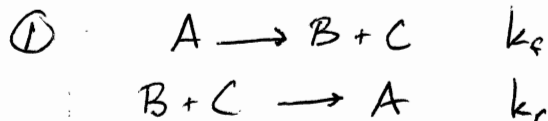


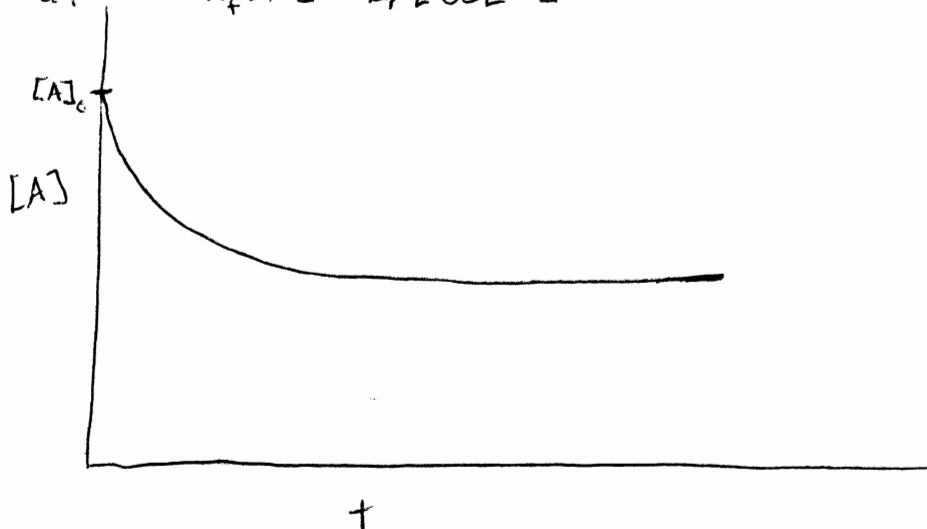
CHM5250 - Exam 1



10

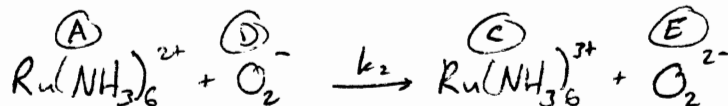
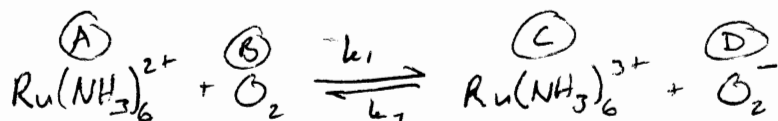
a. $\frac{d[A]}{dt} = -k_f[A] + k_r[B][C]$

b.



30

2



a. $\frac{d[\text{O}_2^-]}{dt} = -k_1[A][B] + k_{-1}[C][D]$

$D = \text{O}_2^- = \text{intermediate} \quad \frac{d[D]}{dt} = 0$
 $\frac{d[D]}{dt} = k_1[A][B] - k_{-1}[C][D] - k_2[A][D] = 0$

$k_1[A][B] = k_{-1}[C][D] + k_2[A][D]$

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

$\frac{d[\text{O}_2^-]}{dt} = -k_1[A][B] + k_{-1}[C] \left(\frac{k_1[A][B]}{k_{-1}[C] + k_2[A]} \right)$

$\frac{d[\text{O}_2^-]}{dt} = k_1[A] \left([B] + \frac{k_{-1}[B][C]}{k_{-1}[C] + k_2[A]} \right) = k_1[A] \left(\frac{-k_2[A][B]}{k_{-1}[C] + k_2[A]} \right)$

$k_{-1}[B][C]$ terms cancel

2 a. (continued)

$$\frac{d[O_2]}{dt} = \frac{-k_1 k_2 [Ru(NH_3)_6^{2+}]^2 [O_2]}{k_{-1} [Ru(NH_3)_6^{2+}] + k_2 [Ru(NH_3)_6^{2+}]}$$

b. If $k_2 \gg k_{-1}$, $k_2 [Ru(NH_3)_6^{2+}] \gg k_{-1} [Ru(NH_3)_6^{2+}]$

$$\text{so, } \frac{d[O_2]}{dt} = - \frac{k_1 k_2 [Ru(NH_3)_6^{2+}]^2 [O_2]}{k_2 [Ru(NH_3)_6^{2+}]}$$

