

Chemistry 163C Final Exam Spring 2013

*Be sure to show all derivations and calculations,
and clearly mark your answers. Good Luck!*

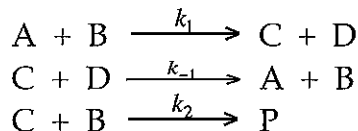
- 1) A 1.0 liter vessel at 300K is filled with O_2 at 1.0 atm. The collisional cross section for O_2 is 0.40 nm^2 . a) Determine the collision frequency $Z_{O_2O_2}$. b) Determine the mean free path, λ . c) Determine the root-mean-squared velocity, v_{rms} . d) What temperature would be required to double $Z_{O_2O_2}$? e) What would be the mean free path at this new temperature?

- 2) Consider a set of distinguishable particles where each has a two-fold degenerate electronic ground state and a four-fold degenerate excited state of energy ϵ , as shown to the right. a) Determine the statistical mechanical expression for the internal energy U . b) Determine the stat mech expression for the entropy S . c) Evaluate S for $T \rightarrow 0$ and for $T \rightarrow \infty$, and briefly interpret your results. d) Sketch a plot of S vs T from 0 K to $T \gg \epsilon/k$.



- 3) Catalase is an enzyme that breaks down hydrogen peroxide (H_2O_2) to oxygen and water. The diffusion constant and radius for catalase are $6.0 \times 10^{-7} \text{ cm}^2/\text{s}$ and 50 \AA , respectively; For H_2O_2 these values are $1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ and 2.0 \AA . a) Determine the diffusion controlled rate constant. b) The experimentally measured rate constant is $5.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. Is this reaction diffusion controlled? c) If the initial concentration of H_2O_2 is 1.0 mM and catalase is $1.0 \mu\text{M}$, what concentration of hydrogen peroxide is left after 1.0 s? (Note: See reverse side for useful equations.)

- 4) Consider the following reaction scheme:



- a) Use the steady state approximation to develop the differential rate law for product P. b) Show that high concentrations of B give a rate law that is first order in [B], whereas at low concentrations of B the rate law is second order in [B]. c) Through the course of the reaction, the concentration of D builds up. What happens to the rate of production of P? At what concentration of [D] will the reaction begin to slow?
- 5) For the bimolecular gas phase reaction:



the activation energy (E_a) and pre-exponential factor (A) are 15.5 kJ/mol and $1.1 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$, respectively. a) Determine the entropy of activation, ΔS^\ddagger . Note: $T = 1000 \text{ K}$ and the standard concentration c° is 1.0 M . b) Is your value consistent with a bimolecular process? c) Briefly explain the significance of the term kT/h in transition state theory. (Note: See reverse side for useful equations.)

1) O_2 300K, 1.0L, 1.0 atm $\sigma = 0.40 \text{ nm}$

$$Z_{O_2O_2} = \frac{1}{\sqrt{2}} \left(\frac{N}{V}\right)^2 \sigma \left(\frac{8kT}{\pi m}\right)^{1/2}$$

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.0}{0.0821 \times 300} = 0.0406 \frac{\text{mol}}{\text{L}}$$

$$\frac{N}{V} = N_A \times 0.0406 \frac{\text{mol}}{\text{L}} \times 10^3 \frac{\text{L}}{\text{m}^3} = 2.44 \times 10^{25} \text{ m}^{-3}$$

$$\begin{aligned} \text{a) } Z_{O_2O_2} &= \frac{1}{\sqrt{2}} (2.44 \times 10^{25})^2 (0.40 \times 10^{-18}) \left(\frac{8 \times 1.38 \times 10^{-23} \times 300 \times N_A}{\pi \times 0.032} \right)^{1/2} \\ &= 7.5 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{b) } \lambda &= \frac{RT}{P N_A \sqrt{2} \sigma} = \frac{8.31 \times 300}{1.01 \times 10^5 \times N_A \times \sqrt{2} \times 0.40 \times 10^{-18}} \\ &= 7.2 \times 10^{-8} \text{ m} = 72 \text{ nm} \end{aligned}$$

