Chemistry 271
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University of Maryland, College Park
General Chemistry and Energetics
Final Exam (200 points total)

Your Name: Key

Your SID #:

Your Section # or time:

May 14, 2012

N=176

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:

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

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

$R = 0.08206$ 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

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

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:

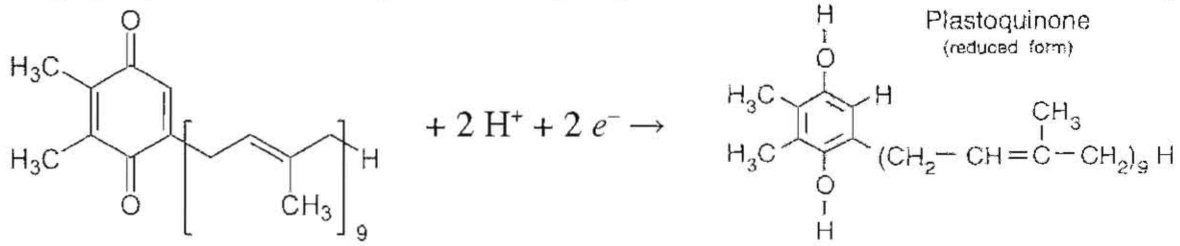
"I pledge on my honor that I have not given or received any unauthorized assistance on this examiuatiou."

1. Short Answer (27 pts)

(a; 3 pts) One word to explain why it is that sometimes the electrochemical reaction that one observes is not the one that one would think should be thermodynamically favorable: Over potential (+3)
(kinetics – (+2))

(b; 6 pts) Eyring (transition state) theory and the Maxwell-Boltzmann distribution both predict a similar functional form for the temperature dependence of the rate constant. The resulting (name of Swedish physical chemist here Arrhenius (+3)) equation is: $\ln k = \ln A - E_a/RT$ (+3) or any variant

(c; 8 pts) The excited state chlorophyll chromophore (P680*) of Photosystem II is a reasonably strong reducing agent, able to reduce a quinone to a hydroquinone via intermediates we will not worry about:



What is the function of the reduced form of the plastoquinone (= hydroquinone)? What is the function of the P680⁺ cation that is the other reaction product?

– The plastoquinone supplies electrons ~~to~~ that eventually re-reduce (+2) oxidized PSI. (+2)

– The P680+ cation oxidizes (+2) water (+2) via the manganese complex.

(d; 6 pts) How does increased CO_2 in the atmosphere lead to global warmiug?

(+3) CO_2 absorbs infra-red radiation emitted by the earth.

(+3) It re-emits the IR in a random direction, so half of it goes toward the earth and heats it.

(e; 4 pts) Why is burning natural gas (CH_4) less bad than burning even the cleanest coal (C) in terms of global warming?

(+2)
CH_4 provides more electrons per carbon atom, so provides more useful energy per molecule of CO_2 sent into the atmosphere (+2)

Score for the page 27/27

2. Electrochemistry (60 pts)

(a; 13 pts) If you hook up the two half cells below, what balanced spontaneous (voltaic) redox reaction occurs? What would you see visually as the reaction proceeded? Calculate E°_{cell}. What balanced electrolytic reaction would occur if you added in a battery that forces electrons in the opposite direction?

Half cell #1: Ag (*s*) electrode / 1 M $Ag^+(aq)$ with 1 M inert spectator anion NO_3^-
Half cell #2: Ni (*s*) electrode / 1 M $Ni^{2+}(aq)$ with 2 M inert spectator anion Cl^-

Reduction potentials:

$Ag^+(aq) + 1\,e^- \rightarrow Ag(s)$ $E^\circ_{red} = 0.80$ V
$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$ $E^\circ_{red} = -0.23$ V

[+2 if not balanced]

(+4) Spontaneous: $Ni(s) + 2\,Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2\,Ag(s)$ $n=2$

(+3) The Ni electrode would dissolve, and the Ag electrode would thicken.

