MASTER

Chemistry 130A	Final Examination	May 11, 1996	3 hours	1	
Name				2	
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Prof. K. Sauer				4	
Total Credit - 250 points	SHOW YOUR WORK			5	
Open textbook and class notes				T	
			Course Grade		

1. (Credit 12+12) Ozone, O_3, is a bent triatomic molecule with two O-O bonds of equal length.

   a) Calculate the average bond dissociation enthalpy for the O-O bond in ozone using data in Tables 2.3 and A.5

   b) Ozone is photochemically decomposed in the atmosphere by light with wavelengths of 350 nm and shorter. It has been proposed that this is initiated by the reaction

   $$O_3(g) + h\nu\ (350\ nm) \rightarrow O_2(g) + O(g)$$

   Determine whether this reaction is possible energetically.

2. (Credit 18 each) For each of the following processes state whether ΔG, ΔH and ΔS of the system ~~increases, decreases or does not change~~ is positive, negative or zero. If there is not enough information given, state what experimental measurements are needed for you to determine the answer. (You may use data in tables in the textbook.) Explain your reasoning.

a) The system contains a 0.1 M NaCl solution and pure water separated by a membrane permeable to water only. A small amount of water is transferred through the membrane from the pure water to the NaCl solution at constant temperature and pressure.

ΔG

ΔH

ΔS

b) Water vapor at 100°C, 1 atm pressure is condensed to liquid water at 100°C, 1 atm pressure.

ΔG

ΔH

ΔS

c) The system consists of ice (pure solid water) at 0°C suspended in a 0.01 M KCl solution at the same temperature, all at 1 atm pressure. Some of the ice is melted into the solution at constant temperature and pressure.

ΔG

ΔH

ΔS

d) A sample of air is allowed to effuse through a pinhole into a large evacuated chamber, all in isolation from the surroundings, until half the air has effused. Because N_2 effuses faster than O_2, the gas in the second chamber is richer in N_2 and the gas in the first chamber is richer in O_2 than the original air. (Assume ideal gas behavior.)

ΔG

ΔH

ΔS

3. (Credit 15+15) In aqueous solution the reaction of A to form B has the following rate expression:

$$-\frac{d[A]}{dt} = k[A](1 + k'[OH^-])$$

Hydroxide is not formed or consumed by the reaction.

a) Propose a mechanism that is consistent with the experimental rate expression. Relate the rate constants in your mechanism to k and k′.

b) From the pH dependence of the reaction, k′ was found to be 2.0×10^5 M^{-1}. In a pH 10.0 buffer it took 10 min for a 0.050 M solution of A to decrease to 0.025 M. Calculate the value of k, including its units.

4. (Credit 18+12+12+12) A buffer is prepared by adding 1.500 g of crystalline glycine hydrochloride ($HOOC\text{-}CH_2\text{-}NH_2 \bullet HCl$; MW 111.5 Da) to 1.000 L of 0.0200 M NaOH. Assume that the volume remains constant.

a) Calculate the pH of this buffer at 25°C using the data in Table 4.1.

b) If the buffer is warmed to 37°C, what will be the pH at this temperature?

c) Calculate the ionic strength of the buffer solution.

d) Using Debye-Hückel theory, calculate the ionic activity coefficient for H^+ in this solution at 25°C.

5. (Credit 12+16+12+10+8+12) The enzyme triose phosphate isomerase catalyzes the reaction

$$\underset{\text{(GAP)}}{\text{Glyceraldehyde-3-phosphate}} \rightarrow \underset{\text{(DHAP)}}{\text{Dihydroxyacetone phosphate}}$$

The enzyme has a catalytic constant $k_{cat} = 4.3 \times 10^3\ s^{-1}$ and a Michaelis constant $k_M = 4.7 \times 10^{-4}$ M for this reaction at pH 7 and 25°C. The enzyme is a symmetrical dimer (MW 53,000 Da) with 2 identical polypeptide chains and 2 independent catalytic sites per molecule.

a) Calculate the turnover number for triose phosphate isomerase.

b) In a particular experiment at pH 7 and 25°C, the initial concentration of GAP was 2.0×10^{-3} M with an enzyme concentration of 1.0×10^{-7} M. Calculate the initial rate of formation of DHAP.

How long will it take for 10% of the GAP initially present to be converted?

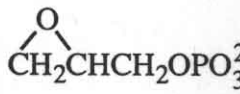
c) The reaction of GAP continues until equilibrium is reached with DHAP. What percentage of the initial GAP is still present when equilibrium is reached at 25°C and pH 7? Relevant data are included in Table 4.2.

d) The Michaelis-Menten mechanism, including the reverse reaction, can be written:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P$$

Use this mechanism to derive an expression for the equilibrium constant between P and S in terms of the four rate constants.

e) Making the assumption that $k_2 << k_{-1}$, calculate a value for k_{-2} for triose phosphate isomerase.

f) The molecule  is a potent inhibitor of triose phosphate isomerase. Addition of a small amount of the inhibitor in a series of experiments containing the enzyme at 1.0×10^{-7} M concentration resulted in $V_{max} = 1.7 \times 10^{-4}$ M sec^{-1} and $v = \frac{1}{2} V_{max}$ at [GAP] $= 4.7 \times 10^{-4}$ M at 25°C and pH 7. Use this evidence to determine the mechanism of inhibition. Explain your reasoning.