Combined 22xx and 23xx Key

Chemistry 271 – 22XX **Your Name:** ______________________
Prof. Jason Kahn
University of Maryland, College Park **Your SID #:** ______________________
General Chemistry and Energetics
Final Exam (200 points total) **Your Section # or time:** ______________________

December 18, 2013

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.

Useful Equations:

$K_a = [H^+][A^-]/[HA]$ $pH = -\log([H^+])$ $K_b = [HA][HO^-]/[A^-]$
$K_w = [H^+][HO^-]$ $pH = pK_a + \log [A^-]/[HA]$ $\Delta G° = -RT\ln K_{eq}$
$R = 0.08206$ L·atm/mole K $k_B = 1.38 \times 10^{-23}$ J/K $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$
$\Delta S - q/T \geq 0$ R = 8.314 J/mole K = 1.987 cal/mole K = $N_A k_B$
$S = k_B \ln W$ $\Delta G = \Delta H - T\Delta S$ $\Delta G = \Delta G° + RT\ln Q$

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 $P(v)dv = Cv^2 exp(-mv^2/2kT)$ $E = E° - 2.303(RT/n\mathcal{F})\log_{10}Q$
$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C $\mathcal{F} = 96500$ C(oulomb)/mole
$\Delta G° = -n\mathcal{F}E°_{cell}$ $\ln k = (-E_a/RT) + \ln A$ 1 Volt = 1 Joule/Coulomb
$[A] = [A]_0 - kt$ $\ln[A] = \ln[A]_0 - kt$ $1/[A] = 1/[A]_0 + 2kt$
Standard hydrogen electrode: $2\,H^+ (aq, 1\,M) + 2\,e^- \rightarrow H_2\,(g)$ 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."

— White exams —

1. Short Answer (40 pts)

(a; 6 pts) Photosystem II in plants uses light energy to create a P680$^+$ cation that is a strong enough +2 oxidizing agent to remove electrons from water +2, the product of which is the oxygen +2 that we use to metabolize food we get from plants.

(b; 6 pts) +2 Voltaic or Galvanic electrochemical cells use chemical energy to make electrical energy, whereas electrolytic +2 cells use an external voltage to drive a/an +2 non-spontaneous, uphill ch. chemical change.

(c; 6 pts) Termolecular reactions in the gas phase are found when an inert collision gas is needed to remove energy +2 from a pair of reacting partners that are forming +2 a bond, which is (circle one) an [✓ exothermic]/endothermic process. +2

(d; 6 pts) The Steady State Approximation applies to (circle one) reactants/[✓ intermediates]/products that +2 (circle all correct answers):

+1 (a) accumulate to a high level during a reaction so that we can measure a steady concentration.

+1 [✓ (b)] are highly reactive so that they decay rapidly.

+1 (c) are always present at vanishingly low concentrations.

+1 [✓ (d)] are created and destroyed at the same rate.

(e; 10 pts) True/False

Statement	T/F
Elementary reactions always get faster as temperature increases.	T
Equilibrium constants always increase as temperature increases	F
Rate laws can be written down by inspection if you know the equilibrium constant for a reaction	F
For a reaction A ⇌ B where the molar free energies of A and B differ such that $\overline{G^o_A} < \overline{G^o_B}$, the minimum free energy state is a pure solution of A.	F
The minimum free energy state of the system corresponds to the minimum enthalpy state of the universe.	F

(f; 6 pts) An oxidizing agent with a standard reduction potential more positive than that of O_2 is +3 thermodynamically unstable in the standard state because it will oxidize water to give O_2

A reducing agent with E_{ox} more positive than that of H_2 is thermodynamically unstable because it will reduce protons to give H_2 +3

Score for the page______________

1. Short Answer (40 pts)

(a; 6 pts) Photosystem I in plants uses light energy to create a P700* excited state that is a strong enough reducing agent (+2) to donate electrons (via intermediates) to $NADP^+$ (+1), which gives NADPH (+1), which in turn ends up reducing CO_2 (+2) to make carbohydrates that we eat.

(b; 6 pts) Termolecular reactions in the gas phase are found when an inert collision gas is needed to remove energy (+2) from a pair of reacting partners that are forming (+2) a bond, which is (circle one) an [✓ exothermic]/endothermic process. +2

(c; 6 pts) Electrolytic (+2) electrochemical cells use an external voltage to drive a/an (+2) uphill / unfavorable / nonspontaneous chemical change, whereas galvanic or voltaic (+2) cells use chemical energy to make electrical energy.

