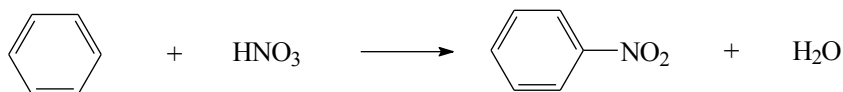


**Marks**  
**5**

- The nitration of benzene to form nitrobenzene may be written with the following stoichiometry.



The reaction was performed in the presence of excess concentrated sulfuric acid and the following data were obtained.

Experiment number	initial [benzene] (M)	initial [nitric acid] (M)	[nitrobenzene] (M) after 100 s
1	0.010	1.0	$1.2 \times 10^{-4}$
2	0.020	1.0	$2.4 \times 10^{-4}$
3	0.020	0.50	$1.2 \times 10^{-4}$

Determine the rate of the reaction for Experiment 1.

As rate =  $\frac{\text{change in concentration}}{\text{change in time}} = \frac{\Delta[\text{nitrobenzene}]}{\Delta t}$ , for experiment 1:

$$\text{rate} = \frac{[\text{nitrobenzene}]_{t_2} - [\text{nitrobenzene}]_{t_1}}{(t_2 - t_1)} = \frac{(1.2 \times 10^{-4} - 0) \text{ M}}{(100 - 0) \text{ s}} = 1.2 \times 10^{-6} \text{ M s}^{-1}$$

Answer:  $1.2 \times 10^{-6} \text{ M s}^{-1}$

What is the rate equation for this reaction?

Between experiments 1 and 2, [nitric acid] is kept constant. [Benzene] is doubled and this leads to a doubling in the [nitrobenzene] produced after 100 s. Between experiments 2 and 3, [benzene] is kept constant. [Nitric acid] is halved and this leads to a halving in the [nitrobenzene] produced after 100 s. Thus,

$$\text{rate} \propto [\text{benzene}][\text{nitric acid}] = k[\text{benzene}][\text{nitric acid}]$$

Rate =  $k[\text{benzene}][\text{nitric acid}]$

What is the value of the rate constant?

As rate =  $k[\text{benzene}][\text{nitric acid}]$ , for experiment 1 so  $k$  and its units are:

$$1.2 \times 10^{-6} \text{ M s}^{-1} = k \times (0.010 \text{ M}) \times (1.0 \text{ M}) \text{ so } k = 1.2 \times 10^{-4} \text{ M s}^{-1}$$

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

$k = 1.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

**Marks**  
**5**

- Consider the following reaction.



A series of experiments gave the rate data shown in the table below.

Experiment number	initial $[\text{ClO}_2]$ (M)	initial $[\text{OH}^-]$ (M)	initial rate of decrease of $[\text{ClO}_2]$ ( $\text{M s}^{-1}$ )
1	0.0500	0.100	$5.75 \times 10^{-2}$
2	0.100	0.100	$2.30 \times 10^{-1}$
3	0.100	0.050	$1.15 \times 10^{-1}$

Determine the rate expression for the above reaction.

Between experiments 1 and 2,  $[\text{OH}^-]$  is kept constant.  $[\text{ClO}_2]$  is doubled and this quadruples the rate: the reaction is second order with respect to  $[\text{ClO}_2]$ . Between experiments 2 and 3,  $[\text{ClO}_2]$  is kept constant.  $[\text{OH}^-]$  is halved and this halves the rate: the reaction is first order with respect to  $[\text{OH}^-]$ . Thus,

$$\text{rate} \propto [\text{ClO}_2]^2[\text{OH}^-] = k[\text{ClO}_2]^2[\text{OH}^-]$$

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]$$

What is the value of the rate constant? Include units in your answer.

Using experiment 1,

$$\text{rate} = k[\text{ClO}_2]^2[\text{OH}^-]$$

$$(5.75 \times 10^{-2} \text{ M s}^{-1}) = k \times (0.0500 \text{ M})^2 \times (0.100 \text{ M}) \quad \text{so } k = 230 \text{ M}^2 \text{ s}^{-1}$$

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

$$k = 230 \text{ M}^2 \text{ s}^{-1}$$

What is the relationship between the rate of decrease of  $[\text{ClO}_2]$  and the rate of increase of  $[\text{ClO}_3^-]$ ?

From the chemical equation, two moles of  $\text{ClO}_2$  are lost for every mole of  $\text{ClO}_3^-$  formed. Thus, the rate of decrease of  $[\text{ClO}_2]$  is twice the rate of increase of  $[\text{ClO}_3^-]$  (or the rate of increase of  $[\text{ClO}_3^-]$  is half the rate of decrease of  $[\text{ClO}_2]$ ).

