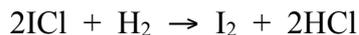


Explain the following terms or concepts.	Marks 1
Heterogeneous catalysis Catalysis that occurs with the reactants and catalyst are in different phases, such as a solid catalysing the reaction of gases.	

- At a certain temperature the following data were collected for the reaction shown.



Experiment	Initial [ICl] (mol L ⁻¹)	Initial [H ₂] (mol L ⁻¹)	Rate of formation of [I ₂] (mol L ⁻¹ s ⁻¹)
1	0.10	0.10	0.0015
2	0.20	0.10	0.0030
3	0.10	0.050	0.00075

Determine the rate law for the reaction.

Between experiments (1) and (2), [ICl] is doubled and [H₂] is constant. This change leads to a doubling of the rate: the rate is proportional to [ICl].

Between experiments (1) and (3), [ICl] is constant and [H₂] is halved. This change leads to a halving of the rate: the rate is proportional to [H₂].

Overall:

$$\text{rate} = k[\text{ICl}][\text{H}_2]$$

What is the value of the rate constant?

Using experiment (1), rate = 0.0015 mol L⁻¹ s⁻¹, [ICl] = 0.10 mol L⁻¹ and [H₂] = 0.10 mol L⁻¹:

$$\text{rate} = k[\text{ICl}][\text{H}_2] = k(0.10 \text{ mol L}^{-1})(0.10 \text{ mol L}^{-1}) = 0.0015 \text{ mol L}^{-1} \text{ s}^{-1}$$

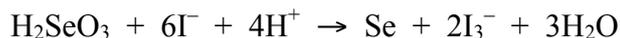
$$k = (0.0015 \text{ mol L}^{-1} \text{ s}^{-1}) / (0.10 \text{ mol L}^{-1})(0.10 \text{ mol L}^{-1}) = 0.15 \text{ L mol}^{-1} \text{ s}^{-1}$$

Answer: 0.15 L mol⁻¹ s⁻¹

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

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



Experiment	Initial $[\text{H}_2\text{SeO}_3]$ (mol L ⁻¹)	Initial $[\text{I}^-]$ (mol L ⁻¹)	Initial $[\text{H}^+]$ (mol L ⁻¹)	Initial rate of increase of $[\text{I}_3^-]$ (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 is of the form:

$$\text{rate} = k[\text{H}_2\text{SeO}_3]^x[\text{I}^-]^y[\text{H}^+]^z$$

Between experiments (1) and (3), $[\text{I}^-]$ and $[\text{H}^+]$ are both constant. The change in rate is due to the change in $[\text{H}_2\text{SeO}_3]$:

$$\frac{\text{rate (3)}}{\text{rate (1)}} = \frac{k(0.075)^x(0.100)^y(0.100)^z}{k(0.100)^x(0.100)^y(0.100)^z} = \frac{(0.075)^x}{(0.100)^x} = \frac{0.750}{1.000} \quad \text{so } x = 1$$

Between experiments (1) and (2), $[\text{H}_2\text{SeO}_3]$ and $[\text{H}^+]$ are both constant. The change in rate is due to the change in $[\text{I}^-]$:

$$\frac{\text{rate (2)}}{\text{rate (1)}} = \frac{k(0.100)^x(0.075)^y(0.100)^z}{k(0.100)^x(0.100)^y(0.100)^z} = \frac{(0.075)^y}{(0.100)^y} = \frac{0.422}{1.000} \quad \text{so } y = 3$$

Between experiments (2) and (4), $[\text{H}_2\text{SeO}_3]$ and $[\text{I}^-]$ are both constant. The change in rate is due to the change in $[\text{H}^+]$:

$$\frac{\text{rate (4)}}{\text{rate (2)}} = \frac{k(0.100)^x(0.075)^y(0.075)^z}{k(0.100)^x(0.075)^y(0.100)^z} = \frac{(0.075)^z}{(0.100)^z} = \frac{0.237}{0.422} \quad \text{so } z = 2$$

Overall:

$$\text{rate} = k[\text{H}_2\text{SeO}_3][\text{I}^-]^3[\text{H}^+]^2$$

What is the value of the rate constant?

