Thermodynamics, pH and Buffers Homework Chem 331 Biochemistry Spring 2022

Name _____ (_____ / 80 points)

For each question show all calculations and simply describe the process. Use complete sentences, bullets or outlines will NOT be accepted. For formula weights, pKa, Ka or other information needed for the problem, start with your book then look for other sources.

1) **(10 pts)** We know that for glycolysis, the bulk of the reactions are reversible. Refer to the information on the link to the Scientific American reading to answer what how the mostly reversible reactions glycolysis in terms of ΔG' and how does this relate to the statement "we hum along smoothly, beneficiaries of a 3 kcal/mol energy window…"?

2) **(10 pts)** Consider the following metabolic reaction important in muscle and nerve cells:

ATP + creatine → phosphocreatine + ADP $\Delta G^{\circ\prime} = +12.6$ kJ/mol

Under intracellular conditions, the Δ*G* for the reaction, which is catalyzed by the enzyme creatine kinase, is ~0 kJ/mol. Which of the following statements is correct?

INDICATE why each of the other answers are incorrect.

- creatine kinase is an unusual enzyme, as it is able to catalyze an endergonic reaction.

- ATP has a greater phosphoryl group transfer potential compared to phosphocreatine.

- at equilibrium, most intracellular creatine is phosphorylated.

- the reaction operates close to equilibrium in cells.

3) Malate Dehydrogenase catalyzes the following reaction in liver mitochondria:

$$\text{Malate} + NAD^+ \rightarrow \text{Oxaloacetate} + NADH + H^+$$

Consider the free energy changes for the following reactions:

Malate $\rightarrow$ Oxaloacetate + 2e-	$\Delta G^{\circ\prime}$ = 249 kJ/mol
$NADH + H^+ \rightarrow NAD^+ + 2H^+ + 2e^-$	$\Delta G^{\circ\prime}$ = 220 kJ/mol

What is the $\Delta G^{\circ\prime}$ for the following coupled reaction: (Show your work) **(5 pts)**

Measured malate in mitochondria is 0.20 mM, NAD+ 1.0 mM and NADH 0.01 mM. oxaloacetate = 1x10-7M (ignore the H+ for this problem)…

What is the Keq for the reaction? **(2 pts)**

What is the ΔG for the reaction? **(3 pts)**

MDH is crucial for mitochondrial function. Using the calculations you've conducted, would you expect for a mitochondria and its host cell to survive using the standard state free energy? **(5 pts)**

What happens to allow cells to function? What reaction is coupled to MDH to allow this physiological condition to exist? **(5 pts)**

4) **(10 pts)** The free energy change ($\Delta G'$) for the oxidation of the cellulose molecules in a sheet of paper into CO_2 and H_2O is large and negative (the = $\Delta G^{o'}$ – 2833 kJ/mol). Explain why paper is stable at room temperature in the presence of oxygen (O_2) because:

5) **(5 points)** Calculate the pH of a 0.5 L solution containing 50 mM sodium phosphate dibasic acid and 70 mM sodium phosphate monobasic before and after adding 1ml of 0.01M NaOH. How much would the pH have changed if the NaOH were added to 1 liter of pure water?

6) **(5 points)** Draw the structure **and** net charge of aspartate for the predominant molecular species at **each** of the following pHs 1, 7, and 10

7) **(10 points)** The pKa's of amino acid functional groups can change depending on microenvironment. Explain the impact of the side chain of Asp when placed in a non-polar environment such as a hydrophobic pocket of a protein. How would you predict the pKa to shift? If the pH remains the same, what happens to the ratio of charged to uncharged species of Asp when in a hydrophobic pocket?

8) An enzyme-catalyzed reaction was carried out in 250 ml of a 50 mM Tris buffer, pH 7.7. As a result of the reaction, 0.05 mole/liter of H^+ was produced.

a) **(2.5 points)** What were the concentrations of each form of the buffer at the start of the reaction?
b) **(5 points)** What was the pH at the end of the reaction?
c) **(2.5 points)** Was this an appropriate buffer for this experiment? Why?

9) **(5 points)** Draw the reaction for the bicarbonate buffer system. Describe what happens to the equilibria of this reaction when a person has severe COVID-19 disease and is yet to be on a respirator. Write the clinical description of what this person will be in and then describe how the patient's biochemistry/physiology will compensate. What happens to the blood pH when the patient is then placed on a ventilator? Be specific in terms of biochemistry.