

**PART I**

Attempt any **FOUR** of the following **SIX** questions. You are advised to spend about **18 minutes** on each of the four questions. Each question carries 10 per cent of the total marks for this examination.

**Question 1**

(a) Show that for a first-order reaction of the type:



the reaction half-life ( $t_{1/2}$ ) is given by the following expression:

$$t_{1/2} = (\ln 2)/k_R = 0.693/k_R \quad (2)$$

where  $k_R$  is the rate constant for the reaction.

(b) Table 1 lists current estimates of the atmospheric lifetimes ( $\tau$ ) of some of the halocarbons that are controlled under the terms of the Montreal Protocol.

**Table 1** A selection of the compounds controlled by the Montreal Protocol: formulae and atmospheric lifetimes ( $\tau$ ).

Compound	Formula	$\tau$ /years
CFC-11	$\text{CFCl}_3$	65
CFC-113	$\text{CCl}_2\text{FCClF}_2$	90
HCFC-141b	$\text{CH}_3\text{CCl}_2\text{F}$	10
methyl bromide	$\text{CH}_3\text{Br}$	12

(i) If the mechanism that removes CFC-113 from the atmosphere is treated as a first-order process with a half-life  $t_{1/2}$ , then:

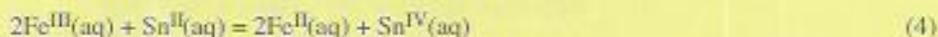
$$\tau = t_{1/2}/0.693 \quad (3)$$

On this basis, estimate how long it will take for the atmospheric concentration of CFC-113 to fall to one-quarter of the level it has reached when emissions cease. Explain your answer.

(ii) The last two compounds in Table 1 have much shorter atmospheric lifetimes than the CFCs. Suggest a plausible explanation for this difference.

**Question 2**

The reaction between  $\text{Fe}^{\text{III}}$  and  $\text{Sn}^{\text{II}}$  in aqueous solution at 298 K has the following time-independent stoichiometry:



One mechanism proposed for the reaction is as follows:



With reference to the mechanism, explain what is meant by a 'pre-equilibrium'.

Derive a chemical rate equation for the proposed mechanism, assuming that the first step is a pre-equilibrium.

Which step in the proposed mechanism must be rate-limiting if it is found experimentally that a plot of  $\ln([\text{Fe}^{\text{III}}]/[\text{Sn}^{\text{II}}])$  versus time is linear for more than 60% reaction? Explain your reasoning.