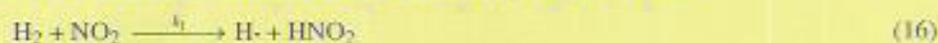


**Question 9**

The reaction between hydrogen,  $\text{H}_2$ , and nitrogen dioxide,  $\text{NO}_2$ , in the gas phase at  $400^\circ\text{C}$  has the following time-independent stoichiometry:



A possible mechanism for this reaction is a chain reaction, as follows:



(a) (6 marks) With reference to this mechanism, explain what is meant by a chain reaction, paying particular attention to the role played by each of the steps 16 to 19. In your answer, identify the chain carriers in the mechanism.

(b) (14 marks) By applying the steady-state approximation to  $\text{HO}\cdot$  and  $\text{H}\cdot$ , show that

$$[\text{HO}\cdot] = k_1[\text{H}_2]/k_4 \quad (20)$$

and hence show that the chemical rate equation predicted by the mechanism has the following form:

$$J = \frac{d[\text{H}_2\text{O}]}{dt} = k_R[\text{H}_2]^2 \quad (21)$$

Include in your answer a brief description of the rationale underlying the steady-state approximation.

**Question 10**

(a) (8 marks) The Langmuir isotherm for single-site adsorption of a gas A can be written as follows:

$$\theta = \frac{bp_A}{1 + bp_A} \quad (22)$$

State the assumptions involved in the derivation of this expression, and explain the significance of the quantity  $b$ .

Would you expect the value of  $b$  to increase or decrease with increasing temperature? Explain your answer.

(b) (12 marks) Write down, and briefly describe, each step in the Langmuir-Hinshelwood mechanism for the following heterogeneously catalysed reaction, involving the two reactants A and B:



and indicate which step is taken to be rate-limiting.

At room temperature, the experimental rate equation for reaction 23 is found to be of the form

$$r = -\frac{dp_A}{dt} = k_R \frac{p_B}{p_A}$$

whereas at higher temperatures it takes the form

$$r = -\frac{dp_A}{dt} = k_R p_A p_B$$

How can these results be rationalized in terms of the mechanism you have proposed? Explain your reasoning.