

Chemistry 130A	Second Midterm Exam	Oct. 18, 1999	50 min	1	
Name				2	
Prof. K. Sauer				3	
Total Points - 100				4	
SHOW YOUR WORK				T	

Data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$

Faraday constant $F = 9.6485 \times 10^4 \text{ C mol}^{-1} = 9.6485 \times 10^4 \text{ J volt}^{-1} \text{ mol}^{-1}$

Thermodynamic data at 298K

Substance	$\Delta \bar{H}_f^\circ (\text{kJ mol}^{-1})$	$\bar{S}^\circ (\text{J K}^{-1} \text{ mol}^{-1})$	$\Delta \bar{G}_f^\circ (\text{kJ mol}^{-1})$
H ₂ (g)	0	130.684	0
N ₂ (g)	0	191.61	0
NH ₃ (g)	-46.11	192.45	-16.45

1. (Credit 8 + 8 + 7 + 7)

One of the great efforts in chemistry during the early part of the 20th century was to “fix nitrogen” by converting a mixture of N₂ (g) and H₂ (g) to ammonia NH₃ (g), which is valuable as a fertilizer and source of nitrogen for plants.

- a) Calculate the equilibrium constant for this reaction at 298K. (Be sure to write the stoichiometric reaction associated with your value of K.)

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- b) This reaction does not occur spontaneously at 298 K and 1 atm pressure. Is this for thermodynamic or kinetic reasons? Explain your conclusion.
- c) An inventor proposes to make the reaction go by raising the temperature to 800K. Evaluate this proposal critically, using thermodynamic reasoning.
- d) Suggest an alternative approach to obtaining the desired reaction to go spontaneously. (Historically, a method was discovered by Fritz Haber, for which he received the Nobel Prize in 1918.) Explain the reasoning underlying your alternative approach.

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2. (Credit 15 + 10)

- a) If two states of the air in the atmosphere at different altitudes are isentropic, which of the following is/are zero between the two states: ΔT , q_{rev} , $\Delta \bar{V}$, $\Delta \bar{S}$? Explain your reasoning.

- b) Critically evaluate the following statement. Is the statement reasonable, or does it violate a basic thermodynamic principle?

“Supercooled liquid water cannot go spontaneously to ice in an isolated system because supercooled water (below 0°C) has a higher entropy than does ice.”

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3. (Credit 12 + 8)

A solution was prepared using 10.0 mL of 0.0100 M malonic acid, HOOC-CH₂-COOH, plus 10.0 mL of 0.0140 M NaOH. To this was added 1.00 mL of 1.0 × 10⁻⁶ M hydroxylamine, NH₂OH, all at 25°C.

_____	pK
HOOC-CH ₂ -COOH → HOOC-CH ₂ -COO ⁻ + H ⁺	2.85
HOOC-CH ₂ -COO ⁻ → ⁻ OOC-CH ₂ -COO ⁻ + H ⁺	5.70
⁺ NH ₃ OH → NH ₂ OH + H ⁺	5.96

a) Calculate the pH of this solution, assuming that all activity coefficients are 1.0.

b) Calculate the fraction of hydroxylamine present in the form ⁺NH₃OH in the above solution.

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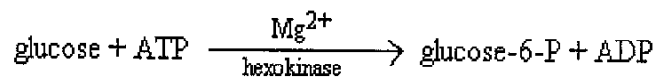
Name _____

Data: Standard free energies of reaction at 25°C, pH 7 for steps in the metabolism of glucose

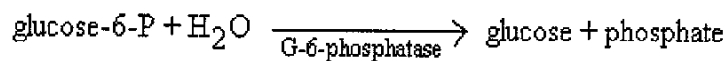
	$\Delta\bar{G}^{0'} \text{ (kJ mol}^{-1}\text{)}$
D-glucose + ATP → D-glucose-6-phosphate + ADP	-16.7
ATP + H ₂ O → ADP + phosphate	-31.0

4. (Credit 8 + 10 + 7)

An important step in the glycolytic path is the phosphorylation of glucose by ATP, catalyzed by the enzyme hexokinase and Mg²⁺:



In the absence of ATP, glucose-6-P is unstable at pH 7, and in presence of the enzyme glucose-6-phosphatase, it hydrolyzes to give glucose:



a) Calculate $\Delta\bar{G}^{0'}$ at pH 7 for the hydrolysis of glucose-6-P at 298 K.

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- b) If the phosphorylation of glucose is allowed to proceed to equilibrium in the presence of equal concentrations of ADP and ATP, what is the ratio (glucose-6-P)/(glucose) at equilibrium? Assume a large excess of ATP and ADP; that is $(ATP) = (ADP) \gg [(glucose) + (glucose-6-P)]$.
- c) In the absence of ATP (and ADP), calculate the ratio (glucose-6-P)/(glucose) at pH 7, if phosphate = 10^{-2} M.