Chemistry 271 **Your Name:** Key

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General Chemistry and Energetics

Final Exam (200 points total) **Your Section # or time:**

December 14, 2012

You have 120 minutes for this exam.

Explanations should be concise and clear. 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.

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

Usefnl Eqnations:

$K_a = [H^+][A^-]/[HA]$ $\quad pH = -\log([H^+])$ $\quad K_b = [HA][HO^-]/[A^-]$

$K_w = [H^+][HO^-]$ $\quad pH = pK_a + \log [A^-]/[HA]$ $\quad \Delta G° = -RT\ln K_{eq}$

$R = 0.08206$ L·atm/mole K $\quad k_B = 1.38 \times 10^{-23}$ J/K $\quad \ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$\Delta S - q/T \geq 0$ $\quad R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$

$S = k_B \ln W$ $\quad \Delta G = \Delta H - T\Delta S$ $\quad E = \Sigma\, n_i\, \varepsilon_i$

$W = N!/(\prod n_i!)$ $\quad n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$ $\quad N = \Sigma\, n_i$

Chemical standard state: 1 M solutes, pure liquids, 1 atm gases

Biochemical standard state: pH 7, all species in the ionic form found at pH 7

$°C = °K - 273.15$ $\quad P(v)dv = Cv^2 exp(-mv^2/2kT)$ $\quad E = E° - 2.303(RT/n\mathcal{F})\log_{10}Q$

$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C $\quad \mathcal{F} = 96500$ C(oulomb)/mole

$\Delta G° = -n\mathcal{F}E°_{cell}$ $\quad \ln k = (-E_a/RT) + \ln A$ $\quad 1$ Volt $= 1$ Joule/Coulomb

$[A] = [A]_0 - kt$ $t_{1/2} = [A]_0/2k$ $\quad \ln[A] = \ln[A]_0 - kt$ $t_{1/2} = \ln 2/k$ $\quad 1/[A] = 1/[A]_0 + 2kt$ $t_{1/2} = \frac{1}{2[A]_0 k}$

Standard hydrogen electrode: $2\,H^+(aq, 1\,M) + 2\,e^- \rightarrow H_2(g)$ $\quad E° = 0.000$ V

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."

1. Kinetics

Chlorofluorocarbon refrigerants (CFCs) were banned because they destroy UV-protective ozone, O_3, in the atmosphere. UV photolysis of CFCs gives chlorine radicals (Cl = Cl·). For complicated reasons, Cl is produced most efficiently in the Antarctic, hence the ozone hole there. One of several ozone-destroying catalytic cycles is described below. There is a significant concentration of both O_3 and O atoms in the upper stratosphere due to photolysis of O_2. We will assume $[O_3] = 2 \times 10^{-9}$ M and $[O] = 3 \times 10^{-12}$ M. Chlorine radicals catalyze the recombination of these "odd-oxygen" species to give two molecules of O_2 according to reactions (1) and (2) below. The same recombination can also happen in an uncatalyzed fashion. We will apply the Steady State Approximation (SSA) to the reactive intermediates ClO and Cl and compare the catalyzed and uncatalyzed rates. [Sources: Davis and Davis, *Fundamentals of Chemical Reaction Engineering*, and www.ccpo.odu.edu/~lizsmith/SEES/ozone/oz_class.htm]

(1) $Cl\ (g) + O_3\ (g) \rightarrow ClO\ (g) + O_2\ (g)$ $k_1 = 3 \times 10^{10}\ M^{-1}s^{-1} \exp(-1200\ (J/mole)/RT)$

(2) $ClO\ (g) + O\ (g) \rightarrow Cl\ (g) + O_2\ (g)$ $k_2 = 6 \times 10^{10}\ M^{-1}s^{-1} \exp(-1800\ (J/mole)/RT)$

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(3) $O_3\ (g) + O\ (g) \rightarrow 2\ O_2\ (g)$ net rxn, uncatalyzed $k_3 = 1 \times 10^{10}\ M^{-1}s^{-1} \exp(-19000\ (J/mole)/RT)$

(a; 3 pts) Write down the differential expression for the rate law for the uncatalyzed loss of O_3 according to reaction (3), assuming that it is an elementary reaction.

