

Chemistry 271, Section 22xx
General Chemistry and Energetics
Final Exam (201 points total)

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December 15, 2009

You have 120 minutes for this exam.

Explanations should be concise and clear. I have given you more space than you should need. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Partial credit will be given, *i.e.*, if you don't know, guess.

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

Key

Your Name: _____

Your SID #: _____

Viewing: Wednesday, December 16, 3:00-5:00 p.m., Chemistry 2507

Useful Equations:

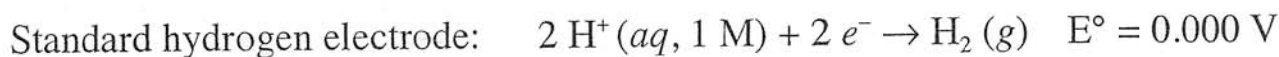
$$\Delta S - q/T \geq 0$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$K_a = [H^+][A^-]/[HA]$$

$$^\circ C = ^\circ K - 273.15$$

$$2.303RT/\mathcal{F} = 0.0592 \text{ Volts at } 25^\circ C$$



$$\ln K_{eq} = (-\Delta H^\circ/RT + \Delta S^\circ/R) \quad \ln k = (-Ea/RT) + \ln A \quad 1 \text{ Volt} = 1 \text{ Joule/Coulomb}$$

$$[A] = [A]_0 - kt \quad \ln[A] = \ln[A]_0 - kt \quad 1/[A] = 1/[A]_0 + 2kt$$

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT} = \frac{k_B T}{h} e^{-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT} = \left(\frac{k_B T}{h} e^{\Delta S^\ddagger/R} \right) e^{-\Delta H^\ddagger/RT}$$

$$pH = -\log([H^+])$$

$$\Delta G = \Delta H - T\Delta S$$

$$n_i/n_0 = \exp[-(E_i - E_0)/kT]$$

$$R = 8.314 \text{ J/mole K}$$

$$S = k \ln W$$

$$PV = nRT$$

$$\Delta G = -n\mathcal{F}E$$

$$E = E^\circ - 2.303(RT/n\mathcal{F}) \log_{10} Q$$

$$\mathcal{F} = 96500 \text{ C(oulomb)/mole}$$

CCACA EE

1. Multiple Choice (48 pts): Read carefully and circle the single best answer for each.

(a; 4 pts) The law of detailed balance or microscopic reversibility states that:

- (a) All elementary reactions have the same rate constants for the forward and backward reactions.
- (b) The mechanism of the reverse reaction is the exact reversal of the mechanism of the forward reaction.
- (c) The product of forward rate constants in a cyclic reaction is equal to the product of reverse rate constants.
- (d) At equilibrium, each elementary step in a complex reaction mechanism is individually at equilibrium.

(e) b, c, and d are all true.

(b; 4 pts) If we could break the law of microscopic reversibility, we could create a/an

- (a) Catalyst that acts at infinite speed.
- (b) Perpetual motion machine.
- (c) Spaceship that travels faster than light.
- (d) Way to text in class without any possibility of detection.
- (e) None of the above.

(c; 4 pts) The steady state approximation applies to

- (a) Reactants in complicated mechanisms.
- (b) All intermediates in complicated mechanisms.
- (c) Intermediates with fast rates of decay.
- (d) All species present at low concentration.
- (e) Only intermediates involved in the rate-limiting step.

(d; 4 pts) Photosystem II in green plants functions to

- (a) Re-oxidize the chlorophyll in PS I.
- (b) Generate oxygen.
- (c) Pump sodium ions.
- (d) Reduce CO₂.
- (e) (a) and (d).

(e; 4 pts) Stratification in lake sediments occurs because

- (a) Heavier bacteria sink.
- (b) Creatures that use the available terminal electron acceptor with the largest E°_{red} win.
- (c) There is a gradient in the availability of photons.
- (d) Hydrogen and methane gas created by anaerobes kill the local aerobes.
- (e) It's warmer as you go deeper.