(+3) $E^\circ_{cell} = 0.80 + 0.23 = 1.03$ V

(+3) Electrolytic reaction: $Ni^{+2}(aq) + 2\,Ag(s) \rightarrow 2Ag^+(aq) + Ni(s)$
(+1 if not balanced)

(b; 14 pts) Write down balanced half-reactions for (1) the reduction of protons to give dihydrogen (H_2), and (2) the oxidation of water to give dioxygen (O_2) in acidic solution. We talked about leveling in the context of acid-base chemistry, the idea that no acid stronger than hydronium is stable in water, and no base stronger than hydroxide is stable in water. What is the corresponding idea for electrochemistry in aqueous solution?

$H^+ + e^- \rightarrow H_2 \Rightarrow 2H^+ + 2e^- \rightarrow H_2$ (1) (+4)

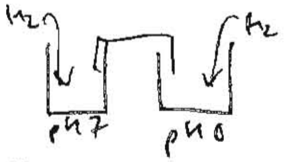
$\underset{2}{}H_2O \rightarrow O_2 \underset{+4H^+ +4e^-}{} \Rightarrow 2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ (2) (+4)

(+3) – Any reducing agent stronger than H_2 (i.e. anything on the RHS of the table and below H_2) will give H_2 in water eventually. [This depends on pH – as pH ↑, proton reduction requires a stronger reducing agent]. So strong reducing agents are unstable in H_2O.

(+3) – Any oxidizing agent stronger than oxygen can oxidize water to give O_2. So strong oxidizing agents are unstable in H_2O.

Score for the page_______ /27

(c: 8 pts) Calculate $E^{\circ\prime}_{red}(H^+)$, i.e. the cell voltage that one would observe for the standard hydrogen electrode (SHE) operated at the biochemical standard state pH 7 instead of pH 0, coupled to a SHE run at the usual chemical standard state.



net rxn

$2H^+(pH7) + H_2(SHE) \rightarrow 2H^+(pH0) + H_2(SHE)$

this is the non-spontaneous direction

(+3 for recognizing the rxn)

$2H^+ + 2e^- \rightarrow H_2$ at pH 7

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

$$= 0 - \frac{0.0592}{2}\log_{10}\left(\frac{[H^+]^2_{SHE}}{[H^+]^2_{pH 7}}\cdot\frac{1\,atm}{1\,atm}\right) \quad (+3)$$

$$= 0 - 0.0296\log_{10}\left(\frac{1}{(10^{-7})^2}\right)$$

$$= 0 - 0.0296\cdot 14 = \underline{-0.414V} \quad (+2)$$

(d; 20 pts) The reduction of mercuric oxide (HgO) is the basis of the mercuric oxide battery, coupled with Zn oxidation to give zinc hydroxide, all under basic conditions.. The battery was banned due to toxicity concerns.

Reduction potentials:

$HgO\ (s) + H_2O\ (l) + 2\ e^- \rightarrow Hg\ (l) + 2\ OH^-\ (aq)$ $E^\circ_{red} = 0.098$ V

$Zn(OH)_2\ (s) + 2\ e^- \rightarrow Zn\ (s) + 2\ OH^-(aq)$ $E^\circ_{red} = -1.249$ V

Write the balanced voltaic redox reaction. Calculate E°_{cell}. Calculate the standard state free energy change per mole of HgO and the equilibrium constant for the reaction. Calculate E_{cell} at pH 8.5 but otherwise standard conditions.

$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$ $E^\circ_{ox} = +1.249V$

$HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$ $E^\circ_{red} = 0.098V$

(+4) $\underline{Zn(s) + HgO(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Hg(l)}$ $\underline{E^\circ_{cell} = 1.347V}$ (+4)

$$\Delta G^\circ = -nFE^\circ_{cell} \ (+2) = -\overset{moles}{2}\cdot 96500\frac{Coulomb}{mole}\cdot 1.347\frac{Joules}{C} = \underline{-2.60\times10^5\frac{J}{mol}} \ (+2)$$

$$K_{eq} = e^{-\Delta G^\circ/RT} \ (+2) = e^{+260000/(8.314\times298)} = e^{105} = \underline{3.72\times10^{45}} \ (+2)$$

$$E_{cell} = 1.347V + \frac{0.0592}{2}\log_{10}(\underset{\substack{\shortparallel\\1}}{Q}) = \underline{1.347V} \ (+4)$$