$$Rate = -\frac{d[O_3]}{dt} = k_3[O_3][O]$$

changing sign of both O and Ox

+1 for writing $d[O_3]/dt$

+2 for correct

(b; 3 pts) Explain how the reactive Cl/ClO species meet the definition of a catalyst. +1

- The reactive chlorine species participate in the reaction but are neither created nor destroyed. +2

(c; 6 pts) For the catalyzed reaction, write down the differential rate equation for the rate of change of [ClO], set it to zero according to the SSA, and solve for [ClO] in terms of k_1, k_2, $[O_3]$, [O], and [Cl].

$$\frac{d[ClO]}{dt} = k_1[Cl][O_3] - k_2[ClO][O] = 0$$

+3 ; SSA

$$k_2[ClO][O] = k_1[Cl][O_3]$$

$$\boxed{[ClO] = \frac{k_1[Cl][O_3]}{k_2[O]}}$$ +3

Score for the page 12

(d; 10 pts) In this scheme, the total concentration of activated chlorine species is equal to a constant we denote $[Cl/ClO]_T = [Cl] + [ClO]$. Use this relationship and your answer to (c) to show that [ClO] in terms of k_1, k_2, $[O_3]$, [O], and $[Cl/ClO]_T$ is given by $[ClO] = (k_1[Cl/ClO]_T[O_3])/(k_2[O] + k_1[O_3])$. Explain in terms of the rates for reactions (1) and (2) why the steady state concentration of [ClO] is decreased when we carry out the experiment at increased [O].

$[Cl/ClO]_T = [Cl] + [ClO]$ so $[Cl] = [Cl/ClO]_T - [ClO]$

$[ClO] = \frac{k_1[Cl][O_3]}{k_2[O]}$ need to substitute for Cl to solve for [ClO] in terms of total reactive chlorine

$[ClO] = \frac{k_1[O_3]}{k_2[O]}([Cl/ClO]_T - [ClO])$ (+3) for substitution

$[ClO]\left(1 + \frac{k_1[O_3]}{k_2[O]}\right) = \frac{k_1[O_3]}{k_2[O]} \cdot [Cl/ClO]_T$

+2 if consistent with a wrong answer from (c)

$[ClO](k_2[O] + k_1[O_3]) = k_1[O_3][Cl/ClO]_T$

$$\boxed{[ClO] = \frac{k_1[O_3][Cl/ClO]_T}{k_2[O] + k_1[O_3]}}$$ ✓ (+3) for path to here

- If [O] ↑ we see from the equation (+1 if no other parts) that [ClO] ↓. Physically this is because the O atoms react with ClO to regenerate Cl; so the higher the [O] the more reactive Cl partitions into Cl· rather than ClO. (+2) (+1 for idea that O shifts ClO → Cl)

Score for the page 10/10

(e; 8 pts) Write down the differential rate law for the loss of $[O_3]$ in the catalytic cycle, and show that the rate law in terms of k_1, k_2, $[O_3]$, $[O]$, and $[Cl/ClO]_T$, starting from the expression in (d), is

$$-\frac{d[O_3]}{dt} = \frac{k_1 k_2 [O][Cl/ClO]_T [O_3]}{k_2[O] + k_1[O_3]} \approx k_2[O][Cl/ClO]_T \text{ for } k_2[O] \ll k_1[O_3]$$

$-\frac{d[O_3]}{dt} = k_1[Cl][O_3] = k_1([Cl/ClO]_T - [ClO])[O_3]$ (+2) (+2) for idea of substitution

$= k_1\left([Cl/ClO]_T - \frac{k_1[Cl/ClO]_T[O_3]}{k_2[O] + k_1[O_3]}\right)[O_3]$

$= k_1[Cl/ClO]_T[O_3]\left(\frac{k_2[O] + k_1[O_3]}{k_2[O] + k_1[O_3]} - \frac{k_1[O_3]}{k_2[O] + k_1[O_3]}\right)$

$-\frac{d[O_3]}{dt} = \frac{k_1 k_2 [Cl/ClO]_T [O_3][O]}{k_2[O] + k_1[O_3]}$ ✓ (+2) (+3) – for any credible work

