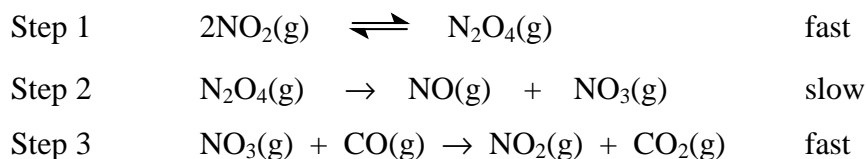


**Marks**  
**4**

- 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:



**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  $T_1 = 303 \text{ K}$ :

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

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

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