

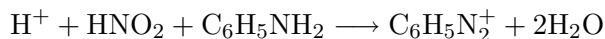
CYL110 2009-2010 MINOR II

Max Marks 100

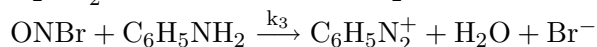
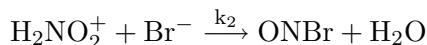
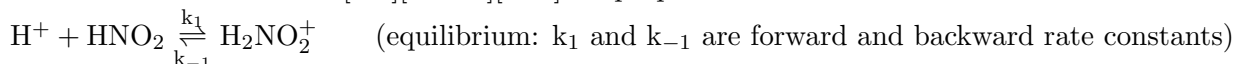
Time 1 hour

PKC, NDK, SP, SS

- Q. 1: (a) State whether the following statements are true or false and provide only a **one line** statement to support your answer:
- (i) The rate law for the elementary reaction  $A + B \longrightarrow$  products in an ideal system must be  $rate = k[A][B]$ .
  - (ii) The rate law for the composite reaction  $C + D \longrightarrow$  products in an ideal system might not be  $rate = k[C][D]$ .
  - (iii) If we know the mechanism of a reaction including the values of the elementary rate constants, we can find the rate law.
  - (iv) The elementary step  $Hg_2^{2+} \longrightarrow 2Hg^+$  can not occur in a reaction mechanism.
  - (v) In the termination step of the hydrogen-bromine reaction, only Br radical recombination is important. (2 × 5 = 10 marks)
- (b) The reaction  $2Fe^{2+} + Tl^{3+} \longrightarrow 2Fe^{3+} + Tl^+$  in aqueous solution has the rate law  $rate = k \frac{[Fe^{2+}]^2[Tl^{3+}]}{[Fe^{2+}] + k'[Fe^{3+}]}$ . Devise a mechanism consistent with this rate law. Explain your steps. (10 + 5 = 15 marks)
- (c) The rate law for the  $Br^-$  catalyzed aqueous reaction



is observed to be  $rate = k[H^+][HNO_2][Br^-]$ . A proposed mechanism is



Derive the observed rate law from the given mechanism. State any approximation you must have made to arrive at your answer. Also can you suggest which of the steps might be the rate determining one and why? (15 marks)

- Q. 2: The concentrations of B and C are slightly increased when the equilibrium  $A \rightleftharpoons B + C$  at 30 °C is subjected to a temperature jump. During the relaxation, the concentration of A reaches half its new equilibrium value in 2.0 μs. The equilibrium constant for the system is  $4.0 \times 10^{-15}$  at 30 °C and the equilibrium concentration of B and C are both  $3.0 \times 10^{-4} \text{ mol dm}^{-3}$ . Calculate the forward ( $k_f$ ) and backward ( $k_b$ ) rate constants. (15 marks)

- Q. 3: Consider a reaction  $A(g) \rightarrow b B(g)$  that is first order in A.

- (a) Sketch the variation in the rate of the reaction with time if this reaction is performed in a rigid, closed container.
- (b) Imagine performing the same reaction in a container, volume  $V_0$  and  $n_0$  moles of A initially, at constant pressure. Obtain an expression for  $-\frac{d[A]}{dt}$ . Determine  $[A](t)$ .
- (c) Are there conditions under which  $[A](t)$  is the same when the reaction is conducted at constant volume and constant pressure? (5+15+10 = 30 marks)

- Q. 4: (a) Based on the Michaelis-Menten mechanism for enzymes discussed in class, draw a graph of the rate of the reaction against substrate concentration. Using the same graph how can you estimate the value of  $K_M$ , the Michaelis-Menten constant.
- (b) Drugs are often used as inhibitors ( $I$ ) to inhibit actions of enzymes during treatment of certain diseases wherein they compete with the substrate ( $S$ ) for the enzyme active site. In such a case, suggest a modified Michaelis-Menten rate mechanism. Also write the key steps (and equations) that will help you derive the final modified Michaelis-Menten rate law. (Please note: The final derivation of the rate law is not required; only steps that will help you to derive it have been asked for in this question) (5+10 = 15 marks)