(+2) for this but can get +8 w/out

$k_2[O] \rightarrow$ small

If $k_2[O] \ll k_1[O_3]$, $k_1[O_3]$ cancels to give $k_2[Cl/ClO]_T[O]$ ✓ if

(f; 8 pts) Calculate initial rates for both the catalyzed and the uncatalyzed destruction of O_3 at 200 K (it's cold up there), with $[Cl/ClO]_T = 10^{-12}$ M, $[O_3] = 2 \times 10^{-9}$ M, and $[O] = 3 \times 10^{-12}$ M. At 200 K, $k_1 = 1.5 \times 10^{10}$ $M^{-1}s^{-1}$, $k_2 = 2 \times 10^{10}$ $M^{-1}s^{-1}$, and $k_3 = 1 \times 10^{5}$ $M^{-1}s^{-1}$.

uncatalyzed: $-\frac{d[O_3]}{dt} = k_3[O_3][O]$

$= \underbrace{1\times10^5\ M^{-1}s^{-1} \cdot 2\times10^{-9}\ M \cdot 3\times10^{-12}\ M}_{(+2)\text{ for plugging in}} = \frac{6\times10^{-16}\ M s^{-1}}{(+2)}$

catalyzed: $k_2[O] = 2\times10^{10}\ M^{-1}s^{-1} \cdot 3\times10^{-12}\ M = 6\times10^{-2}\ s^{-1}$

$k_1[O_3] = 1.5\times10^{10}\ M^{-1}s^{-1} \cdot 2\times10^{-9}\ M = 3\times10^{1}\ s^{-1} >> k_2[O]$

so $-\frac{d[O_3]}{dt} = k_2[O][Cl/ClO]_T = 6\times10^{-2}\ s^{-1} \cdot 10^{-12}\ M$ (+2)

$= \frac{6\times10^{-14}\ M s^{-1}}{(+2)}$ → 100-fold faster than uncatalyzed

Score for the page ____/16

2. Electrochemistry

The standard nonrechargeable ("primary") alkaline cell shown at the right is based on the half reactions below:

$ZnO\,(s) + H_2O\,(l) + 2\,e^- \rightarrow$

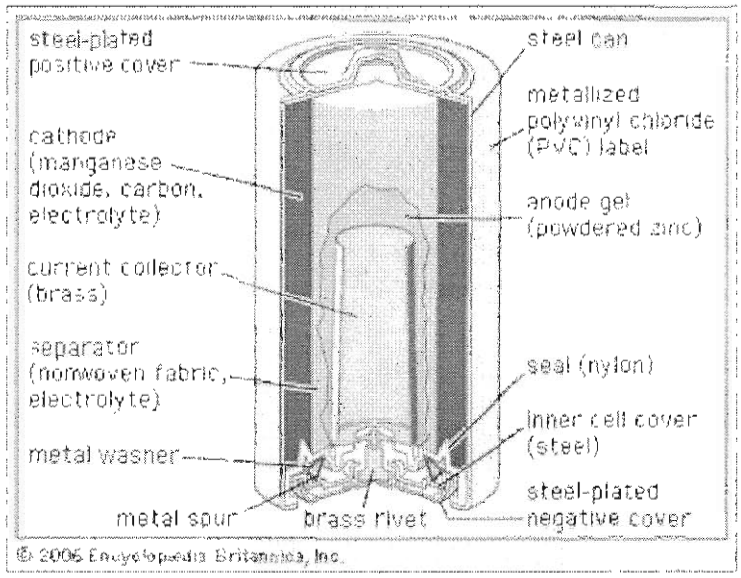
$Zn\,(s) + 2\,OH^-\,(aq) \qquad E°_{red} = -1.28\ V$

$2\,MnO_2\,(s) + H_2O\,(l) + 2\,e^- \rightarrow$

$Mn_2O_3\,(s) + 2\,OH^-\,(aq) \quad E°_{red} = 0.15\ V$

The OH^- comes from the potassium hydroxide electrolyte present in both the anode and the cathode (that's why they call it an alkaline cell). The carbon in the cathode is just for conductivity.

alkaline cell



Cutaway view of an alkaline-manganese dioxide power cell

(a; 10 pts) Write down the overall cell reaction and calculate $E°_{cell}$.

