

(iii) According to the Arrhenius equation (not given on the data sheet), at 300 K

$$k_R(300 \text{ K}) = A \exp \{-E_a/(R \times 300 \text{ K})\}$$

and at 308 K

$$k_R(308 \text{ K}) = A \exp \{-E_a/(R \times 308 \text{ K})\}$$

However,

$$k_R(308 \text{ K})/k_R(300 \text{ K}) = 2$$

so that

$$\frac{k_R(308 \text{ K})}{k_R(300 \text{ K})} = 2 = \frac{\exp\{-E_a/(R \times 308 \text{ K})\}}{\exp\{-E_a/(R \times 300 \text{ K})\}}$$

or, on simplifying

$$2 = \exp \left\{ \frac{-E_a}{(R \times 308 \text{ K})} - \left( \frac{-E_a}{(R \times 300 \text{ K})} \right) \right\}$$

Taking natural logarithms of both sides of the equation,

$$\ln 2 = \frac{-E_a}{R} \left\{ \frac{1}{308 \text{ K}} - \frac{1}{300 \text{ K}} \right\}$$

that is,

$$E_a = -(R \times \ln 2)/(-8.658 \times 10^{-5} \text{ K}^{-1}) = 66.6 \text{ kJ mol}^{-1}$$

### Question 9

(a) The first step (equation 16) is the *initiation* step; this produces one of the radical chain carriers, H•.

The second and third steps (equations 17 and 18) are known as the *propagation* reactions. Summing the second and third steps shows that in these two steps the reactants H<sub>2</sub> and NO<sub>2</sub> are converted into the products H<sub>2</sub>O and NO. The H• atom that we started off with in the second step is regenerated in the third step and can thus duplicate the process, forming more NO and H<sub>2</sub>O.

This is an example of a closed sequence. The cycle of propagation reactions will continue until it is interrupted by a *termination* reaction such as the last step (equation 19). This involves the removal of the second radical chain carrier, HO•.

The average number of times the cycle is repeated between the formation of a particular chain carrier and its termination is known as the *chain length*.

(b) (i) According to the mechanism,

$$d[\text{H}\cdot]/dt = k_1[\text{H}_2][\text{NO}_2] - k_2[\text{H}\cdot][\text{NO}_2] + k_3[\text{HO}\cdot][\text{H}_2]$$

$$d[\text{OH}\cdot]/dt = k_2[\text{H}\cdot][\text{NO}_2] - k_3[\text{HO}\cdot][\text{H}_2] - k_4[\text{HO}\cdot][\text{NO}_2]$$

Applying the steady-state approximation to both chain carriers,

$$0 = k_1[\text{H}_2][\text{NO}_2] - k_2[\text{H}\cdot][\text{NO}_2] + k_3[\text{HO}\cdot][\text{H}_2]$$

$$0 = k_2[\text{H}\cdot][\text{NO}_2] - k_3[\text{HO}\cdot][\text{H}_2] - k_4[\text{HO}\cdot][\text{NO}_2]$$

Adding these two expressions gives:

$$0 = k_1[\text{H}_2][\text{NO}_2] - k_4[\text{HO}\cdot][\text{NO}_2]$$

Thus,

$$[\text{HO}\cdot] = \frac{k_1}{k_4}[\text{H}_2] \text{ (as required)} \quad (\text{A4})$$

From the stoichiometry of the overall reaction (equation 15),

$$J = \frac{d[\text{H}_2\text{O}]}{dt}$$

According to the mechanism, H<sub>2</sub>O is formed in step 3 (equation 18), so

$$\frac{d[\text{H}_2\text{O}]}{dt} = k_3[\text{H}_2][\text{HO}\cdot]$$