- It has been proposed that the reaction  $\text{Cl}_2(\text{g}) + \text{CHCl}_3(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{CCl}_4(\text{g})$  proceeds by the following mechanism:

**Marks**  
**2**



Derive the rate expression for this mechanism.

**As the second reaction is slow, it is rate determining. From the mechanism, the rate of this step is given by:**

$$\text{rate} = k_2[\text{Cl}(\text{g})][\text{CHCl}_3(\text{g})]$$

**As Cl is a highly reactive intermediate, its concentration cannot be included in the rate equation which is to be experimentally tested. As the first step is fast, the equilibrium between  $\text{Cl}_2(\text{g})$  and  $\text{Cl}(\text{g})$  will be set up rapidly and maintained for most of the reaction. For an equilibrium,**

**rate forward reaction = rate backward reaction**

$$k_1[\text{Cl}_2(\text{g})] = k_{-1}[\text{Cl}(\text{g})]^2$$

$$\text{or } [\text{Cl}(\text{g})]^2 = \frac{k_1}{k_{-1}}[\text{Cl}_2(\text{g})]$$

**Hence,**

$$\text{rate} = k_2[\text{Cl}(\text{g})][\text{CHCl}_3(\text{g})] = k_2 \times \sqrt{\frac{k_1}{k_{-1}}[\text{Cl}_2(\text{g})]} \times [\text{CHCl}_3(\text{g})]$$

$$= k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{CHCl}_3(\text{g})][\text{Cl}_2(\text{g})]^{1/2} = k[\text{CHCl}_3(\text{g})][\text{Cl}_2(\text{g})]^{1/2}$$

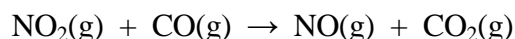
$$\text{where } k = k_2 \sqrt{\frac{k_1}{k_{-1}}}$$

$$\text{Answer: rate} = k[\text{CHCl}_3(\text{g})][\text{Cl}_2(\text{g})]^{1/2}$$

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

**Marks**  
**5**

- The major pollutants NO(g), CO(g), NO<sub>2</sub>(g) and CO<sub>2</sub>(g), which are emitted by cars, can react according to the following equation.



The following rate data were collected at 225 °C.

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

Determine the rate law for the reaction.

**Between experiments (1) and (2), [NO<sub>2</sub>]<sub>0</sub> is constant and [CO]<sub>0</sub> 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]<sub>0</sub> is kept constant and [NO<sub>2</sub>]<sub>0</sub> is doubled. The rate increases by a factor of four: the rate is second order with respect to [NO<sub>2</sub>]. 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 CO<sub>2</sub> when [NO<sub>2</sub>] = [CO] = 0.500 M.

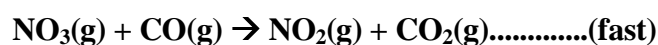
When [NO<sub>2</sub>] = 0.500 M, rate =  $\frac{d[\text{NO}_2]}{dt} = (2.08 \times 10^{-4}) \times (0.500)^2 = 5.20 \times 10^{-5} \text{ M s}^{-1}$

**From the chemical equation, one mole of CO<sub>2</sub> is produced for every mole of NO<sub>2</sub> that is removed. Thus, rate of appearance of CO<sub>2</sub> = rate of loss of NO<sub>2</sub>.**

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

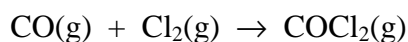
Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

**A possible mechanism is:**



**The first step is slow and is rate determining. For this step, rate  $\propto$  [NO<sub>2</sub>]<sup>2</sup>, 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)].**

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



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

**Marks**  
**5**

Experiment	initial [CO] (M)	initial [Cl <sub>2</sub> ] (M)	Initial rate (M s <sup>-1</sup> )
1	1.00	0.100	$1.29 \times 10^{-29}$
2	0.100	0.100	$1.33 \times 10^{-30}$
3	0.100	1.00	$1.30 \times 10^{-29}$
4	0.100	0.0100	$1.32 \times 10^{-31}$

Determine the rate law for the reaction.

Between experiments (1) and (2), [Cl<sub>2</sub>]<sub>initial</sub> is kept constant and [CO]<sub>initial</sub> is reduced by a factor of 10. The rate decreases by a factor of  $\frac{1.29 \times 10^{-29}}{1.33 \times 10^{-30}} \sim 10$ .

Hence the reaction is first order with respect to CO.