(+3) Battery → $E°_{cell}$ must be > 0 → or any manipulation that 1st rxn is reversed

(+1) (+2) so $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^- \quad E°_{ox} = +1.28V$

(+1) $2MnO_2(s) + H_2O + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq) \quad E°_{red} = 0.15V$

(+3) sum: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s) \quad E°_{cell} = +1.43V$ (+2)

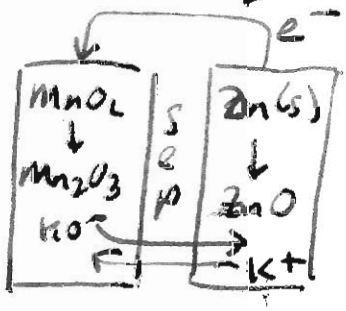
(b; 3 pts) Why are finely powdered Zn(s) and MnO_2(s) used instead of just a chunks o' zinc and manganese dioxide?

– Greater surface area means that more electrons can be transferred, so the cell can provide

(+3) higher current.

(c; 7 pts) The "separator" is analogous to the salt bridge in our standard two-beaker setup. What is its function? How is the electrical circuit completed in the alkaline battery?

(+3) It prevents bulk mixing, i.e. direct contact between MnO_2 and Zn that would short out the battery



e^- through external circuit

(+4) HO^- moves through separator from cathode to anode and/or K^+ moves the other way.

Score for the page_____

(d; 12 pts) Based only on the Nernst equation for the overall cell reaction, how should the voltage change as this battery is depleted? In fact, the cell voltage does drop off gradually as the battery is discharged. Speculate about how/why this occurs, considering that some concentrations may differ in different compartments. In general, why does E_{cell} change only gradually until a battery is nearly completely drained?

(+4) $E = E^\circ - \frac{0.0592}{n} \log Q$ But $Q = 1$ for all solids → no change in voltage

(+4) But in fact $[HO^-]$ is ~~dropping~~ consumed at the anode and produced at the cathode. If there is any movement of K^+ ions instead of HO^-, the concentration of $[HO^-]$ will decrease at the anode and ↑ at cathode, and E ↓.

(+4) Reactions are strongly driven, so Q must be far from 1 for E to change.

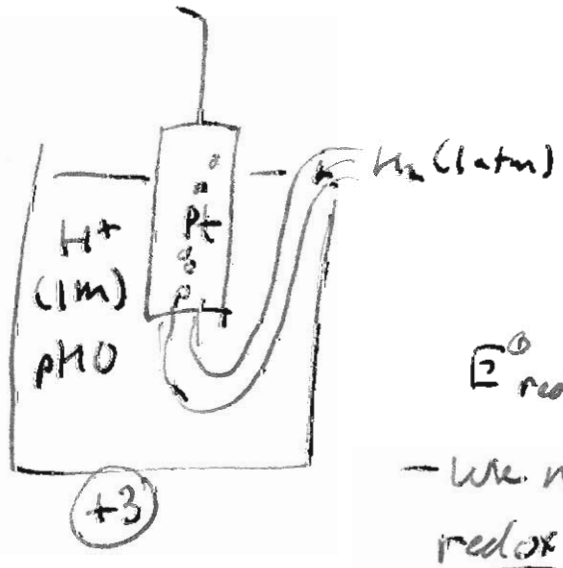
(e; 4 pts) Recharging primary cells is not recommended. Considering the half-reaction for the reduction of ZnO, what undesirable competing reaction could cause problems upon recharging? [Hint: is there something else present that could be reduced?]

$ZnO \rightarrow Zn$ rxn has $E^\circ_{red} = -1.28V$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ has $E^\circ_{red} = -.8V$ — more favorable

(+2) (+2) (+4) Water will be reduced to give H_2 — bad! (value not needed)

(f; 10 pts) (Unrelated) Briefly describe the Standard Hydrogen Electrode and why we need an electrode with an arbitrary reference voltage.



(+3)

The reduction $\frac{1}{2}$ rxn is

(+3) $2H^+(aq) + 2e^- \rightarrow H_2(g)$

But the reaction can go either way without consuming the electrode.

$E^\circ_{red} \equiv 0.000V$, thus $E^\circ_{ox} = 0.000V$ as well

- We need a standard half-cell because redox reactions require an oxidation and a reduction so we can only measure voltage differences.