Using, for example, experiment (1), the initial rate of increase of $[\text{I}_3^-] = 1.000 \text{ mol L}^{-1} \text{ s}^{-1}$. As 2I_3^- are produced in the reaction:

$$\text{rate of reaction} = \frac{1}{2} \times \text{rate of increase of } \text{I}_3^- = 0.5000 \text{ mol L}^{-1} \text{ s}^{-1}$$

Marks
4

$$\begin{aligned} \text{rate} &= k[\text{H}_2\text{SeO}_3][\text{I}^-]^3[\text{H}^+]^2 \\ &= k (0.100 \text{ mol L}^{-1})(0.100 \text{ mol L}^{-1})^3(0.100 \text{ mol}^{-1})^2 = 0.5000 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Hence:

$$k = (0.5000 \text{ mol L}^{-1} \text{ s}^{-1}) / (1.00 \times 10^{-6} \text{ mol}^6 \text{ L}^{-6}) = 5.00 \times 10^5 \text{ L}^5 \text{ mol}^{-5} \text{ s}^{-1}$$

Answer: $5.00 \times 10^5 \text{ L}^5 \text{ mol}^{-5} \text{ s}^{-1}$

- The rate constant of a polymer cross-linking reaction was established as a function of temperature. How can we demonstrate that the kinetics of this reaction follow Arrhenius behaviour? If it does follow Arrhenius behaviour, how can we derive the activation energy for the reaction and the pre-exponential factor A ?

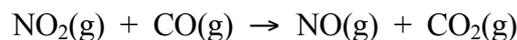
The Arrhenius equation relates the rate constant to the temperature, $k = Ae^{-E_a/RT}$

Taking natural logarithms of this gives $\ln k = \ln A - \frac{1}{T} \left(\frac{E_a}{R} \right)$

A plot of $\ln k$ (on y -axis) versus $\frac{1}{T}$ (on x -axis) will be a straight line if Arrhenius

behaviour is followed. If so, it has a gradient of $-\frac{E_a}{R}$ and a y -intercept of $\ln A$.

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



The following rate data were collected at 215 °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 kept constant and [CO]₀ is halved. There is no effect on the rate. The rate is not dependent on [CO]₀. It is zero order with respect to CO.

Between experiments (2) and (3), [CO]₀ is kept constant and [NO]₀ is doubled. This causes the rate to increase by a factor of $(5.76 \times 10^{-5} / 1.44 \times 10^{-5}) = 4$. The rate depends on the *square* of [NO]. It is second order with respect to NO.

Overall,

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

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

The rate law is determined by the rate of the slowest step. The concentration of the species in this step are determined only by steps before it.

As the rate does not depend on [CO], it must be involved in steps *after* the rate determining step.

The rate depends on [NO₂]² which is consistent with two molecules of NO₂ colliding in the rate determining step.

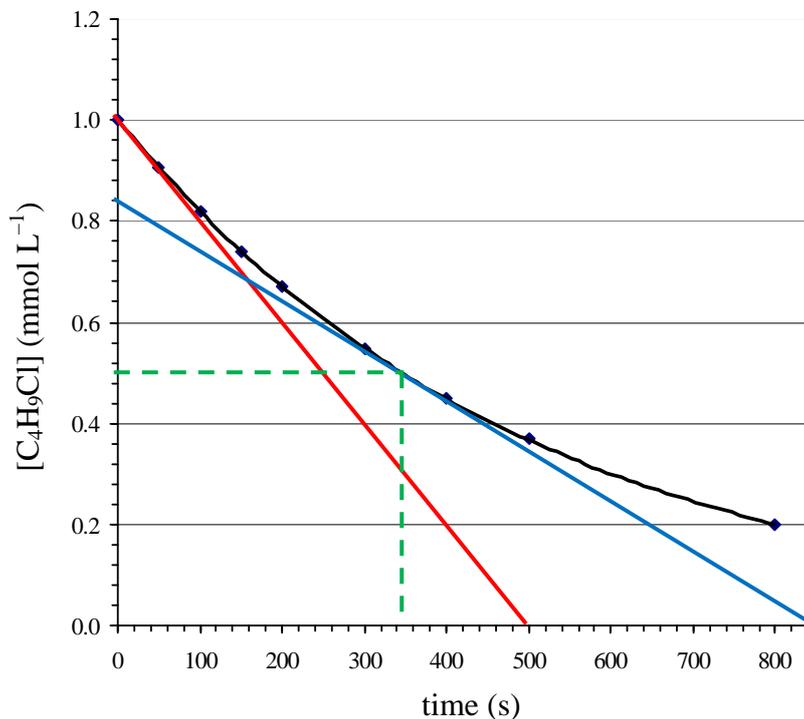
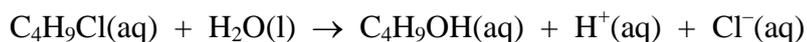
The simplest mechanism which fits these points and is consistent with the overall chemical reaction is:



