Chemistry 271, Section 23xx **University of Maryland, College Park**
General Chemistry and Energetics **Prof. Jason Kahn**
Final Exam (200 points total) **December 14, 2010**

You have 120 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

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."

Your Name: KEY

Your SID #:

Viewing: Friday, December 17, 11-2 Chemistry 1110-1111

Useful Equations:

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

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

$S = k\ln W$

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

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

$PV = nRT$

$K_a = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}]$

$n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$

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

$°\mathrm{C} = °\mathrm{K} - 273.15$

$R = 8.314$ J/mole K

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

$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C

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

Standard hydrogen electrode: $2\,\mathrm{H}^+(aq, 1\,\mathrm{M}) + 2\,e^- \rightarrow \mathrm{H}_2\,(g)$ $E^\circ = 0.000$ V

$\ln K_{eq} = -\Delta H^\circ/RT + \Delta S^\circ/R$

$\ln k = (-E_a/RT) + \ln A$

1 Volt = 1 Joule/Coulomb

$[\mathrm{A}] = [\mathrm{A}]_0 - kt$

$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$

$1/[\mathrm{A}] = 1/[\mathrm{A}]_0 + 2kt$

$P(v)dv = Cv^2\exp(-mv^2/2kT)$

$dS = (c_p/T)\,dT$

$c_p = q_p/dT = dH/dT$

1. Multiple Choice (24 pts)

(i, 4 pts) The Third Law of Thermodynamics gives us a reference state of zero entropy. What else is necessary for measuring absolute entropies of pure substances at non-zero temperature?

- (a) The First Law of Thermodynamics.
- [✓ (b)] Measurements of heat capacity as a function of temperature.
- (c) Calculation of the free energy of formation from tabulated data.
- (d) Enumeration of microstates.
- (e) We cannot measure absolute entropy, only changes in entropy.

(ii; 4 pts) A second-order rate constant

- (a) has units of time^{-1}.
- (b) changes during the course of the reaction as the reactant is depleted.
- (c) can almost never be faster than diffusion-controlled.
- (d) has units of $M^{-1}s^{-1}$.
- [✓ (e)] (c) and (d).

(iii, 4 pts) The Steady State Approximation

- (a) is not useful in enzyme kinetics because substrate concentration is constantly changing.
- (b) can be applied only to reactions of the type $A \rightarrow B \rightarrow C$.
- (c) holds only at equilibrium, when the state of the system is steady.
- [✓ (d)] includes rapid pre-equilibrium as a special case.
- (e) is applicable to the product of any rapid reaction.

4 pts each

(iv; 4 pts) The half life $t_{1/2}$ of a second order reaction $A+A \rightarrow B$

- (a) $= (\ln 2)/k$
- (b) $= 1/\{k([A]_0)^2\}$
- (c) $= [A]_0/k$
- (d) is always shorter than the half life of a first-order reaction.
- [✓ (e)] none of the above

(v, 4 pts) The function of Photosystem I in plants is to

- [✓ (a)] use light energy to reduce NADP$^+$ to NADPH.
- (b) collect light energy and deliver it to Photosystem II.
- (c) oxidize water to provide light.
- (d) re-reduce the reaction center of Photosystem II.
- (e) reduce water to maintain a basic pH.

