



Then as in the example, pg 19, we write

$$\begin{aligned} r_{\text{H}_3\text{PO}_3} &= k_3[\text{X}^*][\text{O}_2] - k_4[\text{H}_3\text{PO}_3] \quad \dots \text{(i)} \\ r_{\text{X}^*} &= k_1[\text{H}_3\text{PO}_2][\text{H}^+] - k_2[\text{X}^*][\text{H}^+] - k_3[\text{X}^*][\text{O}_2] + k_4[\text{H}_3\text{PO}_3] \stackrel{\text{steady state assumption}}{=} 0 \end{aligned}$$

Thus
$$[\text{X}^*] = \frac{k_1[\text{H}_3\text{PO}_2][\text{H}^+] + k_4[\text{H}_3\text{PO}_3]}{k_2[\text{H}^+] + k_3[\text{O}_2]} \quad \dots \text{(ii)}$$

Assuming $k_4 = 0$ (and we are certainly free to do this since this is our model, our brainchild), replacing (ii) in (i) then gives

$$r_{\text{H}_3\text{PO}_3} = \frac{k_1 k_3 [\text{H}_3\text{PO}_2][\text{H}^+][\text{O}_2]}{k_2[\text{H}^+] + k_3[\text{O}_2]} \quad \dots \text{(iii)}$$

Now when $k_3[\text{O}_2] \gg k_2[\text{H}^+]$... i.e. high oxidizer concentration, Eq. (iii) gives

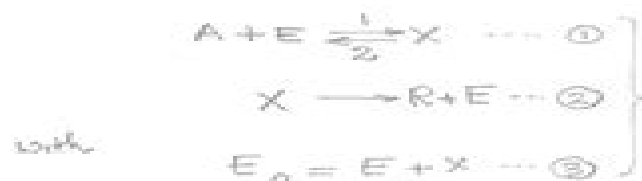
$$r_{\text{H}_3\text{PO}_3} = k_1[\text{H}_3\text{PO}_2][\text{H}^+] \quad \dots \text{(iv)}$$

On the other hand when $k_2[\text{H}^+] \gg k_3[\text{O}_2]$... i.e. low oxidizer concentration Eq. (iii) gives

$$r_{\text{H}_3\text{PO}_3} = \frac{k_1 k_3}{k_2} [\text{H}_3\text{PO}_2][\text{O}_2] \quad \dots \text{(v)}$$

Eqs (iv) & (v) fit the evidence hence the hypothesized model is accepted.

2.23



M-M assume that the reverse reactions of ① approach equilibrium quickly, or

$$K = \frac{\text{X}}{\text{A}\text{E}} = \frac{k_1}{k_2} \quad \dots \text{④}$$

B-H assume that quickly
$$d\text{X}/dt = 0 \quad \dots \text{⑤}$$

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A Gutmann



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