Marks
4

<ul style="list-style-type: none">• Explain the following terms or concepts.	Marks 3
a) Lewis base A Lewis base is a species that donates an electron pair.	
b) Le Châtelier's principle When a chemical system in a state of equilibrium is disturbed, it reattains equilibrium by undergoing a net reaction that reduces the effect of the disturbance.	
c) Heterogeneous catalysis The acceleration of a reaction by the addition of a substance (the catalyst) which is in a different phase state from the reactants. Typically the catalyst is a solid which interacts with liquid or gaseous reactants and products. The solid's surface provides a different reaction pathway and increases the rate at which the reaction attains equilibrium.	

- The following chart shows the concentration of butyl chloride, C_4H_9Cl , as a function of time when it reacts with water according to the following equation:



Determine the instantaneous rate of reaction when $[C_4H_9Cl] = 1.0 \text{ mmol L}^{-1}$.

The rate of the reaction at any point in time is given by:

$$\text{rate} = - \frac{\Delta[C_4H_9Cl]}{\Delta t}$$

The rate when $[C_4H_9Cl] = 1.0 \text{ mmol L}^{-1}$ is given by the gradient of the curve at this point. This is shown by the red line above. Hence,

$$\text{rate} \approx - \frac{(0.0 - 1.0) \text{ mmol L}^{-1}}{(500. - 0.)s} = 0.0020 \text{ mmol L}^{-1} \text{ s}^{-1}$$

Answer: $2.0 \times 10^{-3} \text{ mmol L}^{-1} \text{ s}^{-1}$

Determine the instantaneous rate of reaction when $[C_4H_9Cl] = 0.5 \text{ mmol L}^{-1}$.

The rate when $[C_4H_9Cl] = 0.5 \text{ mmol L}^{-1}$ is given by the gradient of the curve at this point. This is shown by the blue line above. Hence,

$$\text{rate} \approx - \frac{(0.00 - 0.84) \text{ mmol L}^{-1}}{(840. - 0.)s} = 0.001 \text{ mmol L}^{-1} \text{ s}^{-1}$$

Answer: $1.0 \times 10^{-3} \text{ mmol L}^{-1} \text{ s}^{-1}$

THIS QUESTION CONTINUES ON THE NEXT PAGE

What is the order of the reaction with respect to C_4H_9Cl ?

Marks
4

From 2010-N-13, the rate of the reaction is:

$$\text{rate} = 2.0 \times 10^{-3} \text{ mmol L}^{-1} \text{ s}^{-1} \text{ when } [C_4H_9Cl] = 1.0 \text{ mmol L}^{-1}$$

and

$$\text{rate} = 1.0 \times 10^{-3} \text{ mmol L}^{-1} \text{ s}^{-1} \text{ when } [C_4H_9Cl] = 0.5 \text{ mmol L}^{-1}$$

Halving the concentration, halves the rate so the reaction is first order with respect to C_4H_9Cl .

Answer: **first order**

How long would be required for the concentration of C_4H_9Cl to reach 0.01 mmol L^{-1} ?