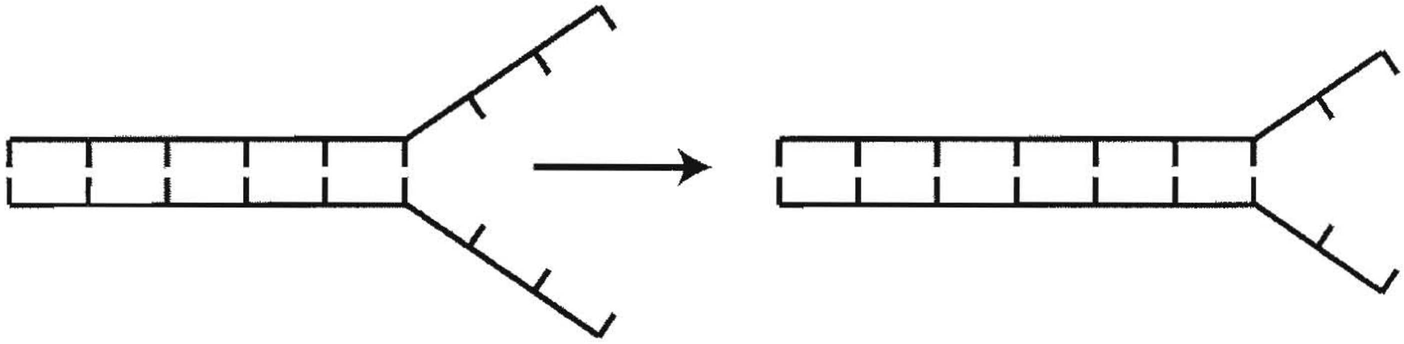
Score for the page ________ /28

(e; 5 pts) In a battery it is often desirable for both the reactants and the products to be solids (in the mercuric oxide battery the HgO/Hg is embedded in graphite for safety and conductivity). Give a reason having to do with voltage.

or any reason why V is constant ← (+2) (+3)

If reactants and products are solids, Q = 1 so voltage remains constant until the battery is exhausted (that's why the HgO/Zn cell was popular for photography)

3. DNA Thermodynamics (24 pts)



(a; 8 pts) The enthalpy change for formation of a base pair in DNA, as in the sketch above, is negative. Why? The entropy change is also negative. Why?

(+4) – $\Delta H < 0$ because stacking + H-bond interactions are forming.

(+4) – $\Delta S < 0$ because conformational freedom of the base pairs is reduced

(b; 6 pts) The free energy turns out to be negative for temperatures below about 95 °C. How can DNA ever melt at temperatures below 95 °C, i.e. what important entropy consideration must also be considered? Why do shorter DNA molecules melt at lower temperatures than longer molecules?

$\Delta G^\circ = \Delta G^\circ(\text{base pairs}) + \Delta G^\circ(\text{initiation})$

↳ the additional entropy cost of bringing ~~the~~ two molecules together is ⊕, so even if $\Delta G^\circ(bp) < 0$, the total ΔG° can be ⊕ (+3)

(+3) – Shorter DNA's have fewer base pairs – less negative $\Delta G^\circ(bp)$ to balance the ⊕ $\Delta G_{\text{initiation}}$

Score for the page /19

(c; 5 pts) Longer PCR primers hybridize more tightly to their target sequences. Why don't we always just make PCR primers as long as we can in order to make the reaction work better?

(+3) - mismatches will also be stabilized also, leading to unwanted hybridization

(+2) → increasing stability comes at the cost of specificity

for either

(d; 5 pts) Give an opinion and very brief reasoning on whether a future pre-natal test that predicts a child's IQ should be available to prospective parents. Assume that the test actually works (whether IQ means anything is a separate issue that we are not concerned with here).

(+1) for a yes or no

(+4) for any thoughtful comment along the lines of

- yes, information wants to be free or
- no, this invites eugenics, which is evil

4. Kinetics (60 pts)

Nitric oxide reacts with hydrogen at elevated temperature according to the following chemical equation (from Oxtoby):

$$2\,NO\,(g) + 2\,H_2\,(g) \rightarrow N_2\,(g) + 2\,H_2O\,(g)$$

(a; 8 pts) It is observed that when the concentration of H_2 is cut in half, the reaction rate is also cut in half. What is the order of the reaction with respect to H_2? When the concentration of NO is increased by a factor of 5, the reaction rate increases by a factor of 25. What is the order of reaction with respect to NO? Write down the differential rate law.