Between experiments (1) and (3), [Cl<sub>2</sub>] is increased by a factor of 10 and [CO]<sub>initial</sub> is decreased by a factor of 10. The rate does not change. As this change in [CO]<sub>initial</sub> is known from above to increase the rate by a factor of 10, the change in [Cl<sub>2</sub>]<sub>initial</sub> must be decreasing the rate by a factor of 10. Hence, the reaction is also first order with respect to Cl<sub>2</sub>.

Hence, overall,

$$\text{rate} = k[\text{CO}][\text{Cl}_2]$$

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

Using experiment (1), when [CO] = 1.00 M and [Cl<sub>2</sub>] = 0.100 M, the rate is  $1.29 \times 10^{-29} \text{ M s}^{-1}$ . Hence from the rate law:

$$1.29 \times 10^{-29} \text{ M s}^{-1} = k \times (1.00 \text{ M}) \times (0.100 \text{ M})$$

$$k = \frac{1.29 \times 10^{-29} \text{ M s}^{-1}}{(1.00 \text{ M}) \times (0.100 \text{ M})} = 1.29 \times 10^{-28} \text{ M}^{-1} \text{ s}^{-1}$$

Answer:  $1.29 \times 10^{-28} \text{ M}^{-1} \text{ s}^{-1}$

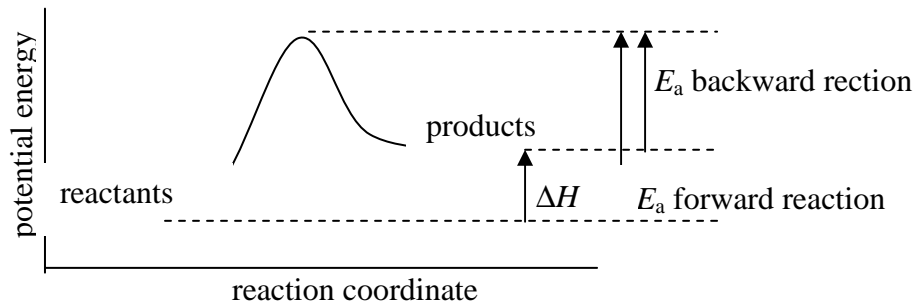
Calculate the rate of appearance of phosgene when [CO] = [Cl<sub>2</sub>] = 1.3 M.

$$\text{rate} = k[\text{CO}][\text{Cl}_2] = (1.29 \times 10^{-28} \text{ M}^{-1} \text{ s}^{-1}) \times (1.3 \text{ M}) \times (1.3 \text{ M}) = 2.2 \times 10^{-28} \text{ M s}^{-1}$$

Answer:  $2.2 \times 10^{-28} \text{ M s}^{-1}$

**Marks**  
**4**

- 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.



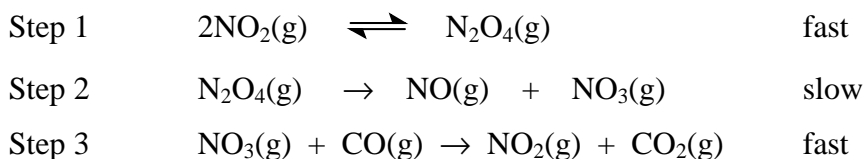
**As the reaction is endothermic, the energy of the products is higher than that of the reactants.**

Would you expect the forward or the reverse reaction to be faster? Why?

**The backward reaction would be faster as it has a lower activation energy.**

**This is a consequence of the reaction being endothermic. As the products have higher energy than the reactants and the same transition state is involved in both the forward and backward reactions, the activation energy for the backward reaction is larger than that for the forward reaction.**

- 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:



**Marks**  
**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  $\text{N}_2\text{O}_4$  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  $\text{NO}_2$  molecules reacting so has a rate:**

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

**The backward reaction involves the decomposition of  $\text{N}_2\text{O}_4$  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:**

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

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

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

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

**ANSWER CONTINUES ON THE NEXT PAGE**

- The rate constant of a particular reaction quadruples when the temperature is increased from 30 °C to 50 °C. Calculate the activation energy,  $E_a$ , for this reaction.

The temperature dependence of the rate constant is given by the Arrhenius equation,  $k = A \exp(-E_a/RT)$ . Taking the natural logarithm of this gives:

$$\ln k = \ln A - \frac{E_a}{RT}$$

The rate constant at one temperature is thus related to that at another temperature by:

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

If the rate constant quadruples then  $\frac{k_2}{k_1} = 4$ . With  $T_2 = 323 \text{ K}$  and  $T_1 = 303 \text{ K}$ :

$$\ln(4) = \frac{E_a}{R} \left(\frac{1}{323} - \frac{1}{303}\right)$$

$$E_a = +56.4 \text{ kJ mol}^{-1}$$

$$E_a = +56.4 \text{ kJ mol}^{-1}$$



**Marks**  
**3**

- Briefly describe collision theory and how it relates to the Arrhenius equation.