(d; 6 pts) The Steady State Approximation applies to (circle one) reactants/[✓ intermediates]/products that (circle all correct answers): +2

+1 [✓ (a)] are highly reactive so that they decay rapidly.

+1 (b) accumulate to a high level during a reaction so that we can measure a steady concentration.

+1 [✓ (c)] are created and destroyed at the same rate.

+1 (d) are always present at vanishingly low concentrations.

(e; 6 pts) An oxidizing agent with a standard reduction potential in water more positive than that of O_2 is thermodynamically unstable in the standard state because it will oxidize water to make O_2 (+3)
A reducing agent with E_{ox} more positive than that of H_2 is thermodynamically unstable because it will reduce H^+ to make H_2 (+3)

(f; 10 pts) True/False

Statement	T/F	
Elementary reactions always get slower as temperature decreases.	F	+2
Rate laws cannot be written down by inspection unless you know the reaction is elementary.	T	+2
Equilibrium constants always increase as temperature increases	F	+2
The minimum free energy state of the system corresponds to the minimum enthalpy state of the universe.	F	+2
For a reaction A ⇌ B where the molar free energies of A and B differ such that $\overline{G^o}_A < \overline{G^o}_B$, the minimum free energy state is a pure solution of A.	F	+2

Score for the page____________

= white

2. Explanations (45 pts)

(a; 15 pts) Derive the Nernst equation using some of the equations on the front of the exam (equations that aren't the Nernst equation!). Conceptually explain why the sign must be negative in the Nernst equation.

(+3) $\Delta G = \Delta G^0 + RT \ln Q$

(+3) $\Delta G^\circ = -nFE^\circ_{cell}$

$\Delta G = -nFE_{cell}$

$-nFE_{cell} = -nFE^0_{cell} + RT \ln Q$

(+3) $E_{cell} = E^0_{cell} - \frac{RT}{nF} \cdot 2.303 \log_{10} Q$

$\frac{2.303\,RT}{F} = 0.0592\,V$ at 25 C

(+3) $E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log_{10} Q$

(+3) As Q ↑, reactn becomes less favorable, so voltage drops - less energy per e^-.

(b; 15 pts) Briefly explain how increasing CO_2 levels in the atmosphere cause global warming, and mention one way in which society could attempt to return the atmosphere to 350 ppm.

(+5) - ~~CO_2~~ Visible light goes through the atmosphere and warms the earth, which gives off infrared radiation

(+5) - CO_2 absorbs IR and then re-emits it back down, warming the earth

(+5) - Hybrid cars, ↑ nuclear energy, CO_2 sequestration, global collapse of all air travel, biofuels, solar/wind/geothermal etc.

Score for the page____________

—Yellow—

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(b; 15 pts) Derive the Nernst equation using some of the equations on the front of the exam (equations that aren't the Nernst equation!). Conceptually explain why the sign must be negative in the Nernst equation.

(+3) $$\Delta G = \Delta G^\circ + RT \ln Q$$

(+3) $$\Delta G^\circ = -nFE^\circ_{cell}$$
$$\Delta G = -nFE_{cell}$$

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln Q$$

(+3) $$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \cdot 2.303 \log_{10} Q$$

$$\frac{2.303\,RT}{F} = 0.0592\,V \text{ at } 25\,C$$

(+3) $$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log_{10} Q$$

(+3) As Q ↑, reaction becomes less favorable, so voltage drops - less energy per e^-.

Score for the page____________

White and Yellow exams are the same.

(15 pts) Explain why DNA hybridization reactions are typically carried out not far below the melting temperature of the desired double-stranded DNA product. In your answer, define the DNA melting temperature, mention mismatch thermodynamics, and speculate on hybridization kinetics.

(+3) The melting temperature is T at which half of the DNA is in ss form and half is ds.

— The reaction is done near Tm to minimize the (+4) amount of mismatched/undesired hybridization, which is thermodynamically less stable ~~but~~ and ∴ melts at lower than Tm (perfect match). Can't go above Tm because signal goes away (+4)

— Also, the kinetics of hybridization are faster at high T — (+4) [mostly because marginally stable mismatches break up faster]

3. Electrochemistry and thermodynamics (55 pts)

There are several parts to this problem. They can frequently be answered even if you have not completed earlier parts.

