1. (10+5+5+5 points) Consider the acid/bromide catalyzed disproportionation reaction:

$$2\,H_2O_2(aq) \xrightarrow[H_3O^+]{Br^-} 2\,H_2O(\ell) + O_2(g)\uparrow$$

for which a postulated mechanism is:

$$H_3O^+ + H_2O_2 \xleftrightarrow{K_{eq}} H_3O_2^+ + H_2O \text{ (fast)}$$
$$H_3O_2^+ + Br^- \xrightarrow{k_1} HOBr + H_2O \text{ (slow)}$$
$$HOBr + H_2O_2 \xrightarrow{k_2} H_3O^+ + O_2 + Br^- \text{ (fast)}$$

A. Write the differential rate law in terms of reactants and catalysts. (10 pts)

$$\text{rate} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k_1[H_3O_2^+][Br^-]$$ 2pts

$$K_{EQ} = \frac{[H_3O_2^+][H_2O]}{[H_3O^+][H_2O_2]}$$ 2pts

$$[H_3O_2^+] = \frac{K_{EQ}[H_3O^+][H_2O_2]}{[H_2O]}$$ 2pts

$$\text{rate} = \frac{k_1 K_{EQ}[Br^-][H_3O^+][H_2O_2]}{[H_2O]}$$ 4pts

can be in K_{EQ}

B. If the overall rate increases by a factor of 4000, calculate the decrease (kJ/mol) in E_a effected by the catalysts. (5pts)

$$\frac{k_1}{k_2} = e^{-\Delta E_a/RT}$$ 3pts

$\ln 4000 = -\Delta E_a / 8.31(300)$

$\Delta E_a = 20{,}677\,J$ or $20.7\,kJ$ 2pts

C. [True or False] If the value of k_2 is ca. $10^{11}\ L\cdot mol^{-1}\cdot s^{-1}$, this solution-phase reaction rate is activation-limited. Explain. (5pts)

False 2pts

this k_2 represents a very fast reaction (diffusion limit) 3p

D. How is the enthalpy of this highly exothermic reaction affected by the catalysts? (5pts)

It is not affected

(Enthalpy is a thermodynamic term)

2. (4+6+5 points) The temperature dependence of the iodine clock reaction was measured in a laboratory.

A. From measured reaction times at three temperatures, a graph of ___ln k___ vs. ___$\frac{1}{T}$___ yielded a straight line with a slope of -1311 K and an intercept of 1.22.

4

B. Calculate E_a from this information.

slope $= -E_a/R \Rightarrow E_a = -\text{slope} \cdot R$

$R = 8.314\ J/mol\cdot K$

$E_a = 10.90\ kJ/mol$

6

*no units -1

C. Calculate the fraction of collisions with energy sufficient to react at 300K.

$$e^{-E_a/RT} = e^{-10899.7\ \text{J/mol}/(8.314\ \text{J/mol·K})(300\text{K})}$$

$$= 0.0126$$

5pts

3. **(10+5+10 points)** The mechanism for the decomposition of NO_2Cl is:

$$NO_2Cl \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

A. By making a steady-state approximation for [Cl], express the rate of appearance of Cl_2 in terms of the concentrations of NO_2Cl and NO_2. (10pt

Define steady-state: $\frac{d[Cl]}{dt} = 0$ 1pt

$$\frac{d[Cl]}{dt} = 0 = k_1[NO_2Cl] - k_{-1}[NO_2][Cl] - k_2[NO_2Cl][Cl]$$ 2pt

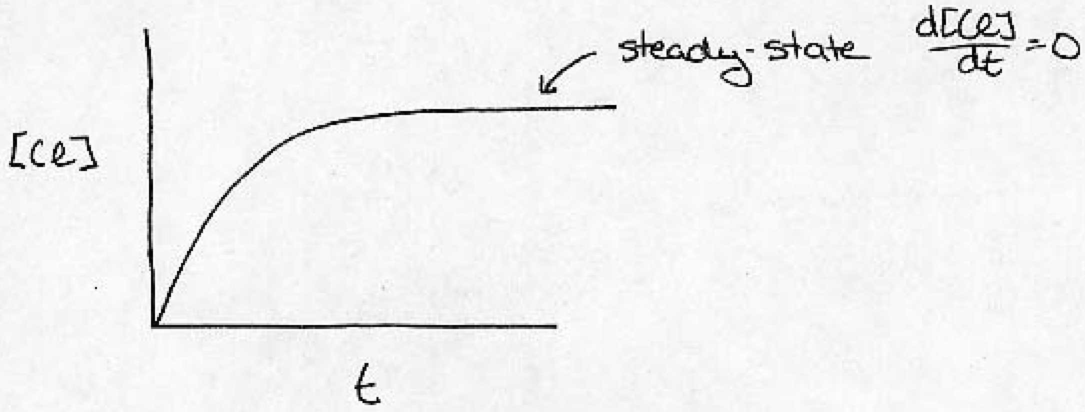
$$[Cl] = \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$ 2pts

$$\frac{d[Cl_2]}{dt} = \text{rate} = k_2[Cl][NO_2Cl]$$ 2pts

$$\text{rate} = \frac{k_2 k_1 [NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$ 3pts