- (f; 4 pts) The continued accumulation of CO_2 at greater than 350 ppm (parts per million) will be harmful to the biosphere because:
- (a) CO_2 accumulation will destroy the ozone layer.
 - (b) CO_2 absorbs visible light and prevents it from getting to the plants that need it.
 - (c) CO_2 absorbs and re-radiates infrared light.
 - (d) CO_2 concentrations of 350 ppm screw up our breathing.
 - (e) Increased CO_2 will accelerate the growth of trees.
- (g; 4 pts) There are fundamental upper limits to second-order rate constants because
- (a) We can't measure them if they are too fast.
 - (b) The speed of molecular vibrations is finite.
 - (c) Molecules must collide to react, and diffusion limits the rate of collision.
 - (d) The reactants can't always be obtained at high concentrations.
 - (e) Not all reactions are catalyzed.
- (h; 4 pts) The overall reaction order (1st, 2nd, 3rd, etc) for the general reaction $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ can
- (a) Never be predicted, only determined by experiment.
 - (b) Be calculated as the product of the orders for individual reactants.
 - (c) Be negative.
 - (d) Be used to prove that the reaction is an elementary reaction.
 - (e) Be used by itself to predict the equilibrium constant.
- (i; 4 pts) One advantage of biofuels (biodiesel, ethanol) over other energy sources is:
- (a) Burning biofuel does not release any CO_2 .
 - (b) Biofuel is currently much cheaper than fossil fuels.
 - (c) You can't use solar/nuclear/wind power to propel a diesel truck.
 - (d) Ethanol production stimulates demand for corn, which makes food cheaper.
 - (e) It can only be made in developed countries, which helps our balance of trade.
- (j; 4 pts) Carbon capture and sequestration (CCS):
- (a) Is necessary partly because as a society we are addicted to coal.
 - (b) Can be retrofitted to existing airplanes.
 - (c) Is currently in use in 50 % of US power plants.
 - (d) Costs a negligible fraction of the energy output from burning the oil that produces the CO_2 to be sequestered.
 - (e) All of the above.

- (k; 4 pts) The "volume of distribution," $V_d = (\text{amount of drug in the body})/(\text{plasma concentration of drug})$
- (a) Is usually larger for fat-soluble drugs than for water-soluble drugs.
 - (b) Reflects the fact that drug may be stored in tissues other than the bloodstream.
 - (c) Affects the rate of elimination.
 - (d) Is \geq plasma volume.
 - (e) All of the above.

- (l; 4 pts) The rate law for a chemical reaction
- (a) Can only be determined experimentally.
 - (b) Cannot depend on the concentrations of products.
 - (c) Must be correctly predicted by any reasonable proposed mechanism.
 - (d) Has no connection to the rate law for the reverse reaction.
 - (e) (a) and (c) are both true.

2. Temperature Dependence of Rates (35 pts)

- (a; 2 pts) We have seen that the Arrhenius rate law and the Eyring rate law both have the form

$$k = A \cdot \exp(-X/RT),$$

- (+2) where $X =$ the activation energy E_a or the enthalpy change ΔH^\ddagger for reaching the (fill in the blank) transition state respectively. The "constant" pre-exponential factor A actually depends on either T or $T^{1/2}$ depending on which theory we use.

- (b; 6 pts) Explain the fundamental basis of the exponential factor in each rate law.

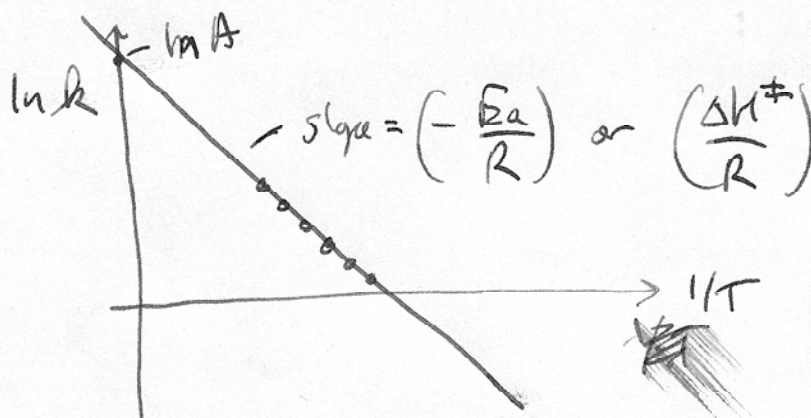
Both derive from the Boltzmann Distribution (+2)

- (+2) The Arrhenius law / collision theory from the Maxwell-Boltzmann distribution of molecular speeds.
Eyring theory from the Req. for forming TS, which is $k \propto e^{-\Delta G^\ddagger/RT}$ - a Boltzmann factor again (+2)

- (c; 4 pts) Why isn't it obvious from experiment exactly what the temperature dependence of A actually is, i.e. which expression for A is correct? [It might help to answer (d) first.]

