- The reaction order for a chemical reaction is given by the sum of the powers in the rate law. Why is the reaction order usually given by a small positive integer, *i.e.* 2 or less?

The rate of a reaction is determined by the slowest step (the rate determining step). This step usually involves 2 species colliding or a single species spontaneously undergoing a change. The rate law for this step then depends on the concentrations on the species involved in this step.

If 2 species are involved, then the rate will be proportional to the concentration of each giving an overall order of 1 + 1 = 2. If 1 species is involved, then the rate will be proportional to its concentration so the overall order will be 1.

Are zero order reactions possible? Explain your answer using examples if possible.

A zero order reaction is one in which the rate does not depend on the concentration of the reactant(s). These are known and typically occur when the reaction is dependent on the availability of a catalyst. For example:

- **A reaction of a gas which occurs on the surface of a metal will become independent of the concentration of the gas if all of the metal surface is saturated with reactants.**
- **A reaction of a substrate on an enzyme will become independent of the concentration of the substrate if the active centres in the enzyme are saturated.**

- Briefly explain how a catalyst works.

**Marks
2**

**A catalyst provides a different reaction pathway which has a lower activation
energy.**

<div style="text-align: right">Marks
8</div>

- The structure of common aspirin, acetylsalicylic acid, is shown below. It has a pK_a value of 3.5.
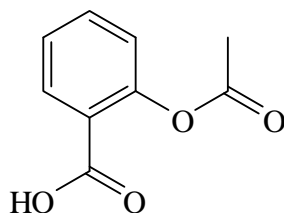
Calculate the pH of a solution in which one normal adult dose (0.65 g) is dissolved in 250 mL of water.

The chemical formula of acetylsalicylic acid is $C_9H_8O_4$. It has a molar mass of $(9 \times 12.01 \text{ (C)} + 8 \times 1.008 \text{ (H)} + 4 \times 16.00 \text{ (O)})$ g mol^{-1} = 180.154 g mol^{-1}.

The number of moles present corresponds to:

  number of moles = mass / molar mass
                = (0.65 g) / (180.154 g mol^{-1}) = 0.00361 mol

The concentration when this amount is dissolved in 250 mL of water is therefore:

  [aspirin] = number of moles / volume
          = (0.00361 mol) / (0.25 L) = 0.0144 M

As aspirin is a weak acid, $[H_3O^+]$ must be calculated using a reaction table:

	$C_9H_8O_4$	H_2O	$\rightleftharpoons$	H_3O^+	$C_9H_7O_4^-$
initial	**0.0144**	**large**		**0**	**0**
change	**-x**	**negligible**		**+x**	**+x**
final	**0.144 –x**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][C_9H_7O_4^-]}{[C_9H_7O_4]} = \frac{x^2}{0.0144-x}$$

As pK_a = -log$_{10}K_a$, $K_a = 10^{-3.5}$ and is very small, $0.0144 – x \sim 0.0144$ and hence:

  $x^2 = 0.0144 \times 10^{-3.5}$ **or** $x = 2.1 \times 10^{-3}$ M = $[H_3O^+]$

Hence, the pH is given by:

  pH = $-$log$_{10}[H_3O^+]$ = $-$log$_{10}(2.1 \times 10^{-3})$ = 2.7

Answer: **2.7**

If blood has a pH of 7.4, what percentage of aspirin is present in the deprotonated form in a solution consisting of one normal adult dose in 250 mL of blood?

Using the Henderson – Hasselbalch equation,

$$\mathbf{pH = p}\textit{K}_\mathbf{a} + \mathbf{log}\frac{\mathbf{[base]}}{\mathbf{[acid]}}$$

At a pH of 7.4

$$\mathbf{7.4 = 3.5 + log}\frac{\mathbf{[base]}}{\mathbf{[acid]}} \quad \mathbf{so} \quad \frac{\mathbf{[base]}}{\mathbf{[acid]}} = \mathbf{10^{3.9} = 7900}$$

The deprotonated, conjugate base form completely dominates at this pH.