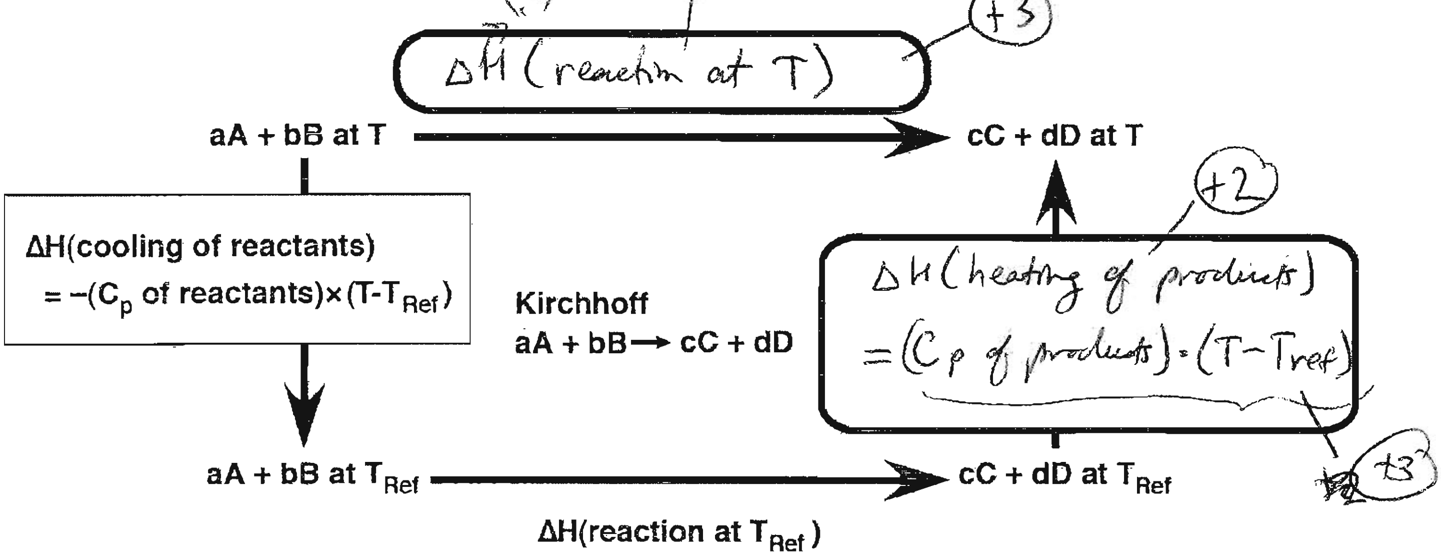
(vi, 4 pts) Assimilation is defined as

- (a) using a substance as a terminal electron acceptor and making no further use of the product.
- [✓ (b)] converting (typically through reduction) inorganic material into biomass.
- (c) nitrogen fixation and all other processes that split diatomic molecules.
- (d) absorption of enemies by an oppressive regime.
- (e) none of the above.

Score for the page____________

2. Heat Capacity (20 pts)

(a; 12 pts) Fill in the boxes in the Kirchhoff cycle below that illustrates why a change in heat capacity (ΔCp) in going from reactants to products implies a temperature-dependent value for the ΔH of the reaction. Derive the expression for ΔH at temperature $T > T_{ref}$ given that we know ΔH at T_{ref} and the relevant heat capacities. 1.5 1.5



$$\left.\begin{aligned}\Delta H(\text{reaction at } T) = &-(\text{Cp of reactants})\cdot(T-T_{ref})\\ &+\Delta H(\text{reaction at } T_{ref})\\ &+(\text{Cp of products})\cdot(T-T_{ref})\end{aligned}\right]$$ (+3)

$$\Delta H(\text{reaction at } T) = \Delta H(\text{reaction at } T_{ref}) + \underbrace{\Delta Cp}_{(+1)}(T-T_{ref})$$

(b; 8 pts) In the example we gave in discussion of calculating the equilibrium constant of the Haber process as a function of temperature, the calculated K_{eq} using the full heat capacity treatment was actually quite close to the K_{eq} calculated with constant $\Delta H°$ and $\Delta S°$, even though the $\Delta H°$ changed substantially. Qualitatively, how is this possible?

(+2) together supporting eqns

$$\left\{\begin{aligned}\Delta G = -RT\ln K_{eq} = \Delta H° - T\Delta S°\\ \ln K_{eq} = -\underbrace{\frac{\Delta H°}{RT}}_{} + \underbrace{\frac{\Delta S°}{R}}_{}\end{aligned}\right\}$$

(+2) for idea that $\Delta H°$ and $\Delta S°$ have same sign + therefore opposing effects

(+3) for idea that they change in the same direction

$\Delta H°$ and $\Delta S°$ both ~~in~~decrease with T (get more ⊖) if $\Delta Cp < 0$.

(+3) And therefore the effects on ΔG and K_{eq} tend to cancel.

