

**Q6.4** Use the information provided to select *two* correct statements from the key.

KEY for Q6.4

- A The rate of reaction 6.2 is given by the following expression:

$$J = \frac{1}{3} \frac{d[A]}{dt}$$

- B When the initial conditions are such that  $[B]_0 \gg [A]_0$ , the time taken for the concentration of A to fall to half its initial value will be independent of  $[A]_0$ .
- C When the initial conditions are such that  $[A]_0 \gg [B]_0$ , a plot of  $\ln [B]$  versus time will yield a straight line with slope equal to  $k_R$ .
- D If concentrations are expressed in  $\text{mol dm}^{-3}$ , then the rate constant  $k_R$  in equation 6.3 has the unit  $\text{mol dm}^{-3} \text{s}^{-1}$ .
- E If the reaction is followed by monitoring the concentration of the product C, then the concentration of A at any time during the reaction can be determined from the following expression:
- $$[A] = 3[A]_0 - 2[C]$$
- where  $[A]_0$  is the initial concentration of A.
- F If the reactants A and B are mixed initially in stoichiometric proportions, then a plot of  $\ln \{[A]/[B]\}$  versus time will yield a straight line with slope equal to  $k_R$ .
- G It is not possible to state the molecularity of reaction 6.2.

**Q6.5** For reaction 6.2, the ratio of the rate constants at 300 K and 310 K,  $k_R(300 \text{ K})/k_R(310 \text{ K})$ , was found to be 0.5. Use this information to estimate the Arrhenius activation energy,  $E_a$ , for reaction 6.2. Select from the key the value that is closest to your answer.

KEY for Q6.5

- |                             |                             |
|-----------------------------|-----------------------------|
| A 0.8 $\text{kJ mol}^{-1}$  | D 53.6 $\text{kJ mol}^{-1}$ |
| B 6.4 $\text{kJ mol}^{-1}$  | E 61.3 $\text{kJ mol}^{-1}$ |
| C 45.5 $\text{kJ mol}^{-1}$ | F 94.7 $\text{kJ mol}^{-1}$ |

**Q6.6** This question is concerned with the following elementary gas-phase reaction:



for which the Arrhenius equation in the temperature range 250–350 K is found to be:

$$k_R = 2.45 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \exp(-5.06 \text{ kJ mol}^{-1}/RT)$$

The hard-sphere molecular diameter of methane,  $\text{CH}_4$ , is 380 pm, and the hard-sphere atomic diameter of fluorine,  $\text{F}^\cdot$ , is 140 pm. For the methyl radical,  $\text{CH}_3^\cdot$ ,  $\Delta H_f^\circ(298.15 \text{ K}) = 145.7 \text{ kJ mol}^{-1}$ . Any other thermodynamic data you need should be taken from the S342 Data Book.

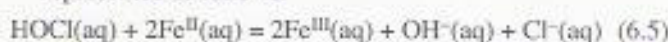
Use the information provided to select *three* correct statements from the key.

KEY for Q6.6

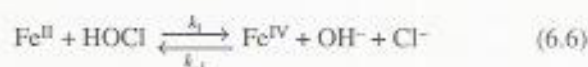
- A Reaction 6.4 is an endothermic process.
- B According to transition state theory, the value of  $\Delta H_m^\ddagger$  for reaction 6.4 sets a lower limit to the activation energy for this reaction.
- C According to transition state theory, the activation energy for reaction 6.4 is less than that for the reverse reaction:
- $$\text{HF} + \text{CH}_3^\cdot \longrightarrow \text{CH}_4 + \text{F}^\cdot$$
- D According to transition state theory, an elementary reaction is one that occurs in a single step and passes through a single transition state.
- E According to the hard-sphere collision theory of chemical reactions, the collision cross-section for reaction 6.4 is 260 pm.
- F According to the hard-sphere collision theory of chemical reactions, the rate of reaction 6.4 can be written as:
- $$\text{rate} = (\text{collision frequency}) \times (\text{fraction of collisions that lead to chemical transformation})$$
- G According to the hard-sphere collision theory of chemical reactions, approximately 13% of the total number of collisions between methane molecules and fluorine atoms will *not* lead to chemical reaction at 300 K.

### PART C (Block 3)

**Q6.7 to Q6.10** The reaction between hypochlorous acid,  $\text{HOCl}$ , and iron(II) ions,  $\text{Fe}^{\text{II}}$ , in aqueous solution exhibits time-independent stoichiometry, and can be represented as follows:



One of the mechanisms proposed for this reaction involves the formation of  $\text{Fe}^{\text{IV}}$  as intermediate:



Analysis of this scheme using the steady-state approximation gives a chemical rate equation that reduces to the following form:

$$J = k_R [\text{Fe}^{\text{II}}]^\alpha [\text{HOCl}]^\beta [\text{OH}^-]^\gamma [\text{Cl}^-]^\delta \quad (6.8)$$

when the conditions are such that:

either  $k_{-1}[\text{OH}^-][\text{Cl}^-]$  is much larger than  $k_2[\text{Fe}^{\text{II}}]$ ;

or  $k_2[\text{Fe}^{\text{II}}]$  is much larger than  $k_{-1}[\text{OH}^-][\text{Cl}^-]$ .

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

KEY for Q6.7 to Q6.9

- |       |        |
|-------|--------|
| A 2   | E -0.5 |
| B 1   | F -1   |
| C 0.5 | G -2   |
| D 0   |        |