(+2)

- We reference all the differences to an arbitrary set point

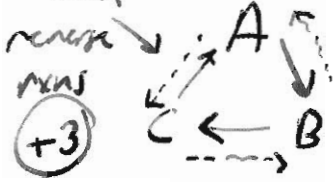
Score for the page_____

3. Metakinetics

(a; 12 pts) Describe the principle of microscopic reversibility. Sketch the connection between microscopic reversibility and the idea that a cyclic reaction cannot proceed unidirectionally without external inputs. If we could violate the principle, what sort of thermodynamically forbidden machine could we build?

(+3) Forward and reverse reactions must traverse the same free energy landscape because at equilibrium (+3) all elementary reactions are balanced.

need reverse rxns (+3)

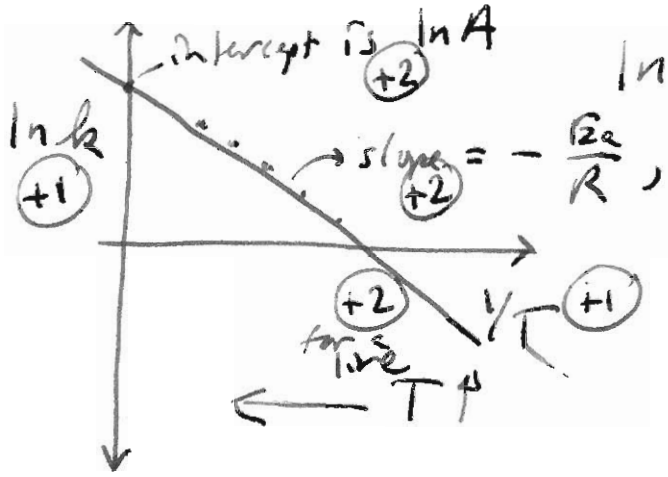


A unidirectional cycle reaction does not have each A↔B, B↔C, and A↔C reaction individually balanced — it cannot work.

We could tap the cycle to make a (+3) perpetual motion machine

(b; 10 pts) Sketch the linear Arrhenius plot and label how one would use it to ~~calculate~~ measure A and Ea.

more space



$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$ (+1)

Ea is always (+) (+1)

Score for the page_____

(c; 4 pts) We have described the Eyring vs. Collision theories for chemical kinetics and shown that they both predict a temperature dependence for the rate constant that agrees with the empirical Arrhenius law, but with different predicted temperature dependences of the preexponential factor, T^1 vs. $T^{1/2}$ vs. T^0 respectively. Why don't the three treatments give us measurably different predictions for the temperature dependence of k?

(+4) - The temperature dependence of the pre-exponential is much weaker than that of the exponential, so we can distinguish it from noise.

not needed — Example: $k = 10^{10} e^{-3000/T} \cdot \{T^{1/2} \text{ vs. } T^{0}\}$ → equal rates at 250 K

For $T = 250$ K $k = 4\times10^{-18}$ · 1 · 1

$T = 350$ K $k = 4\times10^{-13} \times 10^{5}$ · 1.4 · 1.2 · 1] Variation in exponential term dominates, esp for large E_a

(d; 15 pts) Explain why the measured half-life for a second order reaction is not quantitatively useful without more information. Explain why the half-life for a first-order reaction is independent of concentration. Explain why there is no such thing as a truly zero order reaction A → B.

$t_{1/2} = \frac{1}{2k[A]_0}$ for 2nd order reaction –

(+2) The half-life depends on the initial concentration – it actually changes during the measurement. We need to know

(+3) the $[A]_0$ to get the rate constant, which is what's fundamental

$t_{1/2} = \frac{\ln 2}{k}$ for first order – every molecule is an island, so etc. (+4) – lives in a cave,
its properties are independent of the # of neighbors –
the half life depends only on the rate constant

$t_{1/2} = [A]_0/k$ → not needed $-d[A]/dt = k[A]^0$ → no dependence

for A → B the rate must be 0 if there is no A (+3), so at low [A] the rate law must become 1st order or higher in A – it

(+3) looks zero order only when there is a large XS of A over active sites / surface sites etc.

Score for the page 19

4. DNA hybridization

(a; 8 pts) Give two reasons that DNA hybridization has a negative $\Delta S°$.

