Problem Set #8 Solutions

CHM 3400, Dr. Chatfield, Fall 2011

Note that problems 4, 5 and 6 were deferred to the next problem set.

1. (Atkins 11.3)

$$X \xrightarrow[k_1]{22.5\,days} Y \xrightarrow[k_2]{33.0\,days} Z$$

According to eq. 11.6, the intermediate, Y, which have a maximum concentration at time:

$$t = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

Since each of the consecutive reaction is 1st order, we can get k_1 and k_2 from the half lives:

$$k_1 = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{22.5\,days} = 0.0308\,day^{-1}$$

$$k_2 = \frac{\ln 2}{33.0\,days} = 0.0210\,day^{-1}$$

$$t = \frac{1}{(0.0308 - 0.0210)\,day^{-1}} \ln \frac{0.0308}{0.0210} = 39.1\,days$$

2. (Atkins 11.5)

$$A_2 \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} A + A \quad \text{(fast)}$$

$$A + B \xrightarrow{k_b} P \quad \text{(slow)}$$

$$v = \frac{d[P]}{dt} = k_b [A][B]$$

intermediate

Since A is an intermediate, we must replace it in the rate law. To do so, recognize that since the first reaction is fast relative to the second, reactants and products of the first reaction are essentially at equilibrium:

$$\frac{[A]^2}{[A_2]} = K = \frac{k_a}{k_a'}$$

equilibrium constant for 1^{st} rxn

$$[A] = (K[A_2])^{1/2}$$

$$v = k_b K^{1/2} [A_2]^{1/2} [B] = \underbrace{\left(\frac{k_b k_a^{1/2}}{k_a'^{1/2}} \right)}_{k_{eff}} [A_2]^{1/2} [B]$$

3. (Atkins 11.7)

(1) $O_3 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} O_2 + O$

(2) $O + O_3 \xrightarrow{k_2} O_2 + O_2$

overall: $2O_3 \rightarrow 3O_2$

intermediate

$$r = -\frac{1}{2}\frac{d[O_3]}{dt} = \frac{1}{2}\left(k_1[O_3] - k_1'[O_2][O] + k_2[O][O_3]\right)$$

$$\underbrace{\frac{d[O]}{dt} = 0}_{\text{steady-state approx}} = k_1[O_3] - k_1'[O_2][O] - k_2[O][O_3]$$

$$[O] = \frac{k_1[O_3]}{k_1'[O_2] + k_2[O_3]}$$

$$r = \frac{1}{2}\left(k_1[O_3] + \frac{k_1k_2[O_3]^2 - k_1k_1'[O_2][O_3]}{k_1'[O_2] + k_2[O_3]}\right)$$

$$= \frac{1}{2}\left(\frac{k_1k_1'[O_2][O_3] + k_1k_2[O_3]^2 + k_1k_2[O_3]^2 - k_1k_1'[O_2][O_3]}{k_1'[O_2] + k_2[O_3]}\right)$$

$$\boxed{r = \frac{k_1k_2[O_3]^2}{k_1'[O_2] + k_2[O_3]}}$$

If step 2 is slow, the denominator $\approx k_1'[O_2]$

$$r \approx \frac{k_1k_2[O_3]^2}{k_1'[O_2]} \quad (2^{nd} \text{ order in } O_3,\ -1 \text{ order in } O_2)$$

4. (Atkins 11.15 – deferred to Problem Set #9)

5. (Atkins 11.16 – deferred to Problem Set #9)

6. (Akins 11.23 – deferred to Problem Set #9)

7. (Atkins 11.27)

(1) $AH \xrightarrow{k_1} A\cdot + H\cdot$ Initiation

(2) $A\cdot \xrightarrow{k_2} B\cdot + C$ } Propagation

(3) $AH + B\cdot \xrightarrow{k_3} A\cdot + D$

(4) $A\cdot + B\cdot \xrightarrow{k_4} P$ Termination

rate of decomposition of AH $= -\frac{d[AH]}{dt}$

$$-\frac{d[AH]}{dt} = -k_1[AH] + k_3[AH][B\cdot]$$

$$= (k_3[B\cdot] - k_1)[AH]$$

constant assuming steady-state approx.

To actually solve for $[B\cdot]$ explicitly is difficult because it involves a quadratic equation. For our purposes, though (to show that the rate is 1st-order in AH), it is sufficient to show that the quantity above in parentheses is a constant, as we have done.

We can, though, be more explicit to show this clearly:

steady-state approx:

(a) $0 = \frac{d[B\cdot]}{dt} = k_2[A\cdot] - k_3[AH][B\cdot] - k_4[A\cdot][B\cdot]$

(b) $0 = \frac{d[A\cdot]}{dt} = k_1[AH] - k_2[A\cdot] + k_3[AH][B\cdot] - k_4[A\cdot][B\cdot]$

This is a messy algebraic problem. Adding (a) and (b) yields:

$$0 = k_1[AH] - 2k_4[A\cdot][B\cdot] \Rightarrow [A\cdot] = \frac{k_1}{2k_4}\frac{[AH]}{[B\cdot]}$$

Substituting into (a) yields

$$0 = \frac{k_1k_2}{2k_4}\frac{[AH]}{[B\cdot]} - k_3[AH][B\cdot] - \frac{k_1}{2}[AH]$$

$$0 = -k_3[AH][B\cdot]^2 - \frac{k_1}{k_2}[AH][B\cdot] + \frac{k_1k_2}{2k_4}[AH]$$

Note that [AH] cancels, yielding

$$0 = -k_3[B\cdot]^2 - \frac{k_1}{k_2}[B\cdot] + \frac{k_1k_2}{2k_4}$$

We can solve explicitly:

$$[B\cdot] = \frac{\frac{k_1}{k_2} \pm \sqrt{k_1^2/k_2^2 + 2k_1k_2k_3/k_4}}{-2k_3}$$

However, it is not necessary to solve this. We have shown that [B·] depends only on the rate constants, and thus [B·] is a constant (for a given temperature), as stated above.