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

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

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

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Thermodynamic data at 298K

| Substance | $\Delta\bar{H}^\circ_f$(kJ mol$^{-1}$) | $\bar{S}^\circ$(J K$^{-1}$mol$^{-1}$) | $\Delta\bar{G}^\circ_f$(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 |

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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 $N_2$ (g) and $H_2$ (g) to ammonia $NH_3$ (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.)

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.

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: $\Delta T$, $q_{rev}$, $\Delta \overline{V}$, $\Delta \overline{S}$? 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."

3. (Credit 12 + 8)

A solution was prepared using 10.0 mL of 0.0100 M malonic acid, $HOOC\text{-}CH_2\text{-}COOH$, plus 10.0 mL of 0.0140 M NaOH. To this was added 1.00 mL of $1.0 \times 10^{-6}$ M hydroxylamine, $NH_2OH$, all at 25°C.

| | pK |
|---|---|
| $HOOC\text{-}CH_2\text{-}COOH \rightarrow HOOC\text{-}CH_2\text{-}COO^- + H^+$ | 2.85 |
| $HOOC\text{-}CH_2\text{-}COO^- \rightarrow {}^-OOC\text{-}CH_2\text{-}COO^- + H^+$ | 5.70 |
| ${}^+NH_3OH \rightarrow NH_2OH + H^+$ | 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 ${}^+NH_3OH$ in the above solution.

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

| | $\Delta\bar{G}^{0\prime}$ (kJ mol$^{-1}$) |
|---|---|
| D-glucose + ATP → D-glucosc-6-phosphate + ADP | -16.7 |
| ATP + $H_2O$ → 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 $Mg^{2+}$:

$$\text{glucose} + \text{ATP} \xrightarrow[\text{hexokinase}]{Mg^{2+}} \text{glucose-6-P} + \text{ADP}$$

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:

$$\text{glucose-6-P} + H_2O \xrightarrow[\text{G-6-phosphatase}]{} \text{glucose} + \text{phosphate}$$

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

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) >> [(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.