Score for the page__________

3. Photosynthesis and atmospheric chemistry (40 pts)

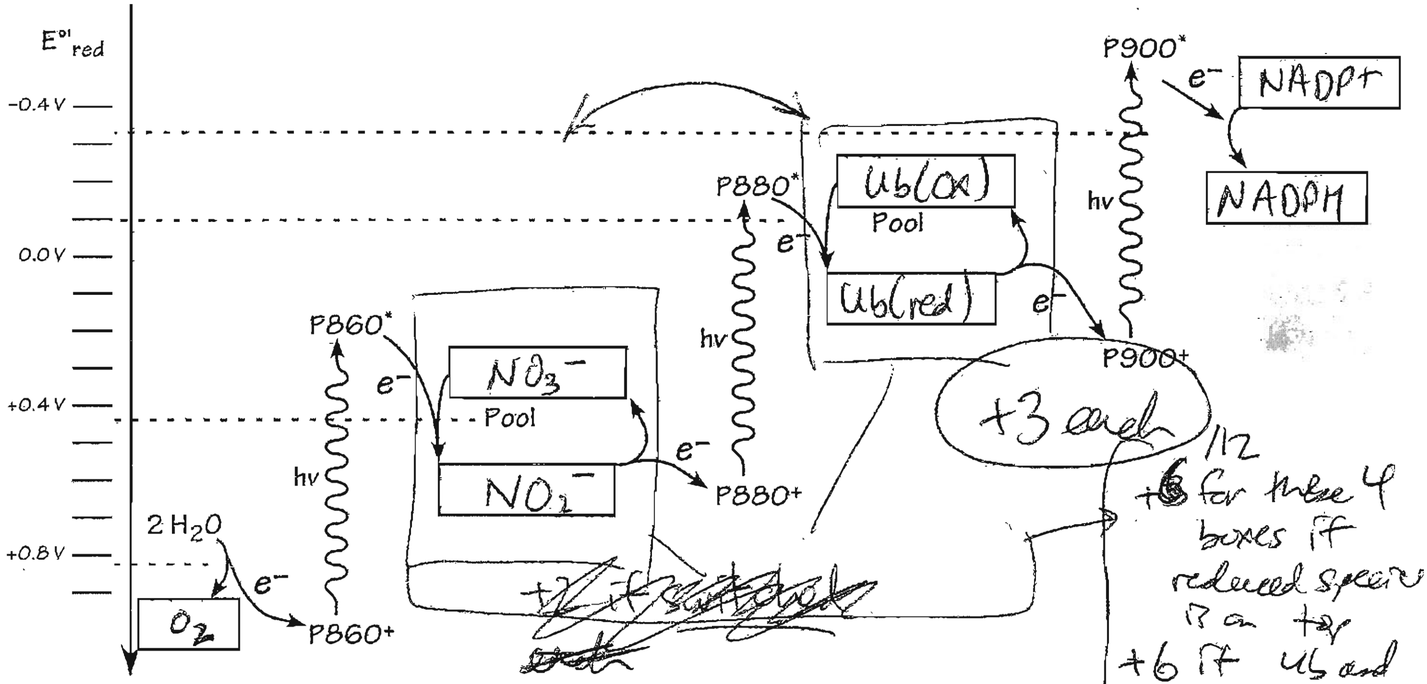
(a; 21 pts) Imagine a world orbiting a star that emits in the infra-red region of the spectrum. The plants on this world are found to have three photosystems (P860, P880, and P900) rather than two. P860 oxidizes water and P900 reduces NADP⁺ to NADPH as on Earth. The two intermediate electron pools are nitrate/nitrite and ubiquinone/ubiquinol, with standard reduction potentials at the biochemical standard state shown below. Complete the "ZZ" scheme below by entering each one of the underlined species below in one box in the diagram.

$\underline{O_2} + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$ $E^{\circ\prime} = 0.815$ V

$\underline{NO_3^-} + 2\,e^- + 2\,H^+ \rightarrow \underline{NO_2^-} + H_2O$ $E^{\circ\prime} = 0.43$ V

$\underline{\text{UbiQ}}\text{ (ox)} + 2\,e^- + 2\,H^+ \rightarrow \underline{\text{UbiQ}}\text{ (red)}$ $E^{\circ\prime} = 0.10$ V

$\underline{NADP^+} + 2\,e^- + 2\,H^+ \rightarrow \underline{NADPH}$ $E^{\circ\prime} = -0.315$ V



+6 for these 4 boxes if reduced species is on top
+6 if Ub and NO3 are switched

(b; 6 pts) Why do these plants need three photosystems to do what our plants do with two?

