## 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:

$$A \longrightarrow \text{products} \qquad (1)$$

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

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

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 | $CFCl_3$ | 65 |
| CFC-113 | $CCl_2FCClF_2$ | 90 |
| HCFC-141b | $CH_3CCl_2F$ | 10 |
| methyl bromide | $CH_3Br$ | 12 |

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

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

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

$$2Fe^{III}(aq) + Sn^{II}(aq) = 2Fe^{II}(aq) + Sn^{IV}(aq) \qquad (4)$$

One mechanism proposed for the reaction is as follows:

$$Fe^{III} + Sn^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{II} + Sn^{III} \qquad (5)$$

$$Fe^{III} + Sn^{III} \xrightarrow{k_2} Fe^{II} + Sn^{IV} \qquad (6)$$

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 $\ln([Fe^{III}]/[Sn^{II}])$ versus time is linear for more than 60% reaction? Explain your reasoning.