Hydrogen peroxide, H_2O_2, is a moderately strong oxidizing agent. A H_2O_2 in aqueous solution is unstable, eventually decaying to give water and O_2 as follows:

$$H_2O_2\ (aq) \rightarrow H_2O\ (l) + O_2\ (g)\ \ \text{[not balanced]}$$

(a; 15 pts) Given the standard reduction potentials below, calculate E°_{cell} for the reaction above in acidic solution, and give the balanced equation for the overall reaction.

$H_2O_2\ (aq) + 2\ H^+\ (aq) + \underline{2}\ e^- \rightarrow 2\ H_2O\ (l)$ $E^\circ_{red} = 1.76$ V

$O_2\ (g) + 4\ H^+\ (aq) + \underline{4}\ e^- \rightarrow 2\ H_2O\ (l)$ $E^\circ_{red} = 1.23$ V

(+3) $2H_2O_2 + \cancel{4H^+} + \cancel{4e^-} \rightarrow 4H_2O$ $E^\circ_{red} = 1.76V$

(+3) [$2H_2O \rightarrow O_2 + \cancel{4H^+} + \cancel{4e^-}$ $E^\circ_{ox} = -1.23V$

$2H_2O_2 \rightarrow 2H_2O + O_2$ (+3) $E^\circ_{cell} = 1.76-1.23V = 0.53V$ (+3) (+3)

Score for the page______________

- White exam -

(b; 10 pts) Without doing a calculation, give $E^{\circ\prime}_{cell}$ = the potential at pH 7 and also E°_{cell} under basic conditions, and explain your reasoning.

(+3) $E^{\circ\prime}_{cell} = E^{\circ}_{cell}$ (basic conditions) $= E^{\circ}_{cell}$ (acidic) $= 0.53\,V$ (+3)

(+4) The overall reaction does not take up or liberate protons or hydroxide so the ΔG° and therefore E°_{cell} is independent of pH

(c; 30 pts) Calculate the standard state free energy change ΔG° for the H_2O_2 decay reaction under acidic conditions, at 298 K. Calculate the equilibrium constant for the reaction at 298 K. What would the concentration of H_2O_2 be at equilibrium with the air at $PO_2 = 0.21$ atm? Why is a measurement of E°_{cell} a better way to measure this K_{eq} than attempting to measure the K_{eq} directly? Speculate on the sign of ΔS°. Does this tell you whether the equilibrium constant will go up or down as temperature increases?

(+2) $\Delta G^{\circ} = -nFE^{\circ}_{cell}$

(+3) $\Delta G^{\circ} = -4 \cdot 96500 \frac{\text{Coulombs}}{\text{mole}} \cdot 0.53 \frac{\text{Joules}}{\text{Coulomb}} = \underline{-204600\ \text{J/mole}}$

(+2) $K_{eq} = e^{-\Delta G^{\circ}/RT}$

(+3) $K_{eq} = e^{+204600\,\text{J/mole}/(8.314\,\text{J/mole K} \cdot 298\,K)} = \underline{7.26 \times 10^{35}}$

(+3) $K_{eq} = \frac{P_{O_2} \cdot [H_2O]^2 \rightarrow 1}{[H_2O_2]^2} = \frac{0.21}{[H_2O_2]^2}$

(+3) $[H_2O_2] = \sqrt{\frac{0.21}{7.26 \times 10^{35}}} = \sqrt{2.89 \times 10^{-37}} = \underline{5.38 \times 10^{-19}}\ M$

(+4) It would be extremely hard to measure 10^{-19} M - it would be about 30000 molecules in 20 ml. Much easier to measure a voltage.

(+3) ΔS° is probably positive because a molecule of gas (+2) is generated. But this does not tell us the sign of ΔH° (it's negative), so we don't know (+3) whether (+2) K_{eq} will increase or decrease.

Score for the page_____________

(b; 10 pts) Without doing a calculation, give E°'$_{cell}$ = the potential at pH 7 and also E°$_{cell}$ under basic conditions, and explain your reasoning.

