

Question 2

Referring to the given mechanism, if the reverse of the first step forming the intermediate (Sn^{III}) is very rapid compared with the rate at which the intermediate reacts to form products in the second step (that is $k_{-1} \gg k_2$), then the first step can be considered to be an established or 'pre-equilibrium'. In this case, the concentration of the intermediate Sn^{III} will be determined solely by the equilibrium constant for this first step. In general, steps in a mechanism that occur before the rate-limiting step are taken to be rapidly established pre-equilibria.

In the proposed mechanism, if the first step is a rapidly established pre-equilibrium then the second step will be rate-limiting, that is

$$J = k_2[\text{Fe}^{\text{III}}][\text{Sn}^{\text{III}}]$$

The concentration of the intermediate Sn^{III} will be governed by the equilibrium constant for the first step

$$[\text{Sn}^{\text{III}}] = \frac{k_1}{k_{-1}} \frac{[\text{Fe}^{\text{III}}][\text{Sn}^{\text{II}}]}{[\text{Fe}^{\text{II}}]}$$

(Alternatively, to arrive at this equation the rate of the forward step can be put equal to that of the reverse step, that is $k_1[\text{Fe}^{\text{III}}][\text{Sn}^{\text{II}}] = k_{-1}[\text{Fe}^{\text{II}}][\text{Sn}^{\text{III}}]$.)

It then follows that

$$J = \frac{k_1 k_2}{k_{-1}} \frac{[\text{Fe}^{\text{III}}]^2 [\text{Sn}^{\text{II}}]}{[\text{Fe}^{\text{II}}]}$$

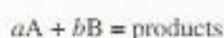
If experimentally a plot of $\ln([\text{Fe}^{\text{III}}]/[\text{Sn}^{\text{II}}])$ versus time is linear for more than 60% reaction then this is typical of a second-order reaction involving only the concentrations of reactant species in the rate equation (see Block 2, Table 7, p. 29). Clearly, given the analysis above, the second step in the proposed mechanism cannot be rate-limiting (even though overall it is second order). However, if the first step is rate-limiting, then

$$J = k_1[\text{Fe}^{\text{III}}][\text{Sn}^{\text{II}}]$$

and this equation – and its integrated form – are consistent with experiment.

The experimental evidence points to the first step in the proposed mechanism as being rate limiting.

[Comment: Note that for a reaction of the general type



with a rate equation that is first order in each reactant, and second order overall,

$$J = k_R[A][B]$$

the appropriate integrated rate equation is given on the data sheet.]

Question 3

(a) A plot of $1/J_0$ versus $1/[S]_0$ is a Lineweaver–Burk plot. It is derived by re-writing the Michaelis-Menten equation (equation 8) in the form of a straight line:

$$J_0 = \frac{V[S]_0}{K_m + [S]_0}$$
$$\frac{1}{J_0} = \frac{K_m + [S]_0}{V[S]_0} = \left(\frac{K_m}{V}\right) \times \frac{1}{[S]_0} + \frac{1}{V}$$

Thus, a plot of $1/J_0$ versus $1/[S]_0$ is a straight line with:

$$\text{slope} = K_m/V \text{ and intercept} = 1/V$$

From Figure 1:

$$\text{intercept} = 5.0 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}; \text{ so } V = 2.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\text{slope} = \frac{(30 - 5) \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}}{(7 - 0) \times 10^3 \text{ mol}^{-1} \text{ dm}^3} = 3.57 \times 10^3 \text{ s}$$