(+2) $\text{Rate} \propto [H_2]^1 \rightarrow \frac{1}{2}\cdot$ [illegible] $[H_2] \rightarrow \left(\frac{1}{2}\right)^1 \text{rate}$

(+2) $\text{Rate} \propto [NO]^2 \rightarrow 5\times [NO] \rightarrow (5)^2 \times \text{rate}$

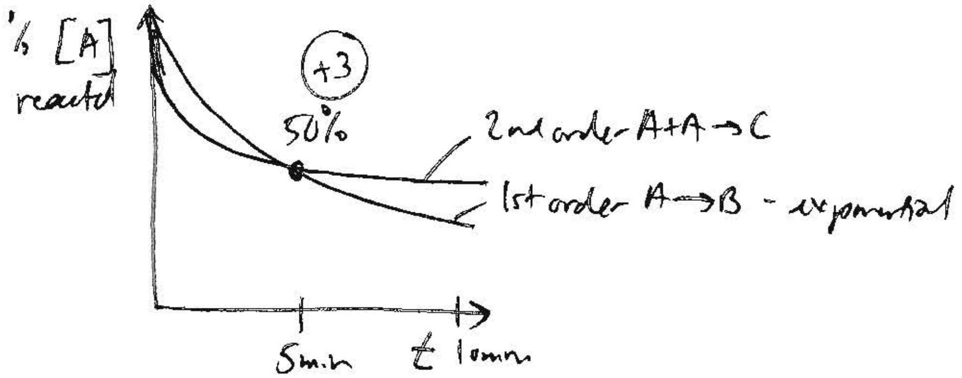
$$\text{Rate} = \underbrace{-\frac{1}{2}\frac{d[NO]}{dt}}_{\text{(+2) for any of the four possibilities}} = \underbrace{k[NO]^2[H_2]}_{(+2)}$$

(b; 7 pts) How does the observed rate law tell us that the NO + H_2 reaction cannot possibly be proceeding through a single elementary step under these conditions? Why would we have guessed *a priori* that this reaction would be very unlikely to be elementary?

- If it were elementary, the rate law would be $k[NO]^2[H_2]^2$, which is not consistent w/ experiment (+2) (+2)

- The reaction as written would be tetramolecular (+2) – these are extremely rare (+1) vs. uni/bi/termolecular reactions (+3)

(c; 20 pts) Sketch the concentration of reactant A as a function of time for the elementary reactions A → B and A + A → C, on one graph, assuming that each reaction has a half-life of 5 minutes. It might be hard to tell the curves apart experimentally. What experiment could you do to determine whether the reaction was first-order or second-order? Sketch the expected result for the concentration of A as a function of time for your proposed experiment.



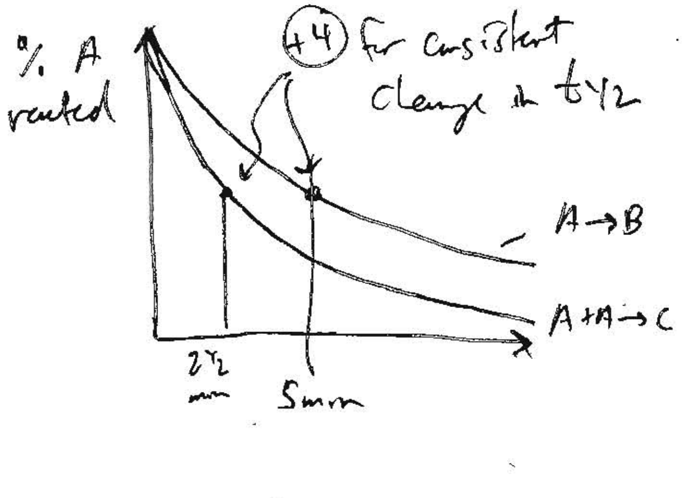
(+3) for idea of curved plots

(+3) for 2nd order being faster at first

- Do a second experiment at double the concentration of $[A]_0$ (+4)

$$\frac{1}{[A]} = \frac{1}{[A_0]} + 2kt \rightarrow t_{1/2} = \frac{1}{2k[A_0]}$$ should ~~get 2x as fast~~ decrease by 2x