From 2010-N-13, the time taken for the concentration to halve from its initial value of 1.0 mmol L^{-1} to 0.5 mmol L^{-1} is approximately 350 s. This is shown by the green dotted line on the figure in 2010-N-13.

The half life is $\approx 350 \text{ s}$. Hence, the rate constant is given by:

$$k = \ln(2) / t_{1/2} = \ln(2) / 350 \text{ s} = 0.0020 \text{ s}^{-1}$$

For a first order reaction, the concentration changes with time according to:

$$\ln[C_4H_9Cl] = \ln[C_4H_9Cl]_0 - kt$$

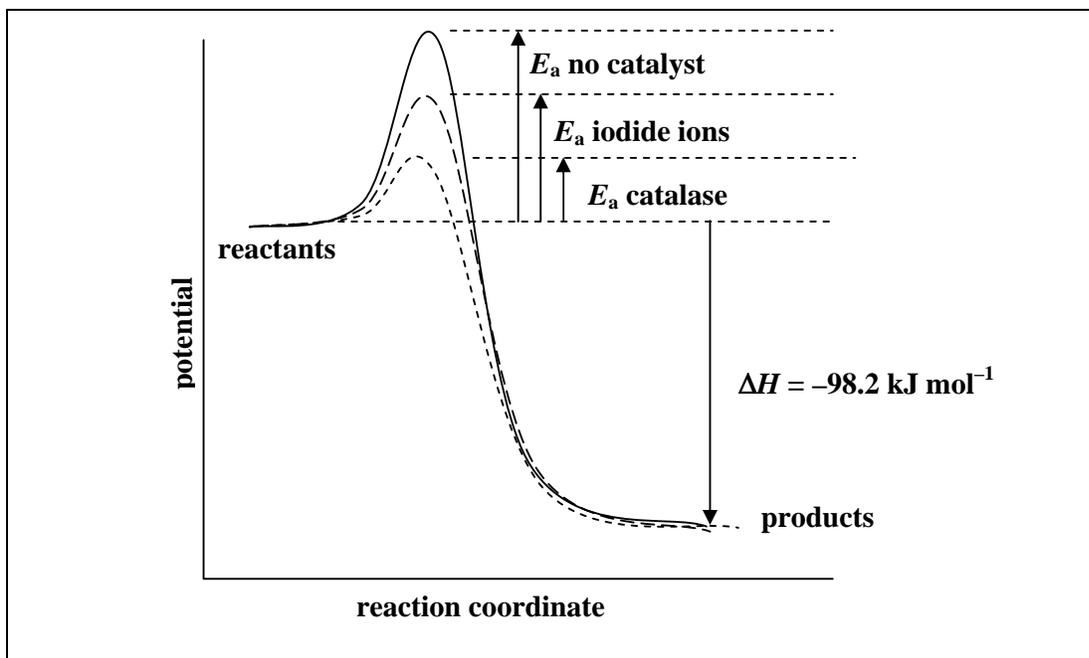
With $k = 0.0020 \text{ s}^{-1}$, the time taken to reduce the concentration its starting value of $[C_4H_9Cl]_0 = 1.0 \text{ mmol L}^{-1}$ to $[C_4H_9Cl] = 0.01 \text{ mmol L}^{-1}$ can be found using:

$$\ln(0.01) = \ln(1.0) - 0.0020t \quad \text{so } t = 2300 \text{ s}$$

Answer: **2300 s**

Marks
6

- The disproportionation of hydrogen peroxide into oxygen and water has an enthalpy of reaction of $-98.2 \text{ kJ mol}^{-1}$ and an activation barrier of 75 kJ mol^{-1} . Iodide ions act as a catalyst for this reaction, with an activation barrier of 56 kJ mol^{-1} . The enzyme, catalase, is also a catalyst for this reaction, and this pathway has an activation barrier of 23 kJ mol^{-1} . Draw a labelled potential energy diagram for this process both without and with each of the catalysts.



Calculate the factor by which the reaction speeds up due to the presence of each of these two catalysts at a temperature of 37°C . Assume that the pre-exponential Arrhenius factor remains constant.

