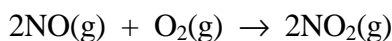


- Nitrogen monoxide, a noxious pollutant, reacts with oxygen to produce nitrogen dioxide, another toxic gas:



The following rate data were collected at 225 °C.

**Marks**  
**7**

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

Determine the rate law for the reaction.

**Between experiments 1 and 2, [NO] is held constant and [O<sub>2</sub>] doubles. This leads to a doubling of the rate: the reaction is 1<sup>st</sup> order with respect to O<sub>2</sub>.**

**Between experiments 1 and 3, [O<sub>2</sub>] is held constant and [NO] doubles. This leads to the rate increasing by a factor of 4: the rate is 2<sup>nd</sup> 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<sup>-2</sup> M, [O<sub>2</sub>] = 1.1 × 10<sup>-2</sup> M and rate = 1.6 × 10<sup>-3</sup> M s<sup>-1</sup>. 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<sup>-2</sup> s<sup>-1</sup>**

Calculate the rate of appearance of NO<sub>2</sub> when [NO] = [O<sub>2</sub>] = 6.5 × 10<sup>-3</sup> 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 NO<sub>2</sub> is *twice* the rate of loss of O<sub>2</sub>:**

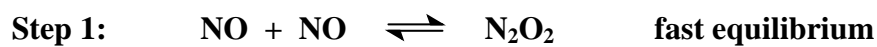
$$\text{d}[\text{NO}_2]/\text{d}t = 2 \times -\text{d}[\text{O}_2]/\text{d}t = (2 \times 2.35 \times 10^{-4} \text{ M s}^{-1}) = 4.7 \times 10^{-4} \text{ M s}^{-1}$$

Answer: **4.7 × 10<sup>-4</sup> M s<sup>-1</sup>**

**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  $k = k_1K$ .**