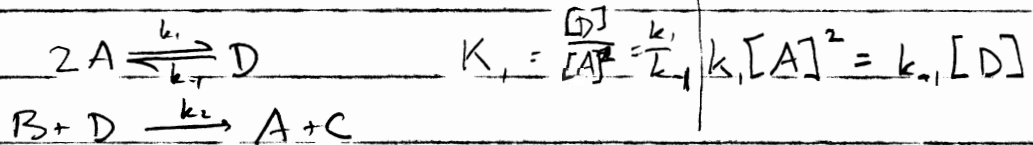
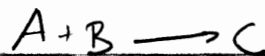


Steinfeld Chp. 2

①

S2.1

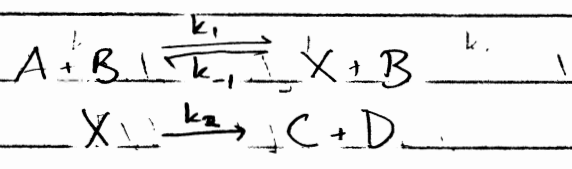


$$\frac{dC}{dt} = k_2 [B][D] \quad [D] = \frac{k_1}{k_{-1}} [A]^2 = K_1 [A]^2$$

$$\frac{dC}{dt} = k_2 [B] \frac{k_1}{k_{-1}} [A]^2 = \left(\frac{k_1 k_2}{k_{-1}} \right) [A]^2 [B] \rightarrow K_1$$

$$\text{or } \boxed{\frac{dC}{dt} = k_2 K_1 [A]^2 [B]}$$

S2.4



a.

$$\frac{d[A]}{dt} = -k_1[A][B] + k_{-1}[X][B]$$

$$\frac{d[X]}{dt} = k_1[A][B] - k_{-1}[X][B] - k_2[X]$$

b.

$$\frac{d[X]}{dt} \approx 0 \quad k_1[A][B] = k_{-1}[X][B] + k_2[X]$$

$$[X] = \frac{k_1[A][B]}{k_{-1}[B] + k_2}$$

$$\frac{dA}{dt} = -k_1[A][B] + k_{-1}[B] \left(\frac{k_1[A][B]}{k_{-1}[B] + k_2} \right)$$

$$= k_1[A][B] \left(-1 + \frac{k_{-1}[B]}{k_{-1}[B] + k_2} \right)$$

$$= k_1[A][B] \left(\frac{-k_{-1}B - k_2}{k_{-1}B + k_2} + \frac{k_{-1}[B]}{k_{-1}[B] + k_2} \right) = k_1[A][B] \left(\frac{-k_2}{k_{-1}B + k_2} \right)$$

Note: [B] is constant since it is not consumed in the rxn!

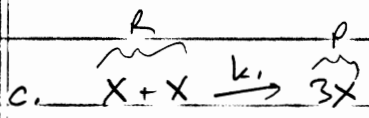
so,

$$\frac{d[A]}{dt} = \left(\frac{-k_1 k_2}{k_{-1}B + k_2} \right) [A][B] = -k_{eff} [A][B] \quad k_{eff} = \frac{k_1 k_2}{k_{-1}[B] + k_2}$$

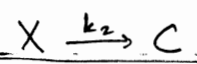
c.

$$k_{eff} = \frac{k_1 k_2}{k_{-1}[B] + k_2} \quad (\text{from above})$$

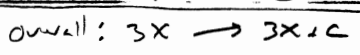
52.5



$k_1 = k_2$



$[X]_0 = \frac{1}{2}, [C]_0 = 0$



$\frac{d[X]}{dt} = -2k[X]^2 + 3k[X]^2 - k_2[X] = k[X]^2 - k_2[X]$

$\frac{d[C]}{dt} = k_2[X]$

$k_1 = k_2 = k$

$\frac{d[X]}{dt} = -2k[X]^2 + 3k[X]^2 - k[X] = k[X]^2 - k[X] = k[X](X-1)$

$\int_{x_0}^{x_+} \frac{dx}{kx^2 - kx} = t$

Need to integrate to get expression for [X] to plug into $\frac{d[C]}{dt}$ expression &

then integrate $\frac{d[C]}{dt}$ to get [C] = ...

