear charge holds the electrons more tightly. Hence, in any period, the Group I element is the one that most easily loses its electron (from the s subshell). This electron is then available to reduce another species.

- The half-life for the first order decomposition of $\text{N}_2\text{O}_5(\text{g})$ is $6.00 \times 10^4 \text{ s}$ at 20°C . Calculate the rate constant, k , at this temperature.

3

For a first-order reaction, the half-life, $t_{1/2}$, is related to the rate constant, k , by:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{(6.00 \times 10^4 \text{ s}^{-1})} = 1.16 \times 10^{-5} \text{ s}^{-1}$$

$$k = 1.16 \times 10^{-5} \text{ s}^{-1}$$

What percentage of the N_2O_5 molecules will have reacted after one hour?

For a first-order reaction:

$$\ln[\text{N}_2\text{O}_5] = \ln[\text{N}_2\text{O}_5]_0 - kt \quad \text{or} \quad \frac{\ln[\text{N}_2\text{O}_5]}{\ln[\text{N}_2\text{O}_5]_0} = -kt$$

Hence for $t = 1 \text{ hour} = (60 \times 60) \text{ s} = 3600 \text{ s}$,

$$\frac{\ln[\text{N}_2\text{O}_5]}{\ln[\text{N}_2\text{O}_5]_0} = -(1.16 \times 10^{-5} \text{ s}^{-1}) \times (3600 \text{ s}) = 0.0418$$

$$\frac{[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]_0} = 0.959 \text{ or } 95.9\% \text{ remains.}$$

The amount that has reacted is $(100.0 - 95.9) = 4.1 \%$

ANSWER: 4.1%