(+3) $E^{o\prime}_{cell} = E^{o}_{cell}$ (basic condition) (+3) $= E^{o}_{cell}$ (acidic) $= 0.53V$

(+4) The overall reaction does not have protons or hydroxide as a reactant or product, so E_{cell} is independent of pH.

$$2H_2O_2 \rightleftharpoons 2H_2O + O_2$$

(c; 30 pts) Calculate the standard state free energy change ΔG° for the H_2O_2 decay reaction under acidic conditions, at 298 K. Calculate the equilibrium constant for the reaction at 298 K. What would the concentration of H_2O_2 be at equilibrium with oxygen at PO_2 = 0.65 atm? Why is a measurement of E°$_{cell}$ a better way to measure this K_{eq} than attempting to measure the K_{eq} directly? Speculate on the sign of ΔS°. Does this tell you whether the equilibrium constant will go up or down as temperature increases?

(+2) $\Delta G^o = -nFE^o_{cell} = -4 \cdot 96500 \frac{\text{Coulombs}}{\text{mole}} \cdot 0.53 \frac{\text{Joules}}{\text{Coulombs}}$

(+3) $\Delta G^o = -204600$ Joules/mole

$K_{eq} \overset{(+2)}{=} e^{-\Delta G^o/RT} = e^{+204600/8.314 \cdot 298} = \cancel{1.38 \times 10^{36}}$ (+3) 7.26×10^{35}

or 55M okay, though wrong

$K_{eq} = \frac{P_{O_2} \cdot [H_2O]^2}{[H_2O_2]^2}$ (+3) $= \frac{0.65}{[H_2O_2]^2} = \cancel{1.38 \times 10^{36}}\ 7.26 \times 10^{35}$

$[H_2O_2] = \sqrt{\frac{0.65}{7.26 \times 10^{35}}} = 9.46 \times 10^{-19}$ M (+3)

(+4) Such an infinitesimal concentration cannot be measured accurately, so it is much better to measure the voltage.

ΔS° is probably positive (+3) ~~(+4)~~ since gas (+2) is produced, but that (+2) ~~(+3)~~ doesn't tell you whether it is exothermic or not (it is), so no info on T-dependence of K. (+3)

Score for the page__________

White

4. Kinetics and Mechanism (60 pts)

The uncatalyzed breakdown of H_2O_2 is difficult to study, because the reaction is catalyzed in a wide variety of ways. The uncatalyzed reaction in the gas phase at high temperature is believed to occur through a series of steps, with the first step being a rate limiting unimolecular homolytic cleavage to give hydroxyl radical:

$H_2O_2\,(g) \rightarrow 2\,HO\bullet\,(g)$ r.l.s.
$HO\bullet\,(g) + H_2O_2\,(g) \rightarrow H_2O\,(g) + HO_2\bullet$ fast
⋮

(a; 10 pts) Give the expected observed rate law for the breakdown of H_2O_2. Also, explain how it is possible to ask you to do this even though I have not shown the rest of the mechanism.

$$\text{Rate} \equiv \underbrace{-\frac{1}{2}}_{\text{OK to omit}}\frac{d[H_2O_2]}{dt} = k_1\,[H_2O_2]$$

(+3) for any rate law
(+3) for correct

(+4) Since step 1 is rate-limiting, all subsequent steps are kinetically invisible, except rate could be multiplied by a constant if the later rapid steps destroy more H_2O_2.

(b; 15 pts) The observed rate constant for this reaction has a preexponential factor of $10^{13}\ s^{-1}$ and an activation energy of 201000 J/mole. Calculate the rate constant at 400 °C and at 100 °C. What would the half-life be at 100°C for H_2O_2 at a concentration of 0.010 M?

(+3) Arrhenius rate law –

$\ln k = -E_a/RT + \ln A$ so $k = Ae^{-E_a/RT}$

(+3) $k = \underset{\substack{\downarrow \\ \text{k unit rxn is first order}}}{10^{+13}\ s^{-1}}\ e^{-(201000\ J/mole)/(8.314\cdot\underbrace{(400+273.15)}_{K})} = 10^{+13}\ s^{-1}\ e^{-35.91}$

$= \underline{2.53 \times 10^{-3}\ s^{-1}}$

(+3) At 100°C $k = 10^{13}\ e^{-201000/(8.314\cdot\overset{373}{\cancel{338}})}$ ~~$= 10^{13}\ e^{-60.74} = 4.16\times10^{-14}\ s^{-1}$~~