+3

+3 for idea IR has less energy

- The IR photons have less energy, and the energy difference between the ground state and excited state sets a limit on the difference in reduction potential. $\Delta G = \frac{hc}{\lambda} = nFE^\circ$

+3 for idea that redox potential change costs free energy

- It requires 3x photon energy to move the electron from $O_2 \rightarrow$ NADPH

Score for the page__________

(c; 4 pts) Two possible failure pathways for photosynthesis are fluorescence, if the electron is not transferred away from the excited state fast enough, or charge recombination, if the electron is not removed from the immediate vicinity fast enough.

(d; 9 pts) How does increased atmospheric CO2 cause global warming?

CO_2 allows visible light from the sun to reach the earth.

(+3) [The visible light is re-radiated as heat, or infra-red (IR).

(+3) [CO_2 absorbs some of the IR and re-radiates it ~~bac~~ randomly, so some of it goes back towards the earth.

The net effect is that less IR is emitted from the earth, and conservation of energy tells us that the earth will warm up. (+3)

4. Kinetics and Thermodynamics (45 pts)

(a; 7 pts) The Maxwell-Boltzmann distribution and Arrhenius equation state that the rate of an elementary reaction always increases with increasing temperature. So how is it possible for the equilibrium constant of a ~~reaction A ⇌~~ B to decrease as temperature increases? Would the reaction be (circle one) [✓ exothermic] or endothermic?

(+2)

A → B gets faster

But so does B → A! (+3) for just this]

(+2) ↗ this statement is +5 by itself

If B → A gets faster faster, $K_{eq} = \frac{k_f}{k_r}$ gets smaller.

If K_{eq} gets smaller as T ↑, rxn must be exothermic by Le Chatelier.

Score for the page____________

3 pts each

(b; 24 pts) Fill in the blanks. A catalyst can change the rate (or rate constant) and/or the mechanism (or pathway) of a reaction but not its equilibrium constant.

The underlined "v^2" factor in the Maxwell-Boltzmann distribution $C\underline{v^2}(\exp(-mv^2/2kT))$ arises because of the ω(ε) factor in the Boltzmann distribution, the degeneracy ~~microstates~~ ~~configuration~~ which is the number of ways in which a particle can have energy ε. The underlined v^2 comes from the surface area ~~volume~~ of a sphere of radius v.

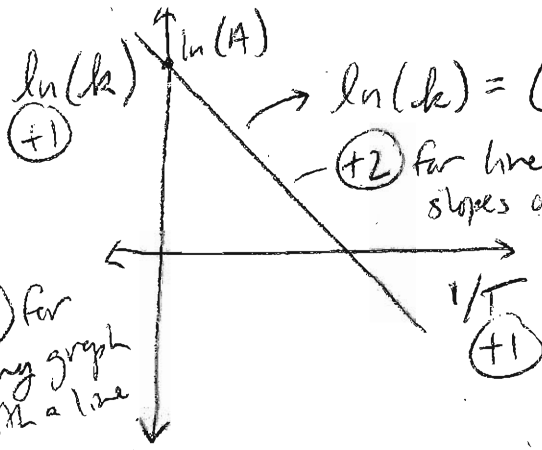
A rate law can be determined by inspection only for a(n) elementary reaction.

The "2" in S_N2 comes from the fact that it's a second order reaction.

two molecules involved

(c; 8 pts) Sketch the Arrhenius plot used to measure activation energy E_a and the preexponential factor A. Label the axes. What is the molecular meaning of Ea according to collision theory for gas phase reactions?

⑤



(+1) for any graph with a line

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

No collide

(+2) for line that slopes down

(+3) − Ea is the energy needed to reach the transition state, or the energy needed for the reaction to occur, provided from kinetic energy of gas.