$$\frac{d[O_2]}{dt} = -k_1 [Ru(NH_3)_6^{2+}] [O_2]$$

↑
one rate constant
underbrace
second order

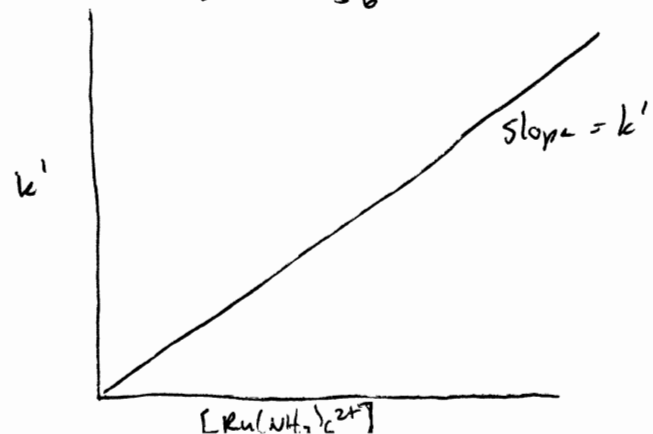
c. Overall rxn. is $2 Ru(NH_3)_6^{2+} + O_2 \rightarrow 2 Ru(NH_3)_6^{3+} + O_2^{2-}$

If $[Ru(NH_3)_6^{2+}] \gg [O_2]$, rate = $k' [O_2] = -\frac{d[O_2]}{dt}$

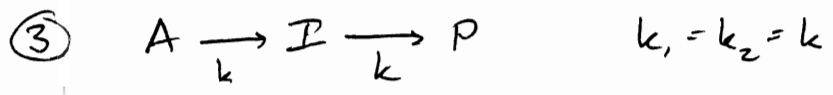
If steady state holds, $-k_1 [Ru(NH_3)_6^{2+}] [O_2] = -k' [O_2]$

so, $k' = k_1 [Ru(NH_3)_6^{2+}]$ If $k_2 \gg k_{-1}$

d. plot k' vs. $[Ru(NH_3)_6^{2+}]$



straight line in this case



① a. $\frac{d[P]}{dt} = k[I]$

20

① b. $[A]_t = [I]_t$ (assume)

$\frac{d[P]}{dt} = k[A]_t \rightarrow$ first order $[A]_t = [A]_0 e^{-kt}$

$d[P] = k[A]_0 e^{-kt} dt$

$\int_0^{[P]_t} d[P] = \int_0^t k[A]_0 e^{-kt} dt$ $\int e^{-kt} = -\frac{1}{k} e^{-kt}$

$[P]_t - 0 = \frac{k[A]_0}{k} (e^{-kt} - e^{-k(0)})$

$[P]_t = [A]_0 (e^{-kt} - 1)$

20

4

$G(\epsilon)d\epsilon = 2\pi \left(\frac{1}{\pi k_B T}\right)^{3/2} \sqrt{\epsilon} \exp\left(\frac{-\epsilon}{k_B T}\right) d\epsilon$

Take derivative ^{with respect to ϵ} and set equal to zero to find maximum probability

$\frac{dG(\epsilon)}{d\epsilon} = 2\pi \left(\frac{1}{\pi k_B T}\right)^{3/2} \left[\exp\left(\frac{-\epsilon}{k_B T}\right) \left(\frac{1}{2} \epsilon^{-1/2}\right) + \left(\epsilon^{1/2}\right) \left(\frac{-1}{k_B T}\right) \exp\left(\frac{-\epsilon}{k_B T}\right) \right]$

$= 2\pi \left(\frac{1}{\pi k_B T}\right)^{3/2} \exp\left(\frac{-\epsilon}{k_B T}\right) \left[\frac{1}{2} \epsilon^{-1/2} - \frac{\epsilon^{1/2}}{k_B T} \right] = 0$

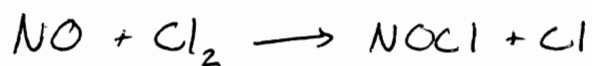
all this cancels when both sides divided by it

$\frac{1}{2} \epsilon^{-1/2} - \frac{\epsilon^{1/2}}{k_B T} = 0$

$\frac{1}{2 \epsilon^{1/2}} = \frac{\epsilon^{1/2}}{k_B T}$

$\frac{k_B T}{2} = \epsilon$

5
20



$\ln k$ vs. $\frac{1}{T} \rightarrow$ Arrhenius plot

$$\ln k = -1.022 \times 10^4 \left(\frac{1}{T} \right) + 22.11$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

so, slope = $-\frac{E_a}{R}$

$$(-1.022 \times 10^4 \text{ K}) = -E_a / (8.3145 \text{ J/mol}\cdot\text{K})$$

$$E_a = -(8.3145 \text{ J/mol}\cdot\text{K}) (-1.022 \times 10^4 \text{ K})$$

$$E_a = 8.497 \times 10^4 \text{ J/mol}$$

$$= \boxed{84.97 \text{ kJ/mol}}$$