(+4) - Two separate molecules move together — ↓ translational entropy

(+4) - Each single strand is locked into a more ordered conformation in the duplex - ↓ conformational entropy

— [Some answers about H_2O might be acceptable]

(b; 20 pts) The equation for DNA melting temperature is $T_m = \Delta H°/(\Delta S° + R \ln(C_T/4))$, where the total strand concentration C_T is taken to be 10^{-6} M. Calculate T_m for Oligonucleotide #1 with $\Delta H°_1 = -38$ kcal/mole and $\Delta S°_1 = -85$ cal/mole K. Calculate T_m for Oligonucleotide #2 with $\Delta H°_2 = -52$ kcal/mole and $\Delta S°_2 = -130$ cal/mole K. At what temperature would the melting curves cross, assuming we have normalized out any differences among extinction coefficients and changes in extinction coefficient with temperature? [Hint: What is the relationship between the K_{eq}s when the curves cross?] Sketch the melting curves for oligonucleotides 1 and 2.

$$T_m = \frac{\Delta H°}{\Delta S° + R \ln(C_T/4)}$$

(1) $$T_m = \frac{-38000 \text{ cal/mole}}{-85 \text{ cal/mole K} + 1.987 \text{ cal/mole K} \ln(10^{-6}/4)}$$ (+3)

$$= \frac{-38000}{-85 + 1.987 \cdot (-15.20)} = 330\text{K} = 56.7\,°\text{C}$$ (+2)

(2) $$T_m = \frac{-52000}{-130 + 1.987(-15.20)} = 324\text{K} = 51.4\,°\text{C}$$ (+2)

For curves to cross, K_{eq}s are equal, so $\Delta G°$'s are equal

(+3) $$\Delta G°_1 = \Delta H°_1 - T\Delta S°_1 = \Delta G°_2 = \Delta H°_2 - T\Delta S°_2$$

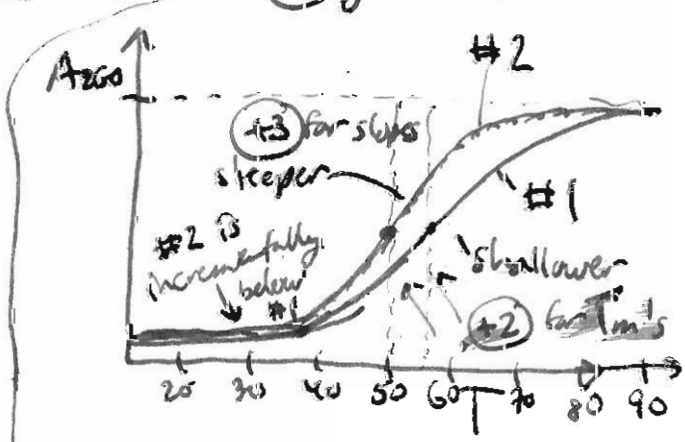
(for reality this is)

$$\Delta H°_1 - \Delta H°_2 = T(\Delta S°_1 - \Delta S°_2)$$

$$T = \frac{\Delta H°_1 - \Delta H°_2}{\Delta S°_1 - \Delta S°_2} = \frac{-38000 + 52000}{-85 + 130}$$

$$= \frac{14000 \text{ cal/mole}}{45 \text{ cal/mole K}} = 311\text{K} = 38\,°\text{C}$$ (+2)

