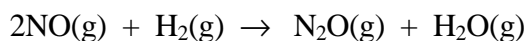


**Marks**  
**5**

- 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] <sub>0</sub> (M)	[H <sub>2</sub> ] <sub>0</sub> (M)	Initial rate (d[NO]/dt, M s <sup>-1</sup> )
1	$6.4 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.6 \times 10^{-5}$
2	$1.3 \times 10^{-2}$	$2.2 \times 10^{-3}$	$1.0 \times 10^{-4}$
3	$6.4 \times 10^{-3}$	$4.4 \times 10^{-3}$	$5.1 \times 10^{-5}$

Determine the rate law for the reaction.

**Between experiments 1 and 2, [H<sub>2</sub>]<sub>0</sub> is constant. Doubling [NO]<sub>0</sub> 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]<sub>0</sub> is constant. Doubling [H<sub>2</sub>]<sub>0</sub> leads to the rate doubling. The rate is second-order with respect to H<sub>2</sub>.**

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

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  $\text{N}_2\text{O}$  when  $[\text{NO}] = [\text{H}_2] = 6.6 \times 10^{-3} \text{ M}$ .

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

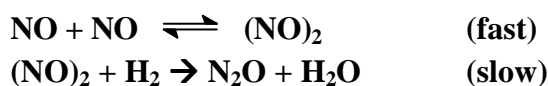
$$-\text{d}[\text{NO}]/\text{dt} = (290 \text{ M}^{-2} \text{ s}^{-1}) \times (6.6 \times 10^{-3} \text{ M})^2 \times (6.6 \times 10^{-3} \text{ M}) = 8.3 \times 10^{-5} \text{ M s}^{-1}$$

From the chemical equation, two NO are lost for every one  $\text{N}_2\text{O}$  that is made. Hence the rate of appearance of  $\text{N}_2\text{O}$  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.