$= 10^{13}\cdot e^{-64.81} = \underline{7.10\times10^{-16}}$

(+3) $t_{1/2} = \ln 2/k$ for 1st order

$= \dfrac{0.693}{\cancel{4.16\times10^{-14}}\ 7.10\times10^{-16}} = \cancel{1.67\times10^{13}}$ sec (+3) 9.76×10^{14} $\equiv$ ~~4~~ 30,000,000 years

4. Kinetics and Mechanism (60 pts)

The uncatalyzed breakdown of H_2O_2 is difficult to study, because the reaction is catalyzed in a wide variety of ways. The uncatalyzed reaction in the gas phase at high temperature is believed to occur through a series of steps, with the first step being a rate limiting unimolecular homolytic cleavage to give hydroxyl radical:

$$k_1 \quad H_2O_2\,(g) \rightarrow 2\,HO\bullet\,(g) \qquad \text{r.l.s.}$$
$$HO\bullet\,(g) + H_2O_2\,(g) \rightarrow H_2O\,(g) + HO_2\bullet \qquad \text{fast}$$
$$\vdots$$

(a; 10 pts) Give the expected observed rate law for the breakdown of H_2O_2. Also, explain how it is possible to ask you to do this even though I have not shown the rest of the mechanism.

$$\text{Rate} = -\frac{1}{2}\cdot\frac{d[H_2O_2]}{dt} = k_1[H_2O_2]$$

(+3) for any rate law
(+3) for correct
) don't need the "½"

If the first step is rate-limiting, none of the subsequent (+4) steps matter to the rate. [Although it could be n·k₁ if the products lead to decay of n molecules of H₂O₂]

(b; 15 pts) The observed rate constant for this reaction has a preexponential factor of 10^{13} s^{-1} and an activation energy of 201000 J/mole. Calculate the rate constant at 500 °C and at 125 °C. What would the half-life be at 125 °C for H_2O_2 at a concentration of 0.020 M?

(+3) Arrhenius rate law: $\ln k = \ln A - \frac{E_a}{RT}$ or $k = Ae^{-E_a/RT}$

(+3) $k = 10^{13}\,s^{-1} \cdot e^{(-201000\,J/mole)/(8.314\,J/mole\,K \cdot 773\,K)}$

(+3) $= 10^{13}\,s^{-1}\,e^{-31.27} = 0.263\,s^{-1}$ @ 500°C

↳ hint that it's first order!

(+3) $= 10^{13}\,s^{-1}\,e^{-201000/(8.314 \cdot 398\,K)} = e^{-60.74} = 4.16 \times 10^{-14}\,s^{-1}$ at 398 K

(+3) $t_{1/2} = \ln 2/k$ for first order

$= 0.693/4.16 \times 10^{-14} = 1.6\cancel{7} \times 10^{13}\,s \approx 5 \times 10^{5}$ years (+3)

– $[H_2O_2]$ is irrelevant –

white and yellow same

You can buy hydrogen peroxide in aqueous solution, and it is reasonably stable on storage. However, there are many ways to catalyze the disproportionation. One example is the reaction with bromide ion under acidic conditions given by the proposed mechanism (= series of elementary reactions) below. The multiple arrows in the third step indicate fast steps that are kinetically invisible after an elementary S_N2 attack on HOBr (hypobromous acid) by H_2O_2.

$$H_2O_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3O_2^+ \qquad \text{fast equilibrium}$$

$$H_3O_2^+ + Br^- \xrightarrow{k_2'} HOBr + H_2O \qquad \text{slow}$$

$$HOBr + H_2O_2 \xrightarrow{k_3} \rightarrow\rightarrow H_2O + H^+ + Br^- + O_2 \qquad \text{fast}$$

(c; 4 pts) Write down the rate of appearance of O_2 just according to the third line of the mechanism above. To move further we will need the concentration of the reactive intermediate HOBr.

(+4) $$\frac{d[O_2]}{dt} = k_3 [HOBr][H_2O_2]$$

(d; 8 pts) Write down the expression for the rate of change of [HOBr] based on the 2nd and 3rd lines, and set the rate of change equal to zero (the SSA). Calculate the concentration of [HOBr]. Now you need to know the concentration of $H_3O_2^+$.

$$\frac{d[HOBr]}{dt} = \underbrace{k_2 [H_3O_2^+][Br^-] - k_3[HOBr][H_2O_2]}_{(+3)} \overset{\text{SSA}}{=} 0 \quad (+2)$$

$$[HOBr] = \frac{k_2 [H_3O_2^+][Br^-]}{k_3 [H_2O_2]} \quad (+3)$$

Score for the page____________

white and yellow are the same

(e; 6 pts) Calculate $[H_3O_2^+]$ in terms of $[H_2O_2]$ and $[H^+]$ from the first line of the mechanism, assuming that $H_3O_2^+$ and H_2O_2 are in rapid equilibrium. Based on your knowledge of chemistry, why is this a reasonable assumption?