(+3) general appearance



(+3) for slope

(+2) for T_m's

Score for the page_____

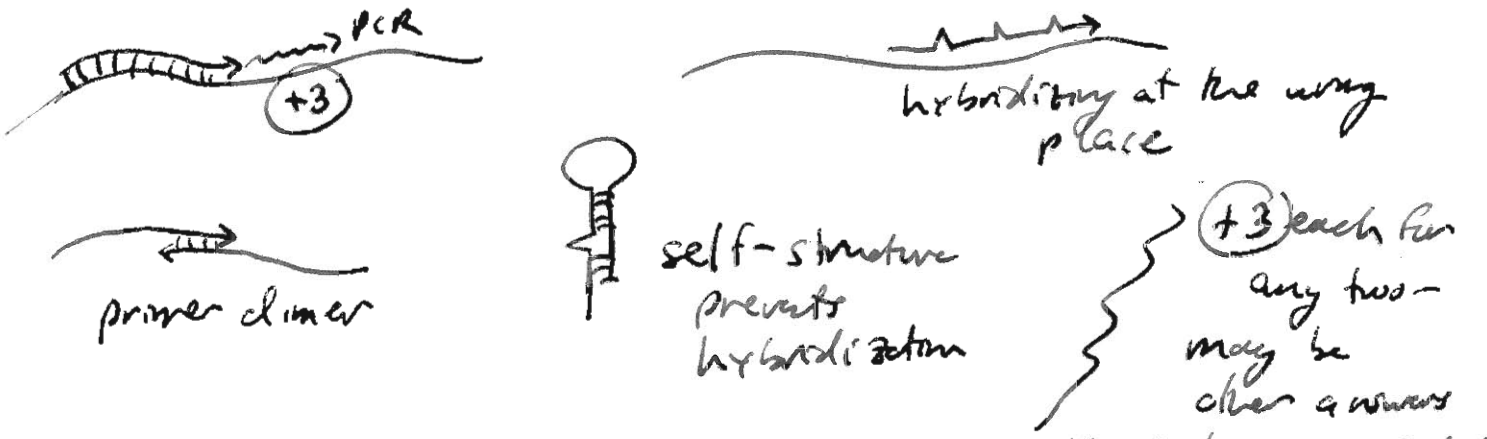
8 pts for curve

(c; 8 pts) Why don't we carry out hybridization reactions either far below or far above the T_m of the desired hybridization?

(+4) - Far below Tm there is no specificity - mismatches are stable

(+4) - Far above Tm there is no signal - nothing is stable.

(d; 9 pts) Sketch the hybridization of a PCR primer to a specific target and sketch two alternative products that could screw up the reaction.



5. Climate change

(a; 6 pts) How does burning fossil fuel to produce CO_2 cause global climate change?

- CO_2 absorbs IR radiated from the earth and re-emits it randomly. (+3) some of it goes back to earth. (+3 for idea of the greenhouse)
- Therefore less IR is emitted to space and the earth warms up. This is the greenhouse effect.

(b; 4 pts) Given that CO_2 emission is bad, the motivation for carbon (= CO_2) capture and sequestration is clear. We already have the technology to liquefy CO_2 under pressure (as in fire extinguishers) and pump it to the bottom of the ocean where it will sit around indefinitely. In terms of thermodynamics, why aren't we already doing this?

(+4) - If it costs more energy to sequester a ton of CO_2 than the energy that we get from producing the CO_2, it's a net waste - more CO_2 is emitted. So the technology is not yet efficient enough.

Score for the page_____

(c; 4 pts) Why does fat have more calories per gram than carbohydrate?

(+4) – more electrons per C-to-C atom
– more efficient packing of C because there's no H_2O with it.
↳ (+2) for only this answer

(d; 8 pts) The fracking boom, whereby natural gas = methane is extracted in copious amounts from previously inaccessible deposits, has caused some degree of schizophrenia among environmentalists. One the one hand, fracking may or may not pollute groundwater and cause earthquakes, which is bad. On the other hand, people say that burning natural gas obtained by fracking buys us time in the race against global warming. How is fracking perhaps buying us time? [Hint: What else do we burn to make electricity?]

(+4) – If we were not burning CH_4, we would still be burning coal to make electricity, so about 2× as much CO_2 would be emitted per kWh.

(+4) – Fracking means that CO_2 emissions are not as large as they would be, so we have more time to create solutions like biofuel / smart grid / wind / nuclear / solar / H_2 that will be sustainable.

(e; 8 pts) Current hydrogen-fueled vehicles may improve air quality in cities, but they don't help with global warming. Why not? What further advance would be needed for them to help reduce CO_2 emission?

(+4) Right now we make H_2 from steam reforming of natural gas or coal + the WGSR → so we are emitting CO_2.

$C + H_2O \longrightarrow CO_2 + H_2$

$CH_4 + O_2 \longrightarrow CO_2 + 2H_2$

(+4) So we would need some way to make H_2 without generating CO_2, like electrolysis of H_2O using nuclear power for electricity.

Page	Score
2	/12
3	/10
4	/16
5	/20
6	/26
7	/22
8	/19
9	/28
10	/27
11	/20
Total	**/200**

Score for the page_____