Steinfeld Chp. 2

S2.1 $A + B \longrightarrow C$

$$2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D \qquad K_1 = \frac{[D]}{[A]^2} = \frac{k_1}{k_{-1}} \qquad k_1[A]^2 = k_{-1}[D]$$

$$B + D \xrightarrow{k_2} A + C$$

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

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

$\rightarrow K_1$

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

S2.4

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + B$$

$$X \xrightarrow{k_2} C + D$$

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. $$\frac{dX}{dt} = 0 \qquad k_1[A][B] = k_{-1}[X][B] + k_2[X]$$

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

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

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

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

<u>Note</u>: [B] is <u>constant</u> since it is not consumed in the rxn!

so, $$\frac{d[A]}{dt} = \left(\frac{-k_1k_2}{k_{-1}B + k_2}\right)[A][B] = \boxed{-k_{eff}[A][B]} \qquad k_{eff} = \frac{k_1k_2}{k_{-1}[B] + k_2}$$

c. $$k_{eff} = \frac{k_1k_2}{k_{-1}[B] + k_2}$$ (from above)

S2.5

c. $\overbrace{X + X}^{R} \xrightarrow{k_1} \overbrace{3X}^{P}$ $k_1 = k_2$

$X \xrightarrow{k_2} C$ $[X]_0 = \frac{1}{2}$, $[C]_0 = 0$

overall: $3X \longrightarrow 3X + C$

$$\frac{d[X]}{dt} = -2k_1[X]^2 + 3k_1[X]^2 - k_2[X] = k_1[X]^2 - k_2[X]$$

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

$k_1 = k_2 = k$

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

$$\int_{X_0}^{X_t} \frac{dX}{kX^2 - kX} = \int_0^t dt$$

← Need to integrate to get expression for [X] to plug into $\frac{d[C]}{dt}$ expression & then rearrange and integrate $\frac{d[C]}{dt}$ to get [C] = ___.

$$\frac{1}{k}\int_{X_0}^{X_t} \frac{dX}{X^2 - X} = t$$

$$\frac{1}{k}\int_{X_0}^{X_t} \frac{dx}{(x+0)(x-1)} = t$$

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

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

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

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

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

↑ 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)

S2.9

$$2O_3 \rightleftharpoons 3O_2$$

① $O_3 \xrightarrow{k_1} O_2 + O$ ② $O + O_2 \xrightarrow{k_2} O_3$ $\Big\}$ $O_3 \rightleftharpoons O_2 + O$

③ $O + O_3 \xrightarrow{k_3} 2O_2$

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

$E_{a,2} = 0$

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

a. $$-\frac{d[O_3]}{dt} = k_1[O_3] - k_2[O][O_2] + k_3[O][O_3]$$

O is intermediate

$$\frac{d[O]}{dt} = k_1[O_3] - k_2[O][O_2] - k_3[O][O_3] \approx 0$$

$$k_1[O_3] = k_2[O][O_2] + k_3[O][O_3]$$

$$[O] = \frac{k_1[O_3]}{k_2[O_2] + k_3[O_3]}$$

$$-\frac{d[O_3]}{dt} = k_1[O_3] - k_2[O_2]\left(\frac{k_1[O_3]}{k_2[O_2]+k_3[O_3]}\right) + k_3[O_3]\left(\frac{k_1[O_3]}{k_2[O_2]+k_3[O_3]}\right)$$

$$= \frac{\cancel{k_1[O_3]k_2[O_2]} + k_1[O_3]k_3[O_3] - \cancel{k_2[O_2]k_1[O_3]} + k_3[O_3]k_1[O_3]}{k_2[O_2] + k_3[O_3]}$$

$$\boxed{-\frac{d[O_3]}{dt} = \frac{k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}}$$

S2.9

b. If $E_a = 0$ $k = Ae^{-E_a/RT}$ $\rightarrow$ 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 $k_2 >> k_3$:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_3[O_3]^2}{k_2[O_2] + \cancel{k_3[O_3]} \rightarrow \sim 0} \rightarrow \boxed{-\frac{d[O_3]}{dt} = \frac{2k_1k_3[O_3]^2}{k_2[O_2]}}$$

c. Using same assumption from b: $k_2 >> k_3$, then $k = \frac{2k_1k_3}{k_2}$
(same as form of k in problem 8 :))

$$k = Ae^{-E_a/RT}$$

$$\frac{2k_1k_3}{k_2} = \frac{2(A_1e^{-E_1/RT})(A_3e^{-E_3/RT})}{(A_2e^{-E_2/RT})}$$

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

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

$\uparrow$

so, for $k = k_1k_2$, $E_a = E_1 + E_2$

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