Question 9 The reaction between hydrogen, H_2, and nitrogen dioxide, NO_2, in the gas phase at 400 °C has the following time-independent stoichiometry:

$$H_2(g) + NO_2(g) = H_2O(g) + NO(g) \qquad (15)$$

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

$$H_2 + NO_2 \xrightarrow{k_1} H\cdot + HNO_2 \qquad (16)$$

$$H\cdot + NO_2 \xrightarrow{k_2} NO + HO\cdot \qquad (17)$$

$$HO\cdot + H_2 \xrightarrow{k_3} H_2O + H\cdot \qquad (18)$$

$$HO\cdot + NO_2 \xrightarrow{k_4} HNO_3 \qquad (19)$$

(*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 HO· and H·, show that

$$[HO\cdot] = k_1[H_2]/k_4 \qquad (20)$$

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

$$J = \frac{d[H_2O]}{dt} = k_R[H_2]^2 \qquad (21)$$

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:

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

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:

$$A(g) + B(g) \xrightarrow[\text{catalyst}]{\text{metal}} C(g) \qquad (23)$$

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.