(+4) for consistent change in $t_{1/2}$



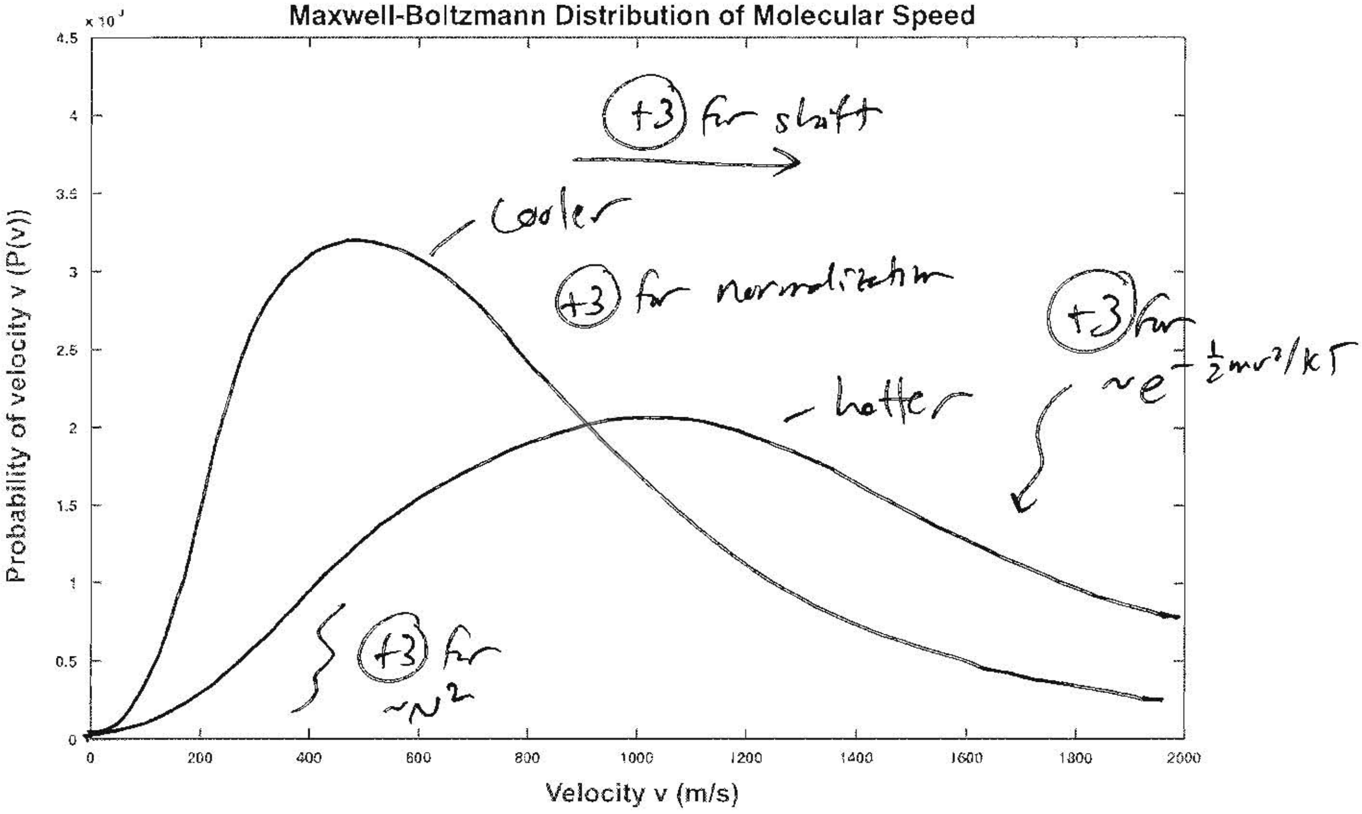
(+3) for idea that 2nd-order curve shifts

Score for the page ____ /27

(d; 7 pts) Explain why the half-life of a zero-order reaction is proportional to reactant concentration. Don't explicate the equation: give a physical rationale.