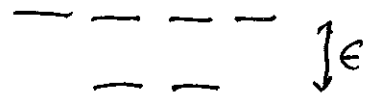
$$\text{c) } v_{\text{rms}} = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3 \times 8.31 \times 300}{0.032}\right)^{1/2} = 483 \frac{\text{m}}{\text{s}}$$

$$\begin{aligned} \text{d) } \text{If } \frac{N}{V} = \text{constant} \quad Z \propto \sqrt{T} \\ \therefore 2Z = 2\sqrt{T} = \sqrt{4T} \quad \therefore T = 1200 \text{ K} \end{aligned}$$

$$\begin{aligned} \text{e) } \text{If } V = \text{constant} \quad T \uparrow \Rightarrow P \uparrow \quad \therefore \text{no change in } \lambda \\ \lambda = 72 \text{ nm} \end{aligned}$$

2)

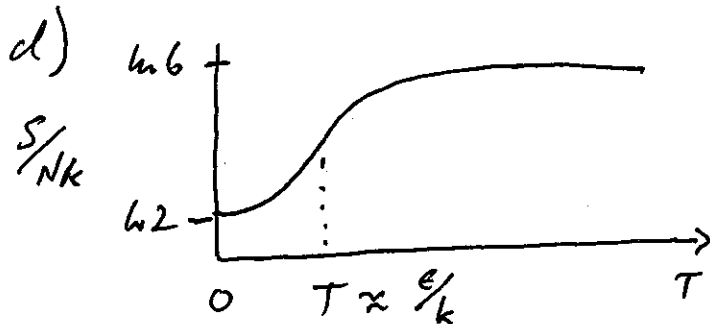
$$g = 2 + 4e^{-\beta\epsilon}$$



$$\begin{aligned} \text{a) } U &= -\frac{\partial \ln Q}{\partial \beta} = -N \frac{1}{2 + 4e^{-\beta\epsilon}} \frac{\partial}{\partial \beta} (2 + 4e^{-\beta\epsilon}) \\ &= \frac{N4\epsilon e^{-\beta\epsilon}}{2 + 4e^{-\beta\epsilon}} = \frac{N4\epsilon}{2e^{\beta\epsilon} + 4} \end{aligned}$$

$$\begin{aligned} \text{b) } S &= \frac{U}{T} + Nk \ln g \\ &= \frac{1}{T} \frac{N4\epsilon}{2e^{\epsilon/kT} + 4} + Nk \ln (2 + 4e^{-\epsilon/kT}) \end{aligned}$$

$$\begin{aligned} \text{c) } T \rightarrow 0 \quad S &= 0 + Nk \ln(2) = Nk \ln(2) \\ T \rightarrow \infty \quad S &= 0 + Nk \ln(6) = Nk \ln(6) \end{aligned} \quad \left. \vphantom{\begin{aligned} T \rightarrow 0 \\ T \rightarrow \infty \end{aligned}} \right\} \begin{array}{l} \text{in each case} \\ S = k \ln W \\ W = \# \text{ of states} \\ \text{occupied} \end{array}$$



3) catalase $D = 6.0 \times 10^{-7} \frac{\text{cm}^2}{\text{s}}$ $r = 50 \text{ \AA}$

H_2O_2 $D = 1.50 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$ $r = 2.0 \text{ \AA}$

a) $k_d = 4\pi N_A (r_A + r_B)(D_A + D_B)$

$$r_A + r_B = (50 + 2.0) \times 10^{-10} \frac{\text{m}}{\text{\AA}} = 52 \times 10^{-10} \text{ m}$$

$$(D_A + D_B) = (6.0 \times 10^{-7} + 1.5 \times 10^{-5}) \times 10^{-4} \frac{\text{m}^2}{\text{cm}^2}$$

$$= 1.56 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$$

$$k_d = 4\pi N_A (52 \times 10^{-10} \text{ m}) (1.56 \times 10^{-9} \frac{\text{m}^2}{\text{s}})$$

$$= 6.1 \times 10^7 \frac{\text{m}^3}{\text{mol} \cdot \text{s}} \times 10^3 \frac{\text{L}}{\text{m}^3} = 6.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

b) $k_d(\text{calc}) \gg k_d(\text{meas})$ $k_d(\text{meas}) = 5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$