A graph of $a \cdot T \cdot e^{-X/RT}$ looks very much like $b \cdot T^{1/2} \cdot e^{-X/RT}$ - the behavior is dominated by the exponential decay. (+4)

(d; 8 pts) Sketch a graph illustrating how we measure E_a or ΔH^\ddagger . Be sure to label the axes.



$k = Ae^{-E_a/RT}$ $\ln k = \ln A - \left(\frac{E_a}{R}\right) \cdot \frac{1}{T}$

] not needed

- +1 for any straight line
- +2 for $\ln k$
- +2 for $1/T$
- +2 for slope
- +1 for y-intercept

(e; 15 pts) A rule of thumb in organic chemistry states that the reaction rate doubles for every 10 degree C (or K) increase in temperature, for temperatures near 300 K. This is a crude approximation: assuming the reaction follows the Arrhenius rate law, what value of E_a makes it true?

$k(300) = Ae^{-E_a/(R \cdot 300)}$ → +2 for clearly Arrhenius eqn

$k(310) = Ae^{-E_a/(R \cdot 310)}$

$\frac{k(310)}{k(300)} = 2 = \frac{Ae^{-E_a/310R}}{Ae^{-E_a/300R}} = e^{\left(\frac{E_a}{300R} - \frac{E_a}{310R}\right)} = e^{\left(\frac{E_a}{R}\right)\left(\frac{1}{300} - \frac{1}{310}\right)}$

+4 for correct equation involving E_a

$\ln 2 = \ln \left[e^{\left(\frac{E_a}{R}\right)\left(\frac{1}{300} - \frac{1}{310}\right)} \right]$

$E_a = \frac{R \ln 2}{\frac{1}{300} - \frac{1}{310}} \quad \left(\frac{J/mol \cdot K}{1/K}\right) = \frac{8.314 \ln 2}{\left(\frac{1}{300} - \frac{1}{310}\right)} \quad J/mol$

$E_a = 53594 \text{ J/mol or } 54 \text{ kJ/mol or } 50 \text{ kcal/mol}$

+2 for numerical answer

3. Miscellaneous bio-redox and (pharmaco)kinetics (57 pts)

(a; 7 pts) There's really no such thing as a zero order reaction. Under what conditions does it become clear that a zero-order reaction is actually a first-order (or higher-order) reaction, and why?

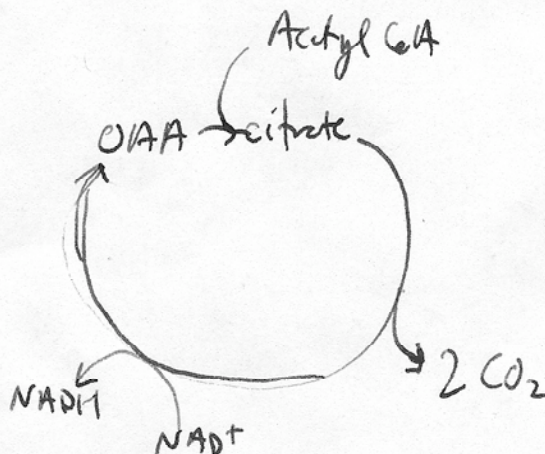
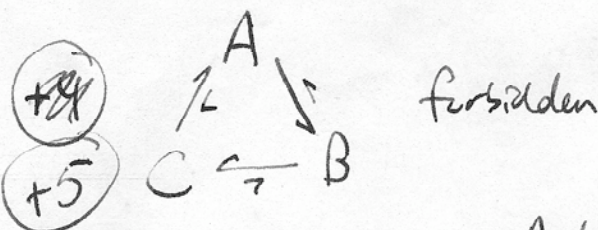
- ~~then~~ Consider $A \rightarrow B$ "zero-order" in A, so $-\frac{d[A]}{dt} = k$

(+3) \rightarrow if β enzyme, +1 otherwise
 - In the reaction can't possibly proceed in the absence of A!