- Zero order reactions are typically catalyzed at (+2) surfaces - as long as the reactant is in large excess, so that it saturates the surface, the (+2) actual concentration doesn't ~~matter~~ affect the rate - (+3) so process of 2x more reactant takes 2x more time

(e; 18 pts) On the axes below, sketch the Maxwell-Boltzmann distribution for the speed of gas molecules at two different temperatures (for the same gas). Identify which is the hotter and which is the cooler temperature. Explain the shape of the curve (why it goes up, why it goes down).



(+3) for shift

(+3) for normalization

(+3) for $\sim e^{-\frac{1}{2}mv^2/kT}$

(+3) for $\sim v^2$

(+3) - Curve goes up due to degeneracy - $4\pi v^2$ ways to have velocity v

(+3) - Curve goes down because of the Boltzmann distribution - $P(E) \propto e^{-E/kT}$

Score for the page_______ /25

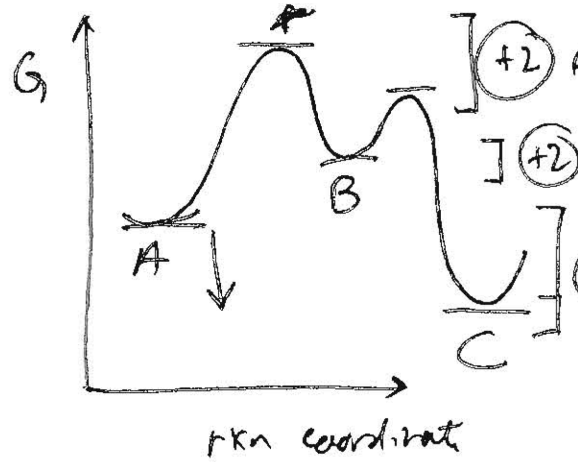
5. Free energy reaction coordinate diagrams (29 pts)

Draw and label free energy reaction coordinate diagrams for the following situations:

(a; 7 pts) A converts to intermediate B slowly, and then B converts to C more rapidly than it (B) goes back to A, and the final product C is more stable than A.

$A \underset{slow}{\rightleftarrows} B \xrightarrow{fast} C$ downhill overall

(+1) for idea



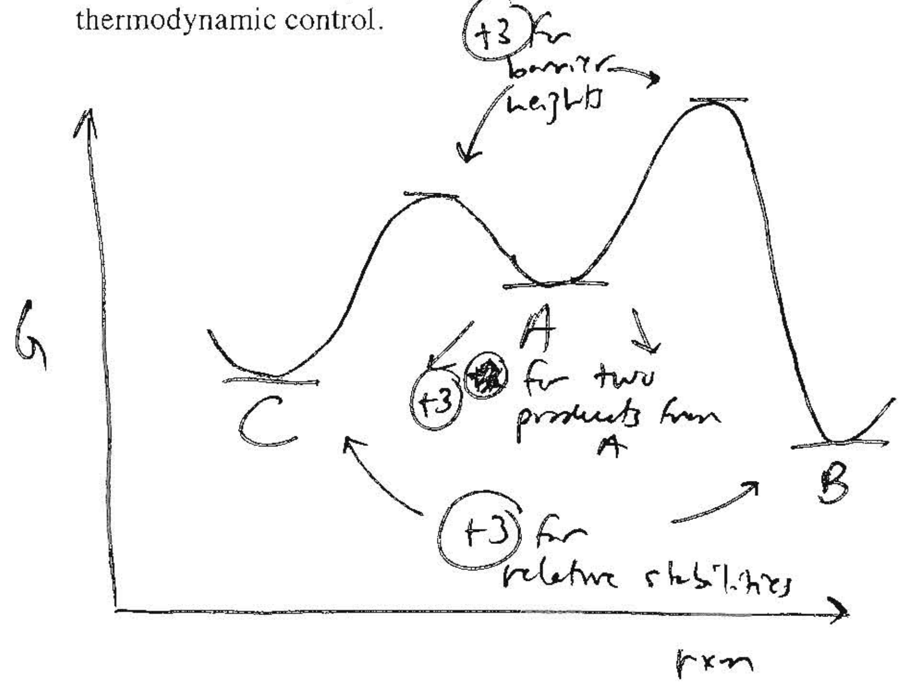
(+2) for first step r.l.s.