Using the Arrhenius equation, $k = A \exp(-E_a / RT)$. Assuming that A is constant, the ratio of the rate constant for the reaction, at the temperature $T = (37 + 273) \text{ K} = 310 \text{ K}$, by a mechanism with activation energy $E_a(1)$ and by a mechanism with activation energy $E_a(2)$ is given by:

$$\frac{k(1)}{k(2)} = \frac{\exp\left(-\frac{E_a(1)}{RT}\right)}{\exp\left(-\frac{E_a(2)}{RT}\right)}$$

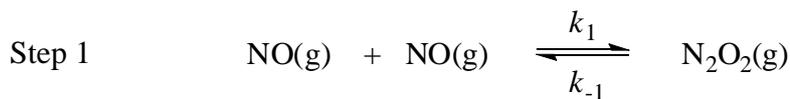
(i) iodide catalysis:

$$\frac{k(1)}{k(2)} = \frac{\exp\left(-\frac{56 \times 10^3}{8.314 \times 310}\right)}{\exp\left(-\frac{75 \times 10^3}{8.314 \times 310}\right)} = 1.6 \times 10^3$$

(ii) enzyme catalysis:

$$\frac{k(1)}{k(2)} = \frac{\exp\left(-\frac{23 \times 10^3}{8.314 \times 310}\right)}{\exp\left(-\frac{75 \times 10^3}{8.314 \times 310}\right)} = 5.8 \times 10^8$$

- A proposed kinetic model for the reaction of NO(g) with Br₂(g) to form NOBr(g) is as follows.



If Step 2 is assumed to be very slow compared to the equilibrium of Step 1, derive the overall rate equation you would expect to see for this mechanism.

If step 1 is at equilibrium, with equilibrium constant, K :

$$K = [\text{N}_2\text{O}_2\text{(g)}]/[\text{NO(g)}]^2$$

$$[\text{N}_2\text{O}_2\text{(g)}] = K [\text{NO(g)}]^2$$

Step 2 involves the bimolecular reaction of a N₂O₂ molecule with a Br₂ molecule. The rate of this step is therefore:

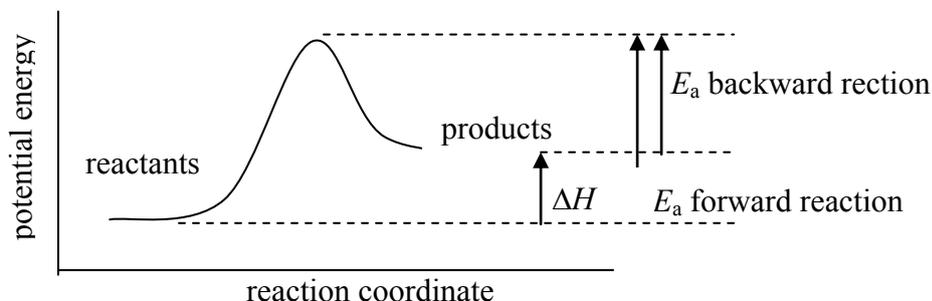
$$\text{rate} = k_2[\text{N}_2\text{O}_2\text{(g)}][\text{Br}_2\text{(g)}]$$

Using the expression for [N₂O₂(g)] from the equilibrium step gives:

$$\text{rate} = k_2K[\text{NO(g)}]^2[\text{Br}_2\text{(g)}] = k[\text{NO(g)}]^2[\text{Br}_2\text{(g)}] \text{ where } k = k_2K$$

- Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reaction, and the enthalpy of reaction.

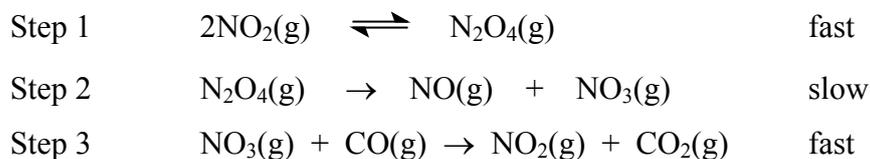
Marks
3



As the reaction is endothermic, the energy of the products is higher than that of the reactants.