\therefore Not diffusion controlled

c) $\frac{d[\text{H}_2\text{O}_2]}{dt} = -5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} [\text{E}][\text{H}_2\text{O}_2]$

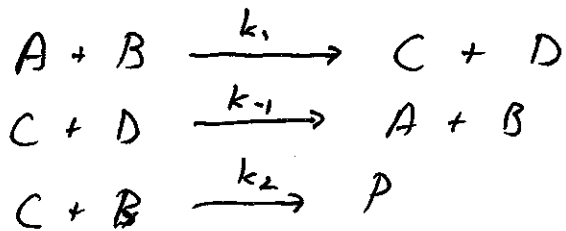
treat $[\text{E}] = \text{const. (enzyme)} = 1.0 \times 10^{-6} \text{ M}$

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = - \underbrace{5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \times 1.0 \times 10^{-6}}_{= -5.0 = \text{const.}} [\text{H}_2\text{O}_2]$$

$$\therefore [\text{H}_2\text{O}_2] = 1.0 \text{ mL} e^{-5.0 \times 1.0}$$

$$= 0.0067 \text{ mL}$$

4)



a) $\frac{d[P]}{dt} = k_2 [C][B]$

~~$\frac{d[A]}{dt}$~~ $\frac{d[C]}{dt} = k_1 [A][B] - k_{-1} [C][D] - k_2 [C][B] \approx 0$

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

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [A][B]^2}{k_{-1} [D] + k_2 [B]}$$

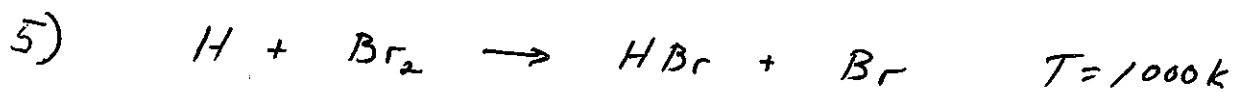
b) $[B]$ large $\frac{d[P]}{dt} \approx \frac{k_2 k_1 [A][B]^2}{k_2 [B]} = k_1 [A][B]$ \leftarrow 1st order in $[B]$

$[B]$ small $\frac{d[P]}{dt} \approx \frac{k_2 k_1 [A][B]^2}{k_{-1} [D]}$ \leftarrow 2nd order in $[B]$

c) as $[D] \uparrow$ $\frac{d[P]}{dt} \downarrow$ rxn slows

this happens when $k_{-1} [D] > k_2 [B]$

$$\text{or } [D] > \frac{k_2}{k_{-1}} [B]$$



$$E_a = 15.5 \frac{kJ}{mol} \quad A = 1.1 \times 10^{11} M^{-1} s^{-1}$$

a) gas phase bimolec. $A = \frac{e^2 k_B T}{h c^0} e^{\frac{\Delta S^\ddagger}{R}}$

$$\therefore \Delta S^\ddagger = R \ln \frac{A h c^0}{e^2 k_B T} \quad c^0 = 1.0 M$$

$$= 8.3 \ln \frac{1.1 \times 10^{11} \times 6.63 \times 10^{-34} \times 1.0}{e^2 \times 1.38 \times 10^{-23} \times 1000}$$

$$= -60.1 \frac{J}{mol \cdot K}$$

b) $\Delta S^\ddagger < 0$ \therefore yes, consistent w/ bimolecular process

c) $\frac{kT}{h}$ is typical for values of A

if $A \gg \frac{kT}{h}$ then usually unimolecular

if $A \ll \frac{kT}{h}$ " " bimolecular