(+3) $K_{eq} = \frac{k_1}{k_{-1}} = \frac{[H_3O_2^+]}{[H_2O_2][H^+]}$ so $\underline{[H_3O_2^+] = \frac{k_1}{k_{-1}} [H_2O_2][H^+]}$ (+2)

- ~~Acid-base~~ Protonation/deprotonation is the fastest chemical reaction (+2)

(f; 7 pts) Write down the overall differential rate law for the production of O_2 according to the mechanism given. Briefly, how could you test experimentally whether this rate law is correct? [You can answer the second part even if you didn't get the rate law].

$$\frac{d[O_2]}{dt} = k_3 [HOBr][H_2O_2]$$

(+2) for any attempt at substitution

$$= \cancel{k_3} \cdot \frac{k_2 [Br^-]}{\cancel{k_3 [H_2O_2]}} \cdot \frac{k_1}{k_{-1}} [H_2O_2][H^+] \cdot \cancel{[H_2O_2]}$$

$$\frac{d[O_2]}{dt} = \frac{k_2 k_1}{k_{-1}} [Br^-][H_2O_2][H^+]$$ (+2)

Reality check - k_3 doesn't matter ✓
same as rapid pre-eq. result ✓

[- Do the reaction at different $[Br^-]$, $[H_2O_2]$, and/or $[H^+]$ and measure initial rates