(d; 6 pts) In discussing gas-phase reactions we frequently discussed the need for a collision gas M to catalyze either dissociation or recombination reactions. It is easy to understand that the collision gas can deliver energy to break apart molecules (think of any parking lot). Why is the collision gas needed to allow atoms/molecules to recombine?

~~For~~ For example, in $I + I + Ar \rightarrow I_2 + Ar$, bond formation is exothermic, ~~so the energy~~ : if the energy liberated is not taken away somehow, the atoms will fall apart again. "M" ~~removes~~ removes the energy liberated, by departing faster than it arrived.

(+3)

(+3)

→ for any mention of why energy needs to be taken away

Score for the page________

5. Kinetics and the Steady State Approximation (35 pts)

Leucine zipper proteins (Z) are monomeric in solution by themselves but they bind to DNA (D) as dimers, with the overall reaction being

$$Z + Z + D \overset{K_{bind}}{\rightleftharpoons} Z_2D$$

There has been debate about the reaction mechanism. One possibility is that a monomer Z must dimerize to form an unstable intermediate Z_2 that either readily falls apart or else binds to DNA. The proposed mechanism is as follows, where we ignore the reverse of the second step (this is reasonable if the complex is very stable):

$$Z + Z \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Z_2$$

$$Z_2 + D \xrightarrow{k_2} Z_2D$$

(a; 5 pts) Write down the differential rate law for the appearance of Z_2D. It includes the unknown $[Z_2]$.

$$\underbrace{\frac{d[Z_2D]}{dt}}_{(+1)} = \underbrace{k_2[Z_2][D]}_{(+4)}$$

Common mistake:

$$\frac{d[Z_2D]}{dt} = k_1[Z]^2 - k_{-1}[\cancel{Z}] - k_2[Z_2][D]$$

(b; 12 pts) Apply the Steady State Approximation to the unstable Z_2 intermediate to determine its steady state concentration during the binding reaction.

$$\underbrace{\frac{d[Z_2]}{dt}}_{(+1)} = \text{synthesis} - \text{breakdown}$$

$$= \overbrace{k_1[Z]^2 - k_{-1}[Z_2] - k_2[Z_2][D]}^{} = 0$$

(+2) for each term → +6
signs must be right

↳ with or without ½ B doing

↑ SSA (+3)

$$[Z_2] = \frac{k_1[Z]^2}{k_{-1} + k_2[D]} \Big\} (+2)$$

Score for the page_______

(c; 4 pts) Substitute your answer for (b) into your answer for (a) to get the rate of production of Z_2D.

$$\frac{d[Z_2D]}{dt} = \underset{\uparrow}{k_2[Z_2][D]} = \frac{k_1k_2[Z]^2[D]}{k_{-1}+k_2[D]} \quad (+3)$$

idea of substitution (+1)

(d; 5 pts) If the Z_2 intermediate is so unstable that it almost always falls apart rather than binding a molecule of D, then the differential rate equation reduces to the expression below. We can also rationalize the form of the rate law below based on the idea that the Z_2 intermediate becomes kinetically irrelevant if it never accumulates or goes on to product: What form would you expect for an overall binding reaction with no intermediates?

$$\frac{d[Z_2D]}{dt} = (k_2(k_1/k_{-1}))[Z]^2[D] \longrightarrow \text{“}k_3\text{”}$$

(+3) A tertiary elementary reaction of Z and D would be very unusual but it would look like

$$\frac{d[Z_2D]}{dt} = k_3[Z]^2[D]$$ as ~~done~~ given above (+2)

(e; 9 pts) From your answer to (c), what is the reaction order with respect to D if the binding of Z_2 dimer to DNA is fast and the DNA is at high concentration? Physically, explain this initially surprising result.

$$\frac{d[Z_2D]}{dt} \approx \frac{k_1k_2[Z]^2[D]}{k_2[D]}$$

$$= k_1[Z]^2$$

if k_2 is large and [D] is large so (+3) ($k_2[D] >> k_{-1}$

zero-order with respect to D (+3)

(+3) (The instant Z_2 forms it reacts with excess [D], so as long as $[D] >> [Z_2]$ the r.l.s. is formation of Z_2, and the concentration of [D] doesn't matter.