- Consider the reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
The experimentally determined rate equation is: $\text{Rate} = k[\text{NO}_2(\text{g})]^2$
Show the rate expression is consistent with the following mechanism:

4



Step 2 is rate determining step and this will determine the rate of the reaction. The subsequent step can be ignored in working out the rate.

Step 2 involves the decomposition of N_2O_4 and depends only on its concentration:

$$\text{rate} = k_2[\text{N}_2\text{O}_4(\text{g})]$$

As this involves the concentration of a reaction intermediate, it is not experimentally testable. The rate law should only involve the concentration of reactants, as their concentrations can be controlled.

As step 2 is slow, step 1 will be able to reach rapid equilibrium.

The forward reaction involves two NO_2 molecules reacting so has a rate:

$$\text{rate of forward reaction} = k_1[\text{NO}_2(\text{g})]^2$$

ANSWER CONTINUES ON THE NEXT PAGE

The backward reaction involves the decomposition of N_2O_4 and so depends only on its concentration:

$$\text{rate of backward reaction} = k_{-1}[\text{N}_2\text{O}_4(\text{g})]$$

If step 1 is at equilibrium then the rate of the forward and backward reactions will be equal:

$$k_1[\text{NO}_2(\text{g})]^2 = k_{-1}[\text{N}_2\text{O}_4(\text{g})] \quad \text{or} \quad [\text{N}_2\text{O}_4(\text{g})] = \frac{k_1}{k_{-1}} [\text{NO}_2(\text{g})]^2 = K_{\text{eq}}[\text{NO}_2(\text{g})]^2$$

Using this expression for $[\text{N}_2\text{O}_4(\text{g})]$ gives:

$$\text{rate} = k_2[\text{N}_2\text{O}_4(\text{g})] = \frac{k_1 k_2}{k_{-1}} [\text{NO}_2(\text{g})]^2 \quad \text{or} \quad \text{rate} = k_2 K_{\text{eq}} [\text{NO}_2(\text{g})]^2$$

This is consistent with the experiment rate law with $k = \frac{k_1 k_2}{k_{-1}} = k_2 K_{\text{eq}}$.

- Nitric oxide reacts with ozone according to the following equation.



The following rate data were collected at a specified temperature.

Marks
3

Trial	Initial[NO] (M)	Initial [O ₃] (M)	Initial rate of reaction (M s ⁻¹)
1	2.1×10^{-6}	2.1×10^{-6}	1.6×10^{-5}
2	6.3×10^{-6}	2.1×10^{-6}	4.8×10^{-5}
3	6.3×10^{-6}	4.2×10^{-6}	9.6×10^{-5}

What is the experimental rate law for the reaction?

$$\text{Rate} = k[\text{NO}]^x[\text{O}_3]^y$$

Between trials (1) and (2), [O₃]_{initial} is constant and [NO]_{initial} is tripled. This leads to the rate tripling: $x = 1$.

Between trials (2) and (3), [NO]_{initial} is constant and [O₃]_{initial} is doubled. This leads to the rate doubling: $y = 1$.

Hence:

$$\text{rate} = k[\text{NO}][\text{O}_3]$$

What is the value of the rate constant of this reaction?

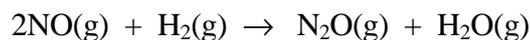
Using trial (1),

$$k = \frac{\text{rate}}{[\text{NO}][\text{O}_3]} = \frac{1.6 \times 10^{-5} \text{ M s}^{-1}}{(2.1 \times 10^{-6} \text{ M})(2.1 \times 10^{-6} \text{ M})} = 3.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

Answer: $3.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$

Marks
5

- 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.

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. Doubling [NO]₀ leads to the rate increasing by a factor of four. The rate is second-order with respect to NO.

Between experiments 1 and 3, [NO]₀ is constant. Doubling [H₂]₀ leads to the rate doubling. The rate is second-order with respect to H₂.