**Collision theory states that molecules must collide to react, and orientation, collision frequency and energy factors determine the reaction rate.**

**Not all collisions are effective - molecules need to be orientated correctly and they need to have enough energy (above the activation energy,  $E_a$ ) for a reaction to occur.**

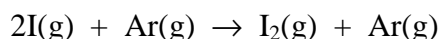
**Increasing the temperature increases the number of collisions that exceed  $E_a$ .**

**Collision theory is summarised in the Arrhenius law,  $k = Ae^{-E_a/RT}$  where A is the “frequency factor”, or pre-exponential factor – related to collision frequency and orientation of colliding molecules.**

**Arrhenius law shows that the higher  $T$ , the larger the rate constant  $k$ , and the higher is the reaction rate.**

- The following data were obtained for the reaction of iodine atoms in the gas phase in the presence of argon.

**Marks**  
**4**



Experiment Number	Initial [I] (M)	Initial [Ar] (M)	Initial Reaction Rate $-\text{d}[\text{I}(\text{g})]/\text{dt}$ ( $\text{M s}^{-1}$ )
1	$1.0 \times 10^{-5}$	$1.0 \times 10^{-3}$	$8.70 \times 10^{-4}$
2	$2.0 \times 10^{-5}$	$1.0 \times 10^{-3}$	$3.48 \times 10^{-3}$
3	$2.0 \times 10^{-5}$	$5.0 \times 10^{-3}$	$1.74 \times 10^{-2}$

Derive an expression for the rate law for the formation of  $\text{I}_2(\text{g})$  and calculate the value of the rate constant for this reaction.

Between experiments (1) and (2),  $[\text{Ar}]$  is constant and  $[\text{I}]$  is doubled. This leads to the rate increasing by  $\frac{3.48 \times 10^{-3}}{8.70 \times 10^{-4}}$ : a factor of 4. The rate is proportional to  $[\text{I}]^2$ .

Between experiments (2) and (3),  $[\text{I}]$  is constant and  $[\text{Ar}]$  is increased by a factor of 5. This leads to the rate increasing by  $\frac{1.74 \times 10^{-2}}{3.48 \times 10^{-3}}$ : a factor of 5. The rate is proportional to  $[\text{Ar}]^1$ .

Overall:

$$-\text{d}[\text{I}(\text{g})]/\text{dt} = k[\text{I}]^2[\text{Ar}]$$

From experiment (1), rate =  $8.70 \times 10^{-4} \text{ M s}^{-1}$  when  $[\text{I}] = 1.0 \times 10^{-5} \text{ M}$  and  $[\text{Ar}] = 1.0 \times 10^{-3} \text{ M}$ . Hence:

$$8.70 \times 10^{-4} \text{ M s}^{-1} = k \times (1.0 \times 10^{-5} \text{ M})^2 \times (1.0 \times 10^{-3} \text{ M})$$

$$k = 8.70 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$$

Rate law:  $-\text{d}[\text{I}(\text{g})]/\text{dt} = k[\text{I}]^2[\text{Ar}]$

Rate constant:  $8.70 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$

Calculate the rate of appearance of  $\text{I}_2(\text{g})$  when  $[\text{I}(\text{g})] = 1.0 \times 10^{-3} \text{ M}$  and  $[\text{Ar}(\text{g})] = 1.0 \times 10^{-2} \text{ M}$ .

$$\begin{aligned} -\text{d}[\text{I}(\text{g})]/\text{dt} &= k[\text{I}]^2[\text{Ar}] \\ &= (8.70 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}) \times (1.0 \times 10^{-3} \text{ M})^2 \times (1.0 \times 10^{-2} \text{ M}) = 87 \text{ M s}^{-1} \end{aligned}$$

From the chemical equation, two I are lost for every  $\text{I}_2$  produced. Hence:

$$\text{d}[\text{I}_2(\text{g})]/\text{dt} = \frac{1}{2} \times -\text{d}[\text{I}(\text{g})]/\text{dt} = \frac{1}{2} \times (87 \text{ M s}^{-1}) = 44 \text{ M s}^{-1}$$

Answer:  $44 \text{ M s}^{-1}$