Score for the page__________

4. Miscellaneous Electrochemistry (36 pts)

A couple of years ago "Blood Falls" in Antarctica had its 15 minutes of fame. Organisms in an anoxic (no O_2) lake under a glacier live by transferring electrons from organic carbon that was buried with them to Fe^{+3} mobilized when the glacier scrapes rust ($Fe_2O_3/Fe(OH)_3$) from rocks, reducing the ferric iron to Fe^{+2}. The "blood" in Blood Falls comes about because every once in a while the glacier moves and squozes out some of the contents of the under-ice lake, and when the dissolved Fe^{+2} hits the air and re-oxidizes.

We will take ethanol as a model for reduced organic carbon food, although presumably being buried in the dark for two million years has made these microbes into a pretty sober bunch.

Some E°′ values:

Acetaldehyde reduction: E°′ = −0.197 V

Acetate reduction to acetaldehyde: E°′ = −0.581 V

Reduction of ferric iron: E° = +0.770 V

Reduction of O_2: $O_2 + 4\,e^- + 4\,H^+ \rightarrow 2\,H_2O$ E°′ = +0.815 V (pH 7)

(a; 12 pts) Write the two half-reactions and the overall balanced chemical reaction for the oxidation of CH_3CH_2OH to CH3CHO (acetaldehyde) and the reduction of Fe^{+3} to Fe^{+2} and determine "*n*." Calculate E°′ for this reaction.

+3 +4

$$CH_3CH_2OH \longrightarrow CH_3CHO + 2H^+ + 2e^- \qquad E^{\circ\prime}_{\text{ox}} = +0.197V$$

$$2(Fe^{+3} + e^- \longrightarrow Fe^{+2}.) \qquad E^{\circ}_{\text{red}} = 0.770V \quad +1$$

+1

$$CH_3CH_2OH + 2Fe^{+3} \longrightarrow CH_3CHO + 2H^+ + 2Fe^{+2} \qquad E^{\circ\prime} = 0.967V$$

$$n = 2 \quad +2$$

+2

+1

MANT USE
-.581

(b; 5 pts) Based on the Nernst equation, explain why, for a typical battery, the voltage does not drop substantially until the battery is nearly entirely dead.

(+2) $$E = E^{\circ} - \frac{0.0592V}{n} \log Q$$

(+3) If $E^{\circ} \sim 1.5V$ and $n = 2$ $E = 1.5 - 0.03 \log Q$

so Q must be 10^5 to make even a 10% difference in E

Score for the page__________

(c; 9 pts) When the lead-acid storage battery is recharged by the alternator of the car, the reduction half- reaction is $PbSO_4(s) + H^+(aq) + 2e^- \rightarrow Pb(s) + HSO_4^-(aq)$ $E^o_{red} = -0.356$ V

We usually just accept this, but on second thought it is surprising that it works given that protons are present in the reaction. What redox reaction, which occurs in the standard hydrogen electrode, might be expected to occur instead of the reduction of $PbSO_4$, and why? (The overpotential (+3) explains why the other redox reactions do not occur readily: for complicated reasons, it requires a much higher voltage to actually get them to go. This is one reason that platinum, the metal used for the SHE electrode, is not used in car batteries. Another reason is that a pound of platinum would cost about as much as the rest of the car.)

(+3) $2H^+ + 2e^- \rightarrow H_2$ $E^0_{red} = 0.000V$

(+3) This reaction is much more favorable than the reduction of $PbSO_4$.

(d; 10 pts) Fill in the blanks. Strong reductants are found at the bottom right (+2) of the typical table of standard reduction potentials (+2)

↳ no credit for "bottom" or "right"

Fat is a denser store of energy than carbohydrate because it has more (+2) electrons (or H) per carbon.

The pH of the biochemical standard state is 7 (+2) whereas the pH of the chemical standard state can be either 0 (+1) or 14 (+1) depending on the reaction in question.

Page	Score
2	/24
3	/20
4	/27
5	/20
6	/38
7	/17
8	/18
9	/17
10	/19
Total	**/200**

Score for the page ____________