(+2) for B above A and C

(+2) for downhill

(b; 10 pts) Reactant A can convert to either B or C, both of which are thermodyuamically more stable than A. B is thermodynamically more stable than C, but C forms faster than B. This is kinetic vs. thermodynamic control.

(+1) for any diagram

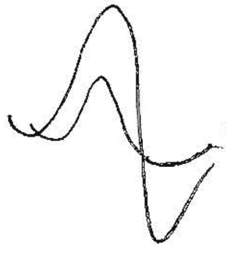


(+3) for barrier height

(+3) for two products from A

(+3) for relative stabilities

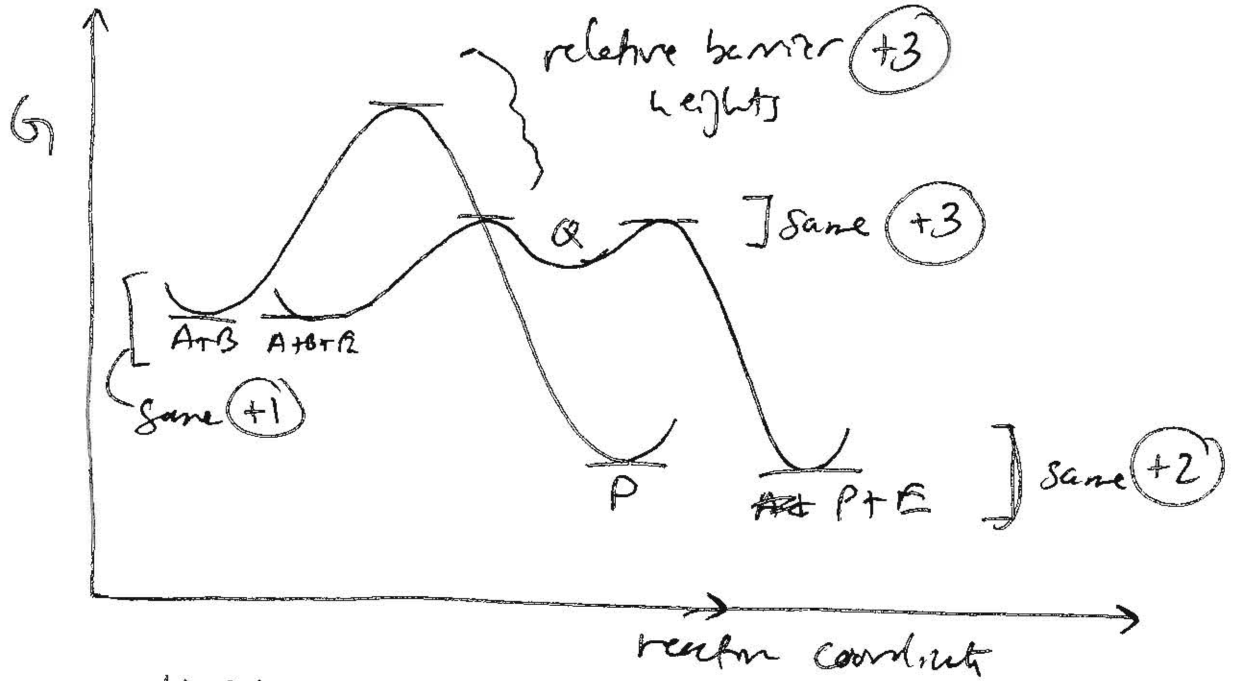
or



OK

Score for the page ____ / 17

(c; 12 pts) A+B converts to P in one slow step. On the same diagram, with the free energy of A+B+E set equal to A+B, A+B+E converts to intermediate Q much more rapidly than A+B -> P, and Q converts to P+E at the same rate with which it goes back to A+B+E. What do we call E?



"E" = enzyme or catalyst (+3)

Page	Score
2	/27
3	/27
4	/28
5	/19
6	/18
7	/27
8	/25
9	/17
10	/12
Total	**/200**

Score for the page_____ /12