$\frac{1}{k} \int_{x_0}^{x_+} \frac{dx}{x^2 - x} = t$

$\frac{1}{k} \int_{x_0}^{x_+} \frac{dx}{(x+0)(x-1)} = t$

Integral #10 $\int \frac{1}{(a+bx)(c+gx)} dx = \frac{1}{ag-bc} \ln \left| \frac{c+gx}{a+bx} \right|$

$a=0 \quad b=1 \quad c=-1 \quad g=1$

$\frac{1}{k} \left[\frac{1}{0+1} \ln \left| \frac{x-1}{x} \right| \right]_{x_0}^{x_+} = t$

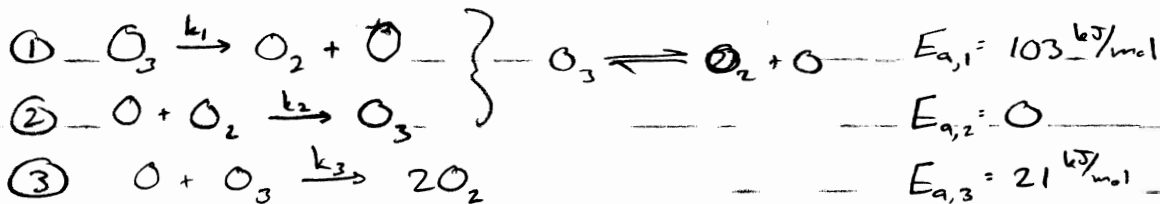
$\frac{1}{k} \left(\ln \left(\frac{x-1}{x} \right) - \ln \left(\frac{1/2-1}{1/2} \right) \right) = t$

$\ln \left(\frac{x-1}{x} \right) - \ln(-1) = kt$

not possible! So, there are no equilib. concs, which makes sense since the overall rxn. does not obey conservation of matter (→ so this entire rxn. is impossible anyway)

(overall: nothing → C)

52.9



$$E_{a,1} = 103 \text{ kJ/mol}$$

$$E_{a,2} = 0$$

$$E_{a,3} = 21 \text{ kJ/mol}$$

$$a. \quad -\frac{d[\text{O}_3]}{dt} = k_1[\text{O}_3] - k_2[\text{O}][\text{O}_2] + k_3[\text{O}][\text{O}_3]$$

O is intermediate

$$\frac{d[\text{O}]}{dt} = k_1[\text{O}_3] - k_2[\text{O}][\text{O}_2] - k_3[\text{O}][\text{O}_3] \approx 0$$

$$k_1[\text{O}_3] = k_2[\text{O}][\text{O}_2] + k_3[\text{O}][\text{O}_3]$$

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_2[\text{O}_2] + k_3[\text{O}_3]}$$

$$\begin{aligned} -\frac{d[\text{O}_3]}{dt} &= k_1[\text{O}_3] - k_2[\text{O}_2] \left(\frac{k_1[\text{O}_3]}{k_2[\text{O}_2] + k_3[\text{O}_3]} \right) + k_3[\text{O}_3] \left(\frac{k_1[\text{O}_3]}{k_2[\text{O}_2] + k_3[\text{O}_3]} \right) \\ &= \frac{k_1[\text{O}_3]k_2[\text{O}_2] + k_1[\text{O}_3]k_3[\text{O}_3] - k_2[\text{O}_2]k_1[\text{O}_3] + k_3[\text{O}_3]k_1[\text{O}_3]}{k_2[\text{O}_2] + k_3[\text{O}_3]} \end{aligned}$$

$$\boxed{-\frac{d[\text{O}_3]}{dt} = \frac{k_1 k_3 [\text{O}_3]^2}{k_2 [\text{O}_2] + k_3 [\text{O}_3]}}$$

S2.9

b. If $E_a = 0$ $k = A e^{-E_a/RT} \rightarrow k_2$ will be very large at all temps (won't follow Arrhen. law); k_3 will be small at low T.

So, at low T $k_2 \gg k_3$:

$$-\frac{d[O_3]}{dt} = \frac{2 k_1 k_3 [O_3]^2}{k_2 [O_2] + k_3 [O_3]} \approx 0 \rightarrow \boxed{-\frac{d[O_3]}{dt} = \frac{2 k_1 k_3 [O_3]^2}{k_2 [O_2]}}$$

c. Using same assumption from b: $k_2 \gg k_3$, then $k = \frac{2 k_1 k_3}{k_2}$
(same as form of k in problem 8.ii)

$$k = A e^{-E_a/RT}$$

$$\frac{2 k_1 k_3}{k_2} = \frac{2 (A_1 e^{-E_1/RT}) (A_3 e^{-E_3/RT})}{(A_2 e^{-E_2/RT})}$$

$$k = (\text{constant}) e^{-(E_1 + E_3 - E_2)/RT}$$

$$E_a = E_1 + E_3 - E_2 = 103 + 21 - 0 = \boxed{124 \text{ kJ/mol}}$$

↑

$$\text{so, for } k = k_1 k_2, E_a = E_1 + E_2$$

$$k = k_1/k_2, E_a = E_1 - E_2$$