(+4) At low [A] the reaction will revert to first order, or whatever the true order is - the surface or catalyst that promotes the reaction will no longer be saturated. (+3)

+7 for this

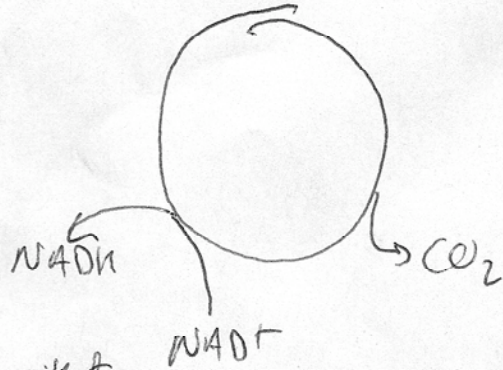
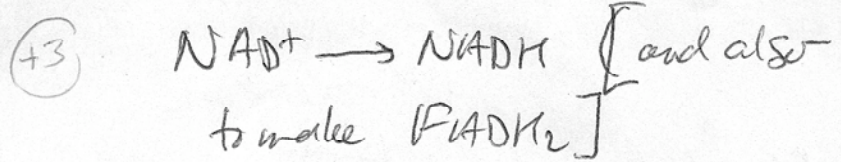
(b; 10 pts) The law of microscopic reversibility forbids cyclic reactions. Sketch what we mean by a forbidden cycle. On the other hand, biochemistry is full of cycles, like the Krebs cycle in intermediary metabolism, which converts citrate through a series of intermediates to oxaloacetate and then back to citrate. How can biology get away with this?



- A cycle is allowed if it is accompanied by spontaneous reactions converting substrate to product. (+5)

(c; 10 pts) The Krebs cycle completes the oxidation of glucose to carbon dioxide. Where are the electrons put during the Krebs cycle, and what happens to the electrons in the end? Why do we call animal metabolism "unwinding the storage of energy from sunlight?"

- Electrons are used to reduce

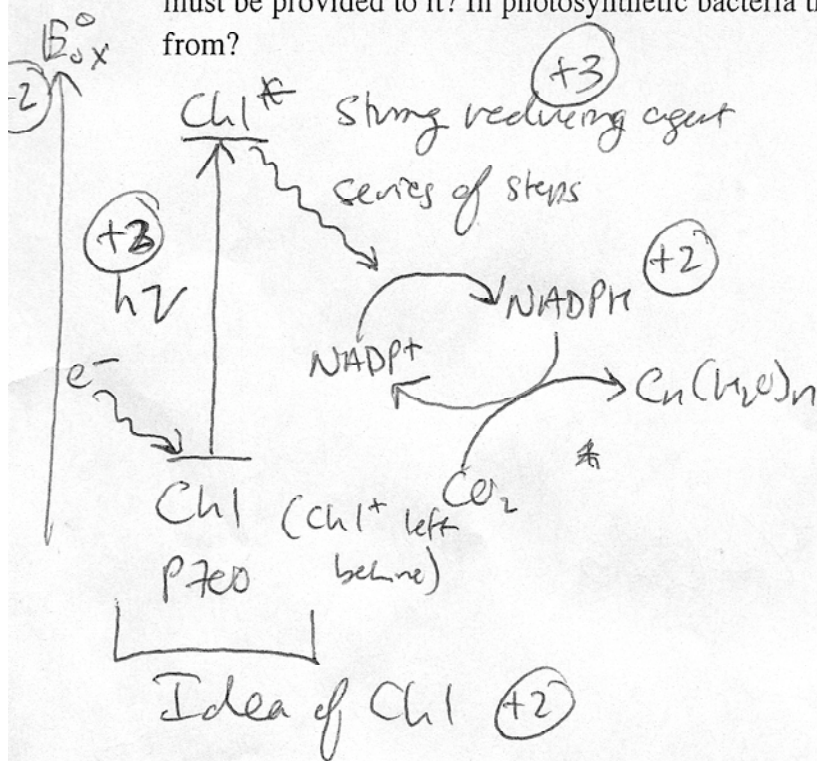


- In the end the electrons are (+2) transferred to O_2 to make H_2O

Idea that we reverse what plants do

- Animals "unwind" the reduction of $CO_2 \rightarrow$ carbohydrates by oxidizing $C_n(H_2O)_n$ (+3/+2) And we unwind the production of O_2 from H_2O (+5)

(d; 15 pts) Sketch Photosystem I (the right-hand side of the Z scheme); don't worry about any intermediate electron carriers. For PS I to act repeatedly to provide reducing power for carbohydrate synthesis, what must be provided to it? In photosynthetic bacteria that lack PS II, where might this something come from?