Answer: **100% base**

Solutions of aspirin are unstable due to hydrolysis. If 0.26 g of a normal adult dose remains after 4 hours, what is the half-life of aspirin?

The number of moles present after 4 hours corresponds to:

    number of moles = mass / molar mass
                    = (0.26 g) / (180.154 g mol^{-1}) = 0.00144 mol

The concentration when this amount is dissolved in 250 mL of water is therefore:

    [aspirin] = number of moles / volume
                = (0.00144 mol) / (0.25 L) = 0.00577 M

The amount present after time t is related to the amount initially present through the equation:

    ln[A] = ln[A]$_0$ - kt

From above, [A]$_0$ = 0.0144 M. As [A] = 0.00577 M with t = 4 hours:

    ln(0.00577) = ln(0.0144) – $k \times$ 4

    k = 0.23

Finally, the half life, $t_{1/2}$, is given by

    $t_{1/2}$ = ln2 / k = 3 hours

Answer: **3 hours**

**Marks
2**

- Assuming aspirin has a half life of around 3 hours in the body, how much of an 80 mg dose will still be in the body after 1 day?

The amount of aspirin halves every 3 hours.

If the initial amount is 80 mg, there will be 40 mg after 3 hours. It continues to halve every 3 hours.

| time / hours	amount / mg
0	80
3	40
6	20
9	10
12	5
15	2.5
18	1.25*
21	0.625*
24	0.3125*

The initial dose of 80 mg was only measured to 1 significant figure and so the answer is also only known to this level of accuracy. There is 0.3 mg left after 1 day.

* To avoid rounding errors, these numbers are given in full and the rounding to 1 significant figure is left until the end.

Answer: **0.3 mg**

|		**Marks**
• The data given in the table below were obtained for the reaction between nitric oxide and chlorine at 1400 K.		**4**

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$
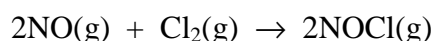
Experiment number	INITIAL $[Cl_2]$ $(mol^{-1} L^{-1})$	INITIAL $[NO]$ $(mol^{-1} L^{-1})$	INITIAL REACTION RATE $(mol^{-1} L^{-1} s^{-1})$
1	0.10	0.10	0.18
2	0.20	0.10	0.36
3	0.10	0.20	0.72

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

RATE LAW	RATE CONSTANT
Between experiments (1) and (2), [NO] is fixed and $[Cl_2]$ is doubled. This leads to the rate doubling: **rate α $[Cl_2]^1$.**	**Using this rate law and the rate from experiment (1),** **$0.18\ M\ s^{-1} = k(0.10\ M)^2(0.10\ M)$**
Between experiments (1) and (3), $[Cl_2]$ is fixed and [NO] is doubled. This leads to the rate increasing by a factor of 4: **rate α $[NO]^2$.**	**Hence,** **$k = 180\ M^{-2}\ s^{-1}$**
Overall, **rate $= k[NO]^2[Cl_2]$.**	**The units of k are such that the units of the left and right hand sides of the equation are the same:** **$M\ s^{-1} = $ (units of k)$(M^2)(M)$** **units of $k = M^{-2}\ s^{-1}$**
Answer: **rate $= k[NO]^2[Cl_2]$**	Answer: **rate constant $= 180\ M^{-2}\ s^{-1}$**

			Marks
			4

- The following data were obtained for the reaction between gaseous nitric oxide and hydrogen at 1280 °C.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$
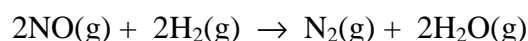
Experiment number	INITIAL [NO] (M)	INITIAL [H$_2$] (M)	INITIAL REACTION RATE (M min^{-1})
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	1.0×10^{-2}	2.0×10^{-3}	5.0×10^{-5}
3	1.0×10^{-2}	4.0×10^{-3}	1.0×10^{-4}

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

RATE LAW

Between experiments 1 and 2, [H$_2$] is constant and [NO] is doubled. The rate increases by a factor of four. The reaction is second order with respect to NO.

