CHAPTER 3

Problem 3.1

3.1 a)

$$k = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{\ln 2}{5730 \text{ years}} = 1.2\times10^{-4} \text{ years}^{-1}$$

3.1 b)

If 73% of ^{14}C remains, $\frac{C}{C_0} = 0.73$

$$\ln\frac{C}{C_0} = -kt$$

$$t = -\frac{\ln(0.73)}{1.2\times10^{-4}\text{ years}^{-1}} = 2,623 \text{ years}$$

Note: For simplicity, this problem assumes a constant input of C-14 (perturbations due to bomb C-14 are not considered).

Problem 3.2

$$V = \frac{V_{max}[S]}{K_M + [S]}$$

$$\frac{1}{V} = \frac{K_M + [S]}{V_{max}[S]} = \frac{K_M}{V_{max}}\cdot\frac{1}{[S]} + \frac{1}{V_{max}}$$

Linear regression gives:

$$y_{int} = \frac{1}{V_{max}} = 8.32\times10^5 \tfrac{s}{M}$$

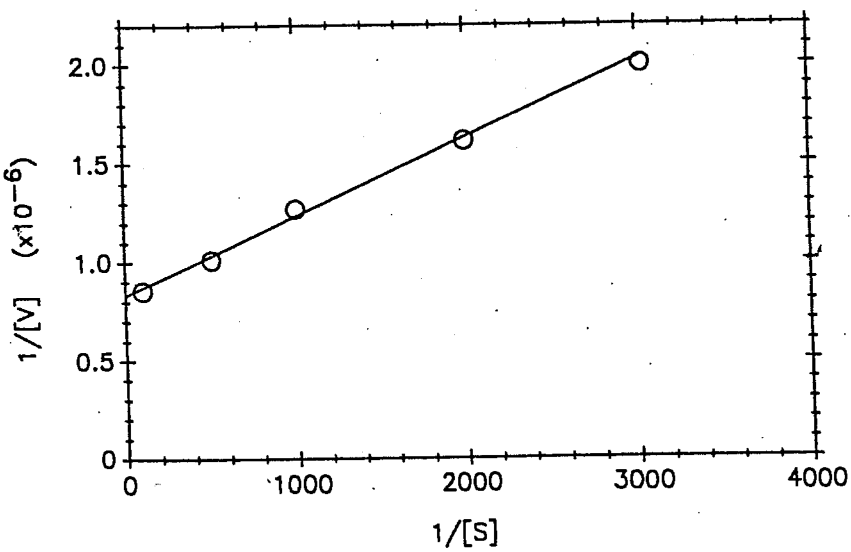
$$V_{max} = 1.20\times10^{-6} \tfrac{M}{s}$$

$$\text{slope} = \frac{K_M}{V_{max}} = 389.5 \text{ s}$$

$$K_M = 4.68\times10^{-4} \text{ M}$$

Plot such that $y = \frac{1}{V}$ and $x = \frac{1}{[S]}$.

Figure 3.2



3.3 a)

Apparent chlorination rate:

$$\frac{-d[C_6H_5OH]_T}{dt} = k^*[C_6H_5OH]_T[HOCl]_T \tag{1}$$

Actual rate law:

$$\frac{-d[C_6H_5O^-]}{dt} = k[C_6H_5O^-][HOCl] \tag{2}$$

Assuming pseudo-equilibrium for acid-base reactions:

$$\frac{-d[C_6H_5O^-]}{dt} = \frac{-d[C_6H_5OH]_T}{dt} \tag{3}$$

Thus

$$\frac{-d[C_6H_5OH]_T}{dt} = k[C_6H_5O^-][HOCl] \tag{4}$$

and from Mass Laws

$$\frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]} = K_{ph}$$

$$\frac{[OCl^-][H^+]}{[HOCl]} = K_{HOCl}$$

Write expressions for $[C_6H_5O^-]$ and [HOCl] in terms of $[C_6H_5OH]_T$ and $[HOCl]_T$:

$$[C_6H_5OH]_T = [C_6H_5O^-]\left(1 + \frac{[H^+]}{K_{ph}}\right) \tag{5}$$

$$[HOCl]_T = [HOCl]\left(1 + \frac{K_{HOCl}}{[H^+]}\right) \tag{6}$$

Substitute (5) and (6) into (4):

$$\frac{-d[C_6H_5OH]_T}{dt} = \frac{k[C_6H_5OH]_T}{\left(1 + \dfrac{[H^+]}{K_{HOCl}}\right)} \frac{[HOCl]_T}{\left(1 + \dfrac{K_{ph}}{[H^+]}\right)} \tag{7}$$

By comparison of (7) and (1):

$$k^* = \frac{k}{\left(1 + \dfrac{[H^+]}{K_{ph}}\right)\left(1 + \dfrac{K_{HOCl}}{[H^+]}\right)} \tag{8}$$

3.3 b)

At low pH ($pH < pK_{HOCl} < pK_{ph}$)

$$\left(1 + \frac{K_{HOCl}}{[H^+]}\right) \approx 1$$

and $$\left(1 + \frac{[H^+]}{K_{ph}}\right) \approx \frac{[H^+]}{K_{ph}}$$

then $$k^* = \frac{kK_{ph}}{[H^+]} \propto \frac{1}{[H^+]}$$

thus k^* increases with increasing pH in this region.

At high pH ($pH > pK_{ph} > pK_{HOCl}$)

$$\left(1+\frac{K_{HOCl}}{[H^+]}\right) \approx \frac{K_{HOCl}}{[H^+]}$$

and $$\left(1+\frac{[H^+]}{K_{ph}}\right) \approx 1$$

then $$k^* = \frac{k[H^+]}{K_{HOCl}} \propto [H^+]$$

Thus k^* decreases with increasing pH in this region. k^* reaches a maximum value in the mid-pH region (see below).

3.3 c)

$$\text{Rate of chlorination} = \frac{k[C_6H_5OH]_T}{\left(1+\frac{[H^+]}{K_{ph}}\right)}\frac{[HOCl]_T}{\left(1+\frac{K_{HOCl}}{[H^+]}\right)}$$

At a given $[C_6H_5OH]_T$ and $[HOCl]_T$,

$$\text{Rate} \propto \frac{1}{\left(1+\frac{[H^+]}{K_{ph}}\right)\left(1+\frac{K_{HOCl}}{[H^+]}\right)}$$

The rate is highest between pH = 7.5 and pH = 10, because it is dependent on the product of the concentrations of $C_6H_5O^-$ and HOCl. Outside of this range, the concentrations of one of the reactants is dropping off rapidly, resulting in a lower reaction rate.

3.3 d)

Rearranging (8):

$$k^* = \frac{kK_{ph}[H^+]}{\left([H^+]+K_{ph}\right)\left([H^+]+K_{HOCl}\right)}$$

solve for maximum k^* or maximum $\log k^*$.

$$\log k^* = \log kK_{ph} + \log[H^+] - \log\left([H^+]+K_{ph}\right) - \log\left([H^+]+K_{HOCl}\right)$$

at maximum $\log k^*$, $\frac{d\log k^*}{d[H^+]} = 0$

$$\frac{d(\log k^*)}{d[H^+]} = \frac{1}{[H^+]} - \frac{1}{[H^+]+K_{ph}} - \frac{1}{[H^+]+K_{HOCl}} = 0$$

Rearranging

$$K_{ph}K_{HOCl} = [H^+]^2$$

This maximum k^* occurs at

$$[H^+] = \sqrt{10^{-10}10^{-7.5}} = 10^{-8.75}$$

or pH = 8.75