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

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

Using experiment 1, the rate is $2.6 \times 10^{-5} \text{ M s}^{-1}$ when $[\text{NO}]_0 = 6.4 \times 10^{-3} \text{ M}$ and $[\text{H}_2]_0 = 2.2 \times 10^{-3}$. Hence,

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

$$k = 290 \text{ M}^{-2} \text{ s}^{-1}$$

The units of k are found by requiring that the units in the rate law balance:

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

$$\text{M s}^{-1} = (\text{units of } k) \times (\text{M})^2 \times (\text{M})$$

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

Answer: $290 \text{ M}^{-2} \text{ s}^{-1}$

THE ANSWER CONTINUES ON THE NEXT PAGE

Calculate the rate of appearance of N_2O when $[\text{NO}] = [\text{H}_2] = 6.6 \times 10^{-3} \text{ M}$.

As $-\text{d}[\text{NO}]/\text{dt} = 290[\text{NO}]^2[\text{H}_2]$,

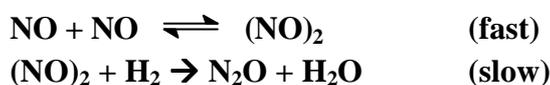
$$-\text{d}[\text{NO}]/\text{dt} = (290 \text{ M}^{-2} \text{ s}^{-1}) \times (6.6 \times 10^{-3} \text{ M})^2 \times (6.6 \times 10^{-3} \text{ M}) = 8.3 \times 10^{-5} \text{ M s}^{-1}$$

From the chemical equation, two NO are lost for every one N_2O that is made. Hence the rate of appearance of N_2O is half this value:

$$-\text{d}[\text{NO}]/\text{dt} = \frac{1}{2} \times 8.3 \times 10^{-5} \text{ M s}^{-1} = 4.1 \times 10^{-5} \text{ M s}^{-1}$$

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

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



The second step is rate determining as it is slow. For this elementary step, the rate law can be written down using the stoichiometry of the reaction equation:

$$\text{rate} = k_2[(\text{NO})_2][\text{H}_2]$$

If the equilibrium in the first step is rapidly obtained then,

$$K_{\text{eq}} = \frac{[(\text{NO})_2]}{[\text{NO}]^2} \quad \text{or} \quad [(\text{NO})_2] = K_{\text{eq}}[\text{NO}]^2$$

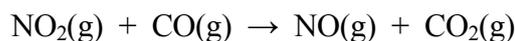
Substituting this back into the rate law for the rate determining step gives,

$$\text{rate} = k_2[(\text{NO})_2][\text{H}_2] = k_2 \times K_{\text{eq}}[\text{NO}]^2 \times [\text{H}_2] = k_{\text{eff}}[\text{NO}]^2[\text{H}_2]$$

This rate law is consistent with the one determined experimentally and so the proposed mechanism is consistent.

Marks
5

- The major pollutants NO(g), CO(g), NO₂(g) and CO₂(g), which are emitted by cars, 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.

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

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

When [NO₂] = 0.500 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: $5.20 \times 10^{-5} \text{ M s}^{-1}$

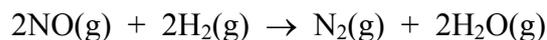
Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

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 affect the overall rate of the reaction and so the rate is independent of [CO(g)].

- Consider the results of the following set of experiments studying the rate of the reaction of nitric oxide with hydrogen at 1280 °C.



Experiment #	[NO] / M	[H ₂] / M	Initial Rate / M s ⁻¹
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	1.0×10^{-2}	2.0×10^{-3}	5.2×10^{-5}
3	1.0×10^{-2}	4.0×10^{-3}	1.0×10^{-4}

Write the rate law expression.

Between experiments 1 and 2, [H₂] is kept constant. Doubling [NO] (from 5.0×10^{-3} to 1.0×10^{-2} M) leads to the rate quadrupling. The reaction is second order with respect to [NO].

Between experiments 2 and 3, [NO] is kept constant. Doubling [H₂] (from 2.0×10^{-3} to 4.0×10^{-3} M) leads to the rate doubling. The reaction is first order with respect to [H₂]. Thus,

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

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

Calculate the rate constant, k . Include units in your answer.

