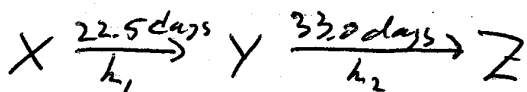


Problem Set #8 Solutions

CHM 3400, Dr. Chatfield, Fall 2011

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

1. (Atkins 11.3)



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

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

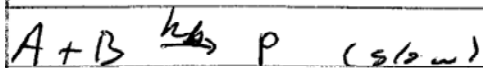
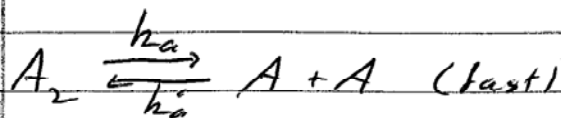
Since each of the consecutive reaction is 1st order, we can get k_1 and k_2 from the half lives:

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

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

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

2. (Atkins 11.5)



$$v = \frac{d[P]}{dt} = k_2 [A][B]$$

↑ 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:

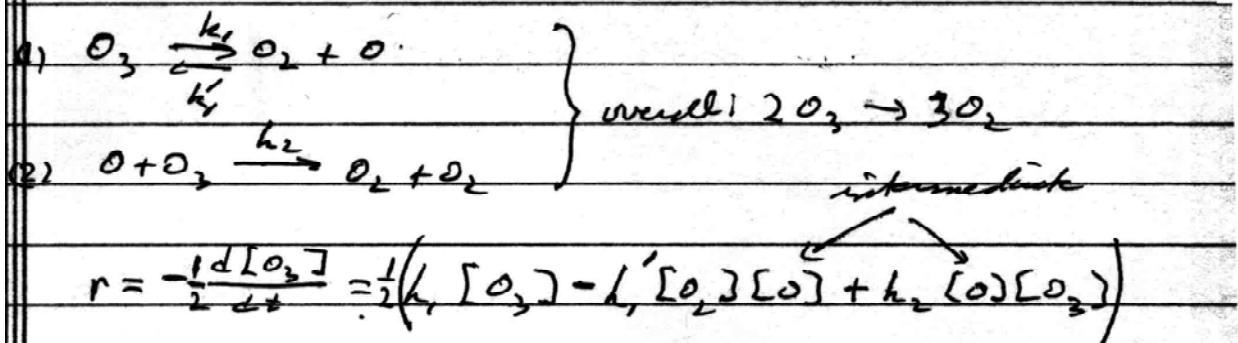
$$\frac{[A]^2}{[A_2]} = K = \frac{k_1}{k_{-1}}$$

↑ equilibrium constant for 1st rxn

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

$$v = k_2 K^{1/2} [A_2]^{1/2} [B] = \underbrace{\left(\frac{k_2 k_1^{1/2}}{k_{-1}^{1/2}} \right)}_{k_{\text{eff}}} [A_2]^{1/2} [B]$$

3. (Atkins 11.7)



$$r = -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{2} (k_1 [\text{O}_3] - k_1' [\text{O}_2][\text{O}] + k_2 [\text{O}][\text{O}_3])$$

$$\frac{d[\text{O}]}{dt} = 0 = k_1 [\text{O}_3] - k_1' [\text{O}_2][\text{O}] - k_2 [\text{O}][\text{O}_3]$$

steady-state approx

$$[\text{O}] = \frac{k_1 [\text{O}_3]}{k_1' [\text{O}_2] + k_2 [\text{O}_3]}$$

$$r = \frac{1}{2} (k_1 [\text{O}_3] + \frac{k_1 k_2 [\text{O}_3]^2 - k_1 k_1' [\text{O}_2][\text{O}_3]}{k_1' [\text{O}_2] + k_2 [\text{O}_3]})$$

$$= \frac{1}{2} \left(\frac{k_1 k_1' [\text{O}_2][\text{O}_3] + k_1 k_2 [\text{O}_3]^2 + k_1 k_2 [\text{O}_3]^2 - k_1 k_1' [\text{O}_2][\text{O}_3]}{k_1' [\text{O}_2] + k_2 [\text{O}_3]} \right)$$

$$r = \frac{k_1 k_2 [\text{O}_3]^2}{k_1' [\text{O}_2] + k_2 [\text{O}_3]}$$

If step 2 is slow, the denominator $\approx k_1' [\text{O}_2]$

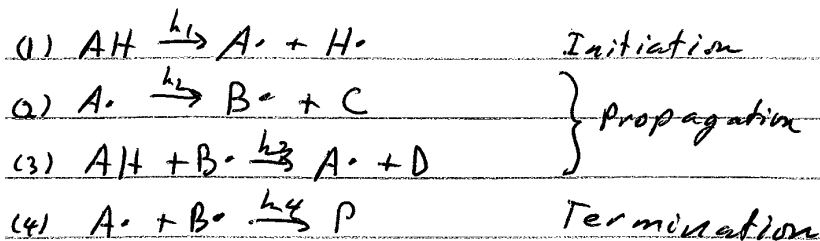
$$r \approx \frac{k_1 k_2 [\text{O}_3]^2}{k_1' [\text{O}_2]} \quad (2 \text{ order in } \text{O}_3, -1 \text{ order in } \text{O}_2)$$

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

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

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

7. (Atkins 11.27)



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

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

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

↑
constant assuming steady-state approx.

To actually solve for $[\text{B}\cdot]$ explicitly is difficult because it involves a quadratic equation.

For one purpose, 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:

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

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

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

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

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

Note that $[AH]$ cancels, yielding

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

We can solve explicitly:

$$[B^{\cdot-}] = \frac{\frac{k_1 k_2}{2k_4} + \sqrt{\left(\frac{k_1 k_2}{2k_4}\right)^2 + 2k_1 k_2 k_3 / k_4}}{-2k_3}$$

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