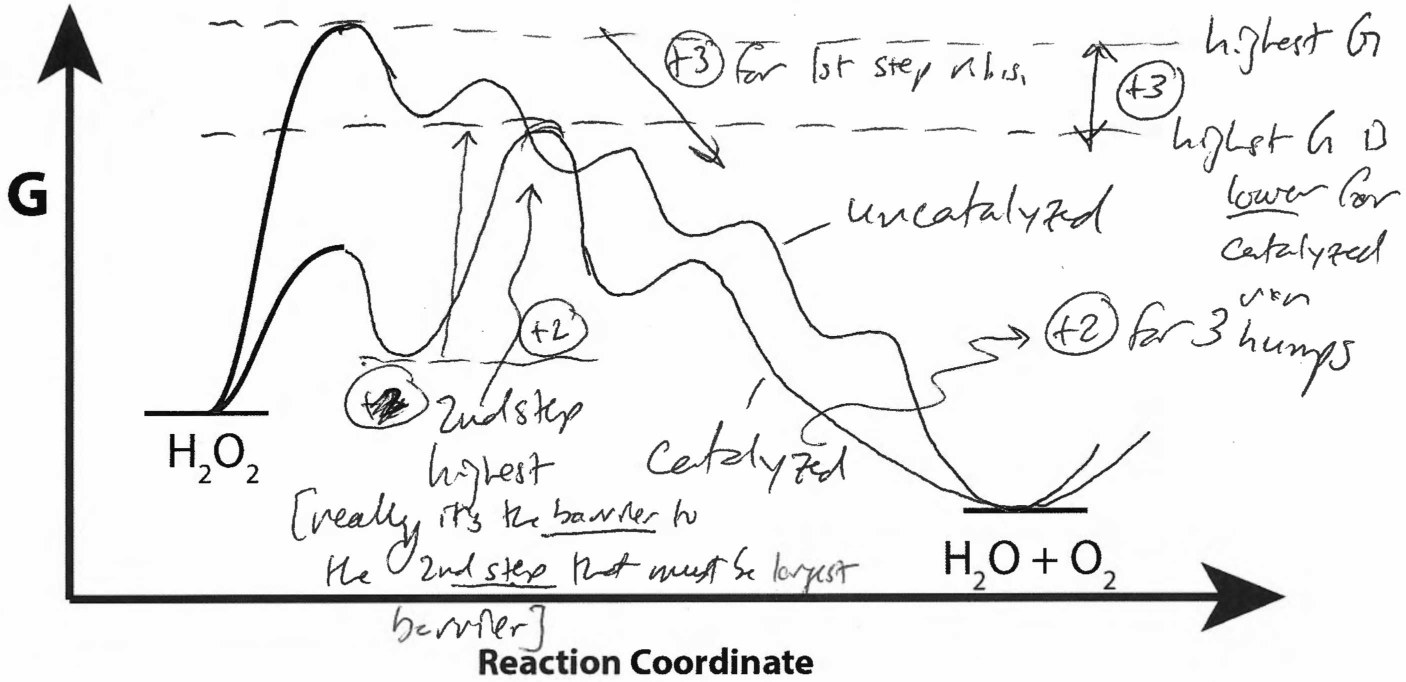
(+3) for either

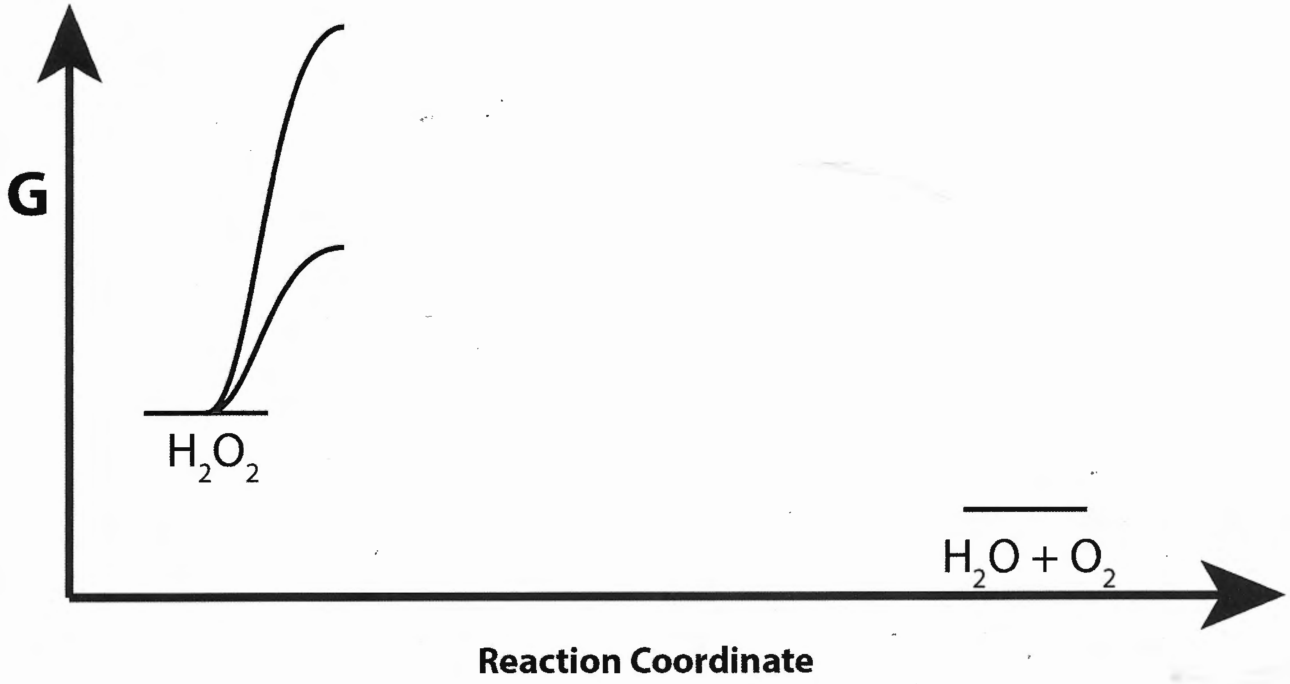
- Curve-fitting to time course of reaction]

Score for the page___________

white (= yellow)

(g; 10 pts) Finally, complete the free energy reaction coordinate diagram comparing the uncatalyzed reaction (with its slow and rate-limiting first step) and the Br⁻-catalyzed reaction. The graph is repeated in case you want to clean up your diagram. Indicate which one you want graded.





Score for the page____________

Extra work space. If you give an answer on this page make sure you write a clear note in the body of the exam telling us to look here.

Page	**Score**
2	/40
3	/30
4	/30
5	/40
6	/25
7	/12
8	/13
9	/10
Total	**/200**

Score for the page_____________