Using experiment 1 and rate = $k[\text{NO}]^2[\text{H}_2]$:

$$(1.3 \times 10^{-5} \text{ M s}^{-1}) = k \times (5.0 \times 10^{-3} \text{ M})^2 \times (2.0 \times 10^{-3} \text{ M}) \quad \text{so } k = 260 \text{ M}^{-2} \text{ s}^{-1}$$

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

$$k = 260 \text{ M}^{-2} \text{ s}^{-1}$$

What is the rate of the reaction when [NO] is 1.2×10^{-2} M and [H₂] is 6.0×10^{-3} M?

Using rate = $(260 \text{ M}^{-2} \text{ s}^{-1})[\text{NO}]^2[\text{H}_2]$:

$$\text{rate} = (260 \text{ M}^{-2} \text{ s}^{-1}) \times (1.2 \times 10^{-2} \text{ M})^2 \times (6.0 \times 10^{-3} \text{ M}) = 2.2 \times 10^{-4} \text{ M s}^{-1}$$

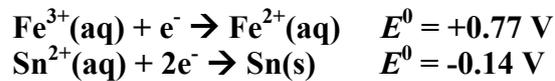
$$\text{Rate} = 2.2 \times 10^{-4} \text{ M s}^{-1}$$

Marks
4

- What is the value of the equilibrium constant for the following reaction at 298 K?



The reduction half cell reactions and E^0 values are:



In the reaction, Sn is being oxidized and so the overall cell potential is:

$$E^0 = ((+0.77) - (-0.14)) \text{ V} = +0.91 \text{ V}$$

The reaction involves 2 electrons so, using $E^0 = \frac{RT}{nF} \ln K$:

$$\ln K = E^0 \times \frac{nF}{RT} = (+0.91 \text{ V}) \times \left(\frac{2 \times 96485 \text{ C mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} \right) = 70.9$$

$$K = e^{70.9} = 6.05 \times 10^{30}$$

Answer: 6.05×10^{30}

- Consider the results of the following set of experiments studying the rate of the chemical reaction: $2A + B \rightarrow 3C + D$

Marks
4

Experiment #	initial [A] / M	initial [B] / M	Rate / M hr ⁻¹
1	0.240	0.120	2.00
2	0.120	0.120	0.500
3	0.240	0.060	1.00

Write the rate law expression.

Between experiment 1 and 2, [B] is kept constant. [A] is halved which causes the rate to be reduced by a factor of four. The rate is second order with respect to [A].

Between experiment 1 and 3, [A] is kept constant. [B] is halved which causes the rate to halve. The rate is first order with respect to [B]. Thus,

$$\text{rate} \propto [A]^2[B] = k[A]^2[B]$$

$$\text{Rate} = k[A]^2[B]$$

Calculate the rate constant, k , with units.

Using experiment 1 and rate = $k[A]^2[B]$:

$$(2.00 \text{ M hr}^{-1}) = k \times (0.240 \text{ M})^2 \times (0.120 \text{ M}) \quad \text{so } k = 289 \text{ M}^{-2} \text{ hr}^{-1}$$

$$(\text{M hr}^{-1}) = (\text{units of } k) \times (\text{M})^2 \times (\text{M}) \quad \text{so the units of } k \text{ are } \text{M}^{-2} \text{ hr}^{-1}$$

$$k = 289 \text{ M}^{-2} \text{ hr}^{-1}$$

What is the rate of the reaction when [A] is 0.0140 M and [B] is 1.35 M?

Using rate = $(289 \text{ M}^{-2} \text{ hr}^{-1})[A]^2[B]$, the rate is:

$$\begin{aligned} \text{rate} &= (289 \text{ M}^{-2} \text{ hr}^{-1}) \times (0.0140 \text{ M})^2 \times (1.35 \text{ M}) \\ &= 0.0766 \text{ M hr}^{-1} = 7.66 \times 10^{-3} \text{ M hr}^{-1} \end{aligned}$$

$$\text{Rate} = 7.66 \times 10^{-3} \text{ M hr}^{-1}$$