B. Graph the concentration of Cl vs. time. (5pts)

5pts

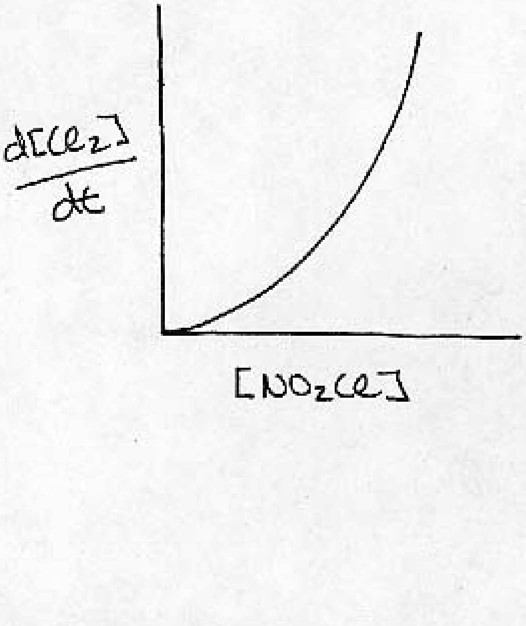


C. Graph $\frac{d[Cl_2]}{dt}$ vs. $[NO_2Cl]$ as expected for high NO_2 concentrations. (10pts)

5pts for high NO_2 concentrations: $k_{-1}[NO_2] \gg k_2[NO_2Cl]$

$$\frac{d[Cl_2]}{dt} = \frac{k_2 k_1 [NO_2Cl]^2}{k_{-1}[NO_2]}$$

5pts



4. **(10 points)** The rate for the reaction

$$OH^-(aq) + NH_4^+(aq) \longrightarrow H_2O(\ell) + NH_3(aq)$$

is first order in both OH^- and NH_4^+ concentrations, and the rate constant k at 20°C is 3.4×10^{10} L mol^{-1} s^{-1}. Suppose 1.00 L of a 0.0010 M NaOH solution is rapidly mixed with the same volume of 0.0010 M NH_4Cl solution. Calculate the time (in seconds) required for the OH^- concentration to decrease to a value of 1.0×10^{-5} M.

4pts

$$-\frac{d[OH^-]}{dt} = rate = k[OH^-][NH_4^+]$$

$$c = [OH^-] = [NH_4^+]$$

$$-\frac{dc}{dt} = kc^2$$

4pts

$$-\int_{c_0}^{c} \frac{dc}{c^2} = \int k\,dt$$

$$\frac{1}{c}\Big|_{c_0}^{c} = kt$$

$$\frac{1}{c} - \frac{1}{c_0} = kt$$

2pts

$$\frac{1}{1\times10^{-5}M} - \frac{1}{0.001M} = 3.4\times10^{10}M^{-1}s^{-1}\cdot t$$

$$t = 2.9\times10^{-6}s$$

5. **(5+5 points)** Certain bacteria use the enzyme penicilinase to decompose penicillin and render it inactive. The Michaelis-Menten constants for this enzyme and substrate are $K_m = 5 \times 10^{-5}$ mol L^{-1} and $k_2 = 2 \times 10^3$ s^{-1}.

A. What is the maximum rate of decomposition of penicillin if the enzyme concentration is 6×10^{-7} M?

$$rate = \frac{k_2[E]_0[S]}{[S]+K_m}$$

$$[S] \gg K_m$$

$$rate \approx \frac{k_2[E]_0[S]}{[S]} = k_2[E]_0 = (2\times10^3 s^{-1})(6\times10^{-7} mol/L)$$

$$= .0012\ mol\cdot L^{-1}\cdot s^{-1}$$

[S] is algebraically eliminated. A value for [S] should not be assumed.

B. At what substrate concentration will the rate of decomposition be half that calculated in part A?

Use rate from part A.

$$\frac{\text{rate}}{2} = 6\times10^{-4}\ \text{mol}\cdot L^{-1}\cdot s^{-1} = \frac{k_2[E]_0[S]}{[S]+K_m}$$

Plug in the known values of k_2, $[E]_0$, and K_m.
Rearrange to solve for $[S]$.
$[S] = 5\times10^{-5}\ \text{mol}\cdot L^{-1}$

6. (15 points) Calculate the rate constant for the abstraction reaction, carried out in the gas phase at 800K:

$$\cdot OH + CH_4 \longrightarrow H_2O + \cdot CH_3$$

The activation energy is 32 kJ/mol. The molecular diameters are 1.10 (OH) 2.90 (CH_4) and 1.70 (H_2O) Angstroms (1 Å = 10^{-10} M). The steric factor is 0.12 and the enthalpy change is -175 kJ/mol.

$$\bar{c} = \sqrt{\frac{8RT}{\pi\mu}}$$

1pt $K = Ae^{-E_a/RT}$

5pts

$$\mu = \frac{(0.017)(0.016)}{(0.017)+(0.016)} = \frac{M_{OH}M_{CH_4}}{M_{OH}+M_{CH_4}} = 8.24\times10^{-3}\ \text{kg/mol}$$

$$\bar{c} = \sqrt{\frac{(8)(8.314)(800)}{\pi\mu}}$$

4pts $e^{-E_a/RT} = e^{-32000/(8.31)(800)}$

5pts

$$K = \sigma P N_0 c\, e^{-32000/(8.31)(800)}$$

$$\sigma = \pi\left(\frac{1.10}{2}+\frac{2.90}{2}\right)^2$$

$P = 0.12$

$K = 8.0\times10^{6}\ \text{m}^3/\text{mol}\cdot\text{s}$