Between experiments 2 and 3, [NO] is constant and [H$_2$] is doubled. The rate increases by a factor of two. The reaction is first order with respect to H$_2$.

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

RATE CONSTANT

Using experiment 1,

$$\textbf{rate} = k\textbf{[NO]}^2\textbf{[H}_2\textbf{]}$$
$$\textbf{1.3}\times\textbf{10}^{-5} = k \times (\textbf{5.0}\times\textbf{10}^{-3})^2 \times (\textbf{2.0}\times\textbf{10}^{-3})$$

$$k = \textbf{260 M}^{-2}\textbf{ min}^{-1}$$

The units of k can be deduced from balancing those of the other terms:

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

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

Answer: **260 M^{-2} min^{-1}**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

**Marks
6**

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

Molecules must collide with sufficient energy to overcome the activation energy of reaction.

Molecules must be oriented correctly for reaction to occur.

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

Experimentally, the rate constant for a reaction is related to the temperature through the Arrhenius equation:

$$k = Ae^{-Ea/RT}$$

where E_a is the activation energy and A is the pre-exponential or just "A" factor.

Higher activation energy results in slower reaction rates.

The rate constant for the decomposition of N_2O_5 increases from 1.50×10^{-5} s^{-1} at 27 °C to 3.80×10^{-3} s^{-1} at 57 °C. Calculate the activation energy for the reaction.

The rate constants at two different temperatures are related through the Arrhenius equation:

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

Thus,

$$\ln\left(\frac{3.80 \times 10^{-3}\text{ s}^{-1}}{1.52 \times 10^{-5}\text{ s}^{-1}}\right) = \frac{E_a}{(8.314\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{(27+273)\text{ K}} - \frac{1}{(57+273)\text{ K}}\right)$$

$$E_a = 151000\text{ J mol}^{-1} = 151\text{ kJ mol}^{-1}.$$

Answer: **151 kJ mol^{-1}**

	Marks
• What are allotropes? Give an example of a pair of allotropes involving carbon and a second example of a pair not involving carbon.	**3**

Allotropes are different molecular forms of the same element. Examples include graphite, diamond and buckminsterfullerene for carbon, white and red phosphorus and O_2 and O_3 for oxygen.

	4
• The following data were obtained for the reaction between gaseous nitric oxide and chlorine at 1400 K.	

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$
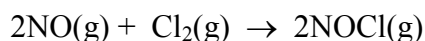
EXPERIMENT NUMBER	INITIAL [NO] $(mol\ L^{-1})$	INITIAL [Cl$_2$] $(mol\ L^{-1})$	INITIAL REACTION RATE $(mol\ L^{-1}\ s^{-1})$
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.10	0.72

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

RATE LAW

In experiments 1 and 2, [NO] is kept constant. Doubling [Cl$_2$] doubles the rate so the reaction is first order with respect to [Cl$_2$].

In experiments 1 and 3, [Cl$_2$] is kept constant. Doubling [NO] leads to the rate increasing by a factor of four so the reaction is second order with respect to [NO].

Therefore:

$$rate\ \alpha\ [NO]^2[Cl_2]$$

$$rate = k[NO]^2[Cl_2]$$

RATE CONSTANT

From experiment 1 and the rate law,

$$rate = k[NO]^2[Cl_2]$$

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

$$= \frac{(0.18\,mol\,L^{-1}\,s^{-1})}{(0.10\,mol\,L^{-1})^2(0.10\,mol\,L^{-1})}$$

$$k = 180\ mol^{-2}\ L^2\ s^{-1}$$

The units can be deduced from the rate law and the units of the rate (mol $L^{-1}\ s^{-1}$) and the concentrations (mol L^{-1}):

$$units\ of\ k = \frac{mol\,L^{-1}\,s^{-1}}{(mol\,L^{-1})^2(mol\,L^{-1})}$$

units of k are $mol^{-2}\ L^2\ s^{-1}$

Answer: **rate = $k[NO]^2[Cl_2]$**

Answer: $k = 180\ mol^{-2}\ L^2\ s^{-1}$