- PS I Chl^+ cation must be re-reduced, \therefore (+3) (+2) need electrons

- The electrons can come from an external reductant like H_2S or H_2 [or from cyclic electron transfer back to Chl - but this can't reduce CO_2]

(e; 15 pts) Consider an individual who has taken a dose of an illegal drug that brings the drug's plasma concentration to its effective level of 48 mg/L. The detection limit of the drug in blood plasma is given as 1.5 mg/L. If the individual has a volume of distribution (Vd) of 150 L, and the clearance rate of the drug (Cl) is 2.25 mL/second, how long does the individual have to wait in order to pass a drug test? [Hint: the equation at the right is a convenient version of the first-order decay equation.]

$Cl = K_{el} \times Vd$ K_{el} = Fraction of drug eliminated per second $t_{1/2} = \frac{0.693}{K_{el}}$ $[Drug] = [Drug]_0 2^{-t/t_{1/2}}$

(+1) $Cl = 2.25 \times 10^{-3} \text{ L/s}$

(+1) $Vd = 150 \text{ L}$

→ conversion (-2)

(+2) (+1) $K_{el} = \frac{Cl}{Vd} = \frac{2.25 \times 10^{-3} \text{ L/s}}{150 \text{ L}} = 1.5 \times 10^{-5} \text{ s}^{-1}$ (+2)

(+2) (+1) $t_{1/2} = \frac{0.693}{K_{el}} = \frac{0.693}{1.5 \times 10^{-5} \text{ s}^{-1}} = 0.462 \times 10^5 \text{ sec}$ (+2)

$[Drug] = [Drug]_0 2^{-t/t_{1/2}}$ (+1)

$\frac{1.5 \text{ mg/ml}}{48 \text{ mg/ml}} = 2^{-t/t_{1/2}}$ (+2)

$-\frac{t}{t_{1/2}} = -5$

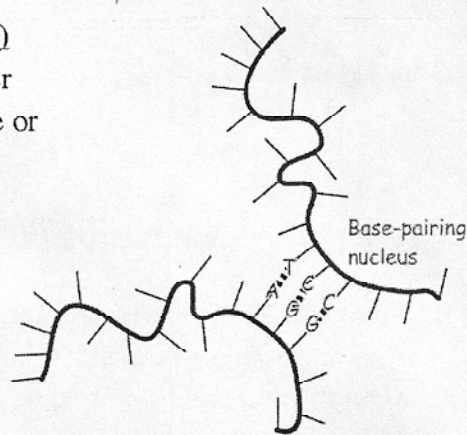
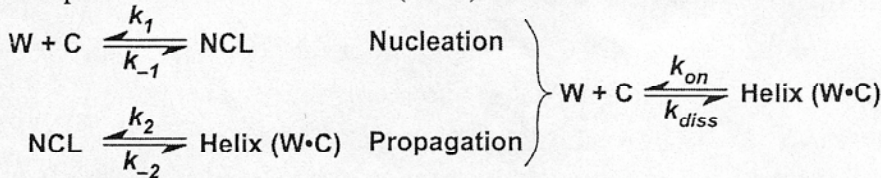
$\frac{1}{32} = 2^{-5}$

$t = 5 t_{1/2}$
 $= 5 \times 0.462 \times 10^5 \text{ sec}$
 ~~$= 2.31 \times 10^5 \text{ sec}$~~
 $= 2.31 \times 10^5 \text{ sec}$
 $= 64 \text{ hours}$

+4 for any correct solution

4. DNA Hybridization and the Steady State Approximation (40 pts)

The hybridization of two DNA strands to make a duplex is a second order reaction. The mechanism is believed to be reversible "Nucleation" of one or a few base pairs to form an unstable short helix ("NCL") followed by rapid formation of the remaining base pairs ("Propagation") to complete the rest of the Helix (W•C):



The observed integrated rate law for equal W and C concentrations is $1/[W] = (1/[W]_0) + k_{on}t$. The observed overall second order rate constant k_{on} for $W + C \rightarrow W•C$ is about $5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for oligonucleotides. This is much slower than the maximal possible (diffusion-controlled) rate constant, which is about $10^9 \text{ M}^{-1}\text{s}^{-1}$.

(a; 4 pts) Physically, why do you think the association reaction is so slow, even at temperatures where the duplex is thermodynamically highly favorable?

(+4) for idea of rare productive collisions
 - It is entropically unlikely that the right base pairs will form upon random collision. Most collisions are unproductive, so the rate is much slower than diffusion.

