

**Q6.8** If  $k_{-1}[\text{OH}^-][\text{Cl}^-] \gg k_2[\text{Fe}^{\text{II}}]$ , what is the value of  $\beta$  in the reduced rate equation 6.8? Select your answer from the key for Q6.7 to Q6.9.

**Q6.9** If  $k_{-1}[\text{OH}^-][\text{Cl}^-] \gg k_2[\text{Fe}^{\text{II}}]$ , what is the value of  $\delta$  in the reduced rate equation 6.8? Select your answer from the key for Q6.7 to Q6.9.

**Q6.10** With reference to the proposed mechanism, select *three* correct statements from the key.

KEY for Q6.10

- A The theoretical rate equation for  $\text{Fe}^{\text{III}}$  provides the most straightforward route to the chemical rate equation predicted by the mechanism.  
 B The rate of change of concentration of  $\text{Fe}^{\text{III}}$  is given by the following expression:

$$\frac{d[\text{Fe}^{\text{III}}]}{dt} = k_2[\text{Fe}^{\text{II}}][\text{Fe}^{\text{IV}}]$$

- C The rate of change of concentration of  $\text{Cl}^-$  arising from the back reaction of the first step (equation 6.6) alone, is given by the following expression:

$$\frac{d[\text{Cl}^-]}{dt} = k_{-1}[\text{Fe}^{\text{IV}}][\text{OH}^-][\text{Cl}^-]$$

- D Applying the steady-state approximation leads to the following expression for the concentration of the intermediate,  $\text{Fe}^{\text{IV}}$ :

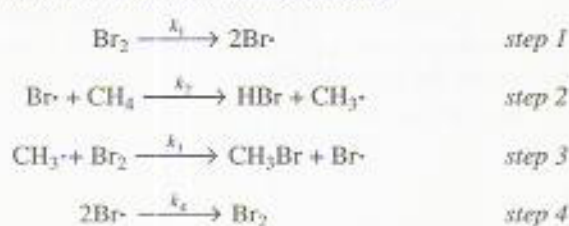
$$[\text{Fe}^{\text{IV}}] = \frac{k_1[\text{Fe}^{\text{II}}][\text{HOCl}]}{k_{-1}[\text{OH}^-][\text{Cl}^-] - k_2[\text{Fe}^{\text{II}}]}$$

- E If  $k_2[\text{Fe}^{\text{II}}] \gg k_{-1}[\text{OH}^-][\text{Cl}^-]$ , the reduced form of the chemical rate equation (equation 6.8) predicts that the overall order of reaction is two.  
 F If  $k_2[\text{Fe}^{\text{II}}] \gg k_{-1}[\text{OH}^-][\text{Cl}^-]$ , the rate constant  $k_R$  in the reduced form of the chemical rate equation (equation 6.8) is given by  $k_R = k_2$ .  
 G If  $k_{-1}[\text{OH}^-][\text{Cl}^-] \gg k_2[\text{Fe}^{\text{II}}]$ , the reduced form of the chemical rate equation (equation 6.8) predicts that doubling the concentration of hydroxide ions,  $\text{OH}^-$ , in the solution will have no effect on the overall rate of reaction.  
 H If  $k_{-1}[\text{OH}^-][\text{Cl}^-] \gg k_2[\text{Fe}^{\text{II}}]$ , then the first step can be considered to be an established pre-equilibrium.

**Q6.11** The gas-phase reaction between bromine,  $\text{Br}_2$ , and methane,  $\text{CH}_4$ , produces bromomethane,  $\text{CH}_3\text{Br}$ , and hydrogen bromide,  $\text{HBr}$ , as major products. The reaction can be considered to have the following time-independent stoichiometry:



In simplified form, a possible mechanism for this reaction is a chain reaction, as follows:



By applying the steady-state approximation to *both* chain carriers,  $\text{Br}\cdot$  and  $\text{CH}_3\cdot$ , it can be shown that this

scheme leads to a chemical rate equation of the following form:

$$J = k_R[\text{CH}_4]^\alpha[\text{Br}_2]^\beta \quad (6.10)$$

With reference to the proposed mechanism and the chemical rate equation in equation 6.10, select from the key the *two* incorrect statements.

KEY for Q6.11

- A Step 1 in the proposed mechanism is an example of an initiation reaction.  
 B Step 3 in the proposed mechanism is an example of a propagation reaction.  
 C According to the proposed mechanism, the rate of change of concentration of  $\text{CH}_3\cdot$  is given by the following expression:

$$\frac{d[\text{CH}_3\cdot]}{dt} = k_2[\text{Br}\cdot][\text{CH}_4] - k_3[\text{CH}_3\cdot][\text{Br}_2]$$

- D According to the proposed mechanism, the rate of change of concentration of  $\text{Br}\cdot$  is given by the following expression:

$$\frac{d[\text{Br}\cdot]}{dt} = k_1[\text{Br}_2] - k_2[\text{Br}\cdot][\text{CH}_4] + k_3[\text{CH}_3\cdot][\text{Br}_2] - k_4[\text{Br}\cdot]^2$$

- E According to the proposed mechanism, the concentration of  $\text{Br}\cdot$  can be expressed by:

$$[\text{Br}\cdot] = \left(\frac{k_1}{k_4}\right)[\text{Br}_2]$$

- F In the chemical rate equation predicted by the proposed mechanism (equation 6.10),  $\alpha = 1$ .  
 G In the chemical rate equation predicted by the proposed mechanism (equation 6.10),  $\beta = 0.5$ .

#### PART D (Block 4)

**Q6.12** Select from the key *three* statements that are correct.

KEY for Q6.12

- A The experimental rate equation for a homogeneously catalysed reaction always has the same form as the experimental rate equation for the corresponding uncatalysed reaction.  
 B In the hydroformylation of a terminal alkene,  $\text{RCH}=\text{CH}_2$ , catalysed by the rhodium complex  $[\text{RhH}(\text{CO})\text{L}_3]$ , changing the nature of the ligand L has no effect on the selectivity of the process for the straight-chain product  $\text{RCH}_2\text{CH}_2\text{CHO}$ .  
 C The process shown in Figure 6.1a is an example of an oxidative addition.  
 D The process shown in Figure 6.1b is an example of a reductive elimination.  
 E If the hydrolysis of an aldehyde,  $\text{RCHO}$ ,  

$$\text{RCHO}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{RCH}(\text{OH})_2(\text{aq})$$
 has an experimental rate equation of the following form in a solution of  $\text{pH} = 2$ :  

$$J = k_R[\text{RCHO}][\text{H}^+]$$
 this suggests that the reaction proceeds via an acid-catalysed pathway under these conditions.  
 F One problem with homogeneous catalysis is the difficulty of separating the catalyst from the reaction mixture.