(b; 8 pts) What is the $t_{1/2}$ for hybridization at $2 \mu\text{M}$ $[W]_0$? [Hint: Slow is relative!]

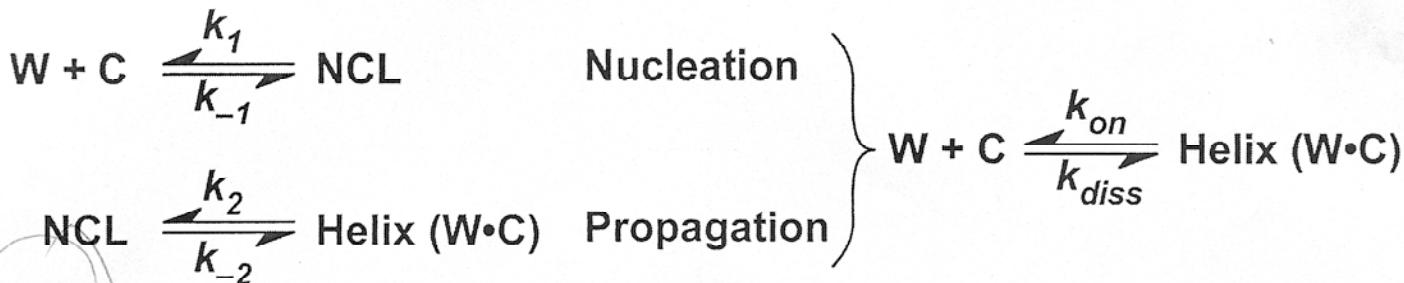
(+1) $\frac{1}{1 \times 10^{-6} \text{ M}} = \frac{1}{\frac{1}{2}[W]_0} = \frac{1}{[W]_0} + k_{on} t_{1/2} = \frac{1}{2 \times 10^{-6} \text{ M}} + 5 \times 10^5 \text{ M}^{-1}\text{s}^{-1} \cdot t_{1/2}$ (+1)

(+2) for equation for $t_{1/2}$
 $t_{1/2} = \frac{\left(\frac{1}{1 \times 10^{-6} \text{ M}} - \frac{1}{2 \times 10^{-6} \text{ M}} \right)}{5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}} = \frac{(10^6 \text{ M}^{-1} - 0.5 \times 10^6 \text{ M}^{-1})}{5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}}$

$= \frac{0.5 \times 10^6}{0.5 \times 10^6 \text{ s}^{-1}} = 1 \text{ second}$ (+2)

(+7) for $t_{1/2} = \frac{1}{2k_{on}[W]_0} = 0.5 \text{ s}$

$\frac{2}{[W]_0} = \frac{1}{[W]_0} + k_{on} t_{1/2}$ $\frac{1}{[W]_0} = k_{on} t_{1/2}$ $t_{1/2} = \frac{1}{k_{on} [W]_0}$ (+4)



(c; 12 pts) The equilibrium constant $K_{association}$ for the overall $W + C \rightleftharpoons W\cdot C$ equilibrium for a particular oligonucleotide pair at 37 °C is $8 \times 10^8 \text{ M}^{-1}$. If $k_{on} = 5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ as above and we consider the hybridization equilibrium to be an elementary reaction, what is the first-order rate constant for dissociation k_{diss} ? This has an impact on the methods of doing a hybridization experiment, in which we mix probe and target oligonucleotides and then wash away mismatched and free probe to increase signal/noise. Specifically, if we assume that mismatched duplexes dissociate only twice as fast as the desired product rates, ESTIMATE how long we have to wait for 95 % of the undesired signal to wash away (4 half-lives): Circle one and give an approximate calculation: 1 min 1 hour 1 day 1 month?

$$K_{assoc} = \frac{k_{on}}{k_{diss}} \quad \Rightarrow \quad k_{diss} = \frac{k_{on}}{K_a} = \frac{5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}}{8 \times 10^8 \text{ M}^{-1}} = (0.625 \times 10^{-3}) \text{ s}^{-1} = 6.25 \times 10^{-4} \text{ s}^{-1}$$

(+1) (+2) (+3 to here)

$$k_{diss}(\text{mismatch}) = 2 \times 6.25 \times 10^{-4} \text{ s}^{-1} = 1.25 \times 10^{-3} \text{ s}^{-1} \quad (+1)$$

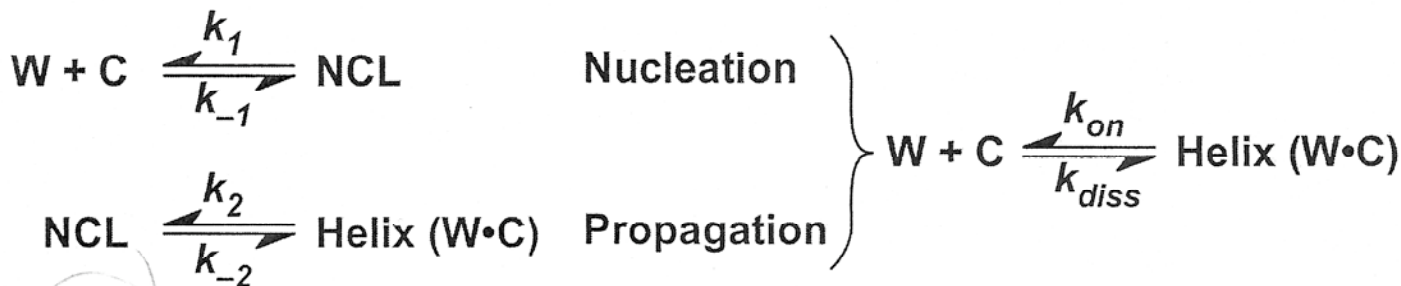
$$[wc] = [wc]_0 e^{-kt}$$

$$(+1) \quad t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{1.25 \times 10^{-3} \text{ s}^{-1}} = 554 \text{ sec}$$

$$4 \times t_{1/2} \approx 2200 \text{ sec}$$

(+2) for any calculation

+3 for missing the x2



(d; 16 pts) Given the mechanism above, apply the steady state approximation (SSA) to the NCL intermediate to derive the differential rate law for helix formation. We will ignore the "unzipping" reaction (k_{-2}) so we consider only the overall forward reaction. Start with the rate of helix formation = $d[\text{Helix}]/dt = k_2[\text{NCL}]$.

If $k_1 \gg k_2$, this mechanism is a type we have seen before, called a rapid pre-equilibrium (+2)

If $k_2 \gg k_1$, then which step of the reaction is rate-limiting? Circle one: First (+2) Second
 [If you're worried, in this case if k_2 is not $\gg k_1$, then the SSA does not apply.]

$$\frac{d[Wc]}{dt} = k_2 [NCL]$$

$$\frac{d[NCL]}{dt} = k_1 [W][C] - k_{-1} [NCL] - k_2 [NCL] \stackrel{SSA}{=} 0$$

$$[NCL] = \frac{k_1 [W][C]}{k_{-1} + k_2}$$

$$\frac{d[Wc]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [W][C]$$

total is 18 -
 can get 16 max

(+2) For any work with k_1, k_2 \rightarrow if rapid pre-eg or key first is wrong
 $k_{-1} \gg k_2 \quad \frac{d[Wc]}{dt} = k_2 \left(\frac{k_1}{k_{-1}} \right) [W][C]$
 $k_2 \gg k_{-1} \quad \frac{d[Wc]}{dt} = k_1 [W][C]$
 = rate of first step = r.l.s.
 Score for the page _____

5. Fundamentals of Catalysis (21 pts): See directions below the table

	<p>(a; 7 pts) Identity: <u>perfect enzyme (+3)</u> Reasoning: - transition state is the first step therefore the r.l.s is the initial binding and the rxn is as fast as it can possibly be (+2)</p>
	<p>(b; 7 pts) Identity: <u>enzyme w/ P release as r.l.s (+3)</u> Reasoning: The last step is the transition state and it must ^{can} correspond to generation of free products. (+4)</p>
	<p>(c; 7 pts) Identity: <u>binding protein (+3)</u> Reasoning: The second intermediate is the free energy minimum - the enzyme will just sit there and not be released. (+2)</p>

Consider the three free energy reaction coordinate diagrams above for the reactions carried out by would-be catalysts. The uncatalyzed reaction for each case is shown in the faint dashed curve. One of the catalysts corresponds to a binding protein, one corresponds to an enzyme for which the rate-limiting step is product release, and one corresponds to a perfect enzyme, i.e. one where the initial binding is the rate-limiting step. Identify which is which and briefly explain your reasoning.

Page	Score
2	/20
3	/20
4	/20
5	/23
6	/17
7	/25
8	/15
9	/12
10	/12
11	/16
12	/21
Total	/201

Score for the page _____