Name: 

Instructions:

Please do not start working on the exam until you are told to begin. Check the exam to make sure that it contains exactly 6 different pages, including this one and a periodic table on the last page.

Some useful constants and equations:

\[ R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \quad 101.3 \text{ J} = 1 \text{ L atm} \]

\[ \Delta U = q + w \quad \Delta H = C_p \Delta T \quad \Delta S = q_{rev}/T \]

\[ H = U + PV \]

\[ \Delta_r G = \Delta_r G^o + RT \ln Q \]

\[ \ln \left( \frac{K_2}{K_1} \right) = \left( \frac{\Delta_r H^o}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{(van’t Hoff equation)} \]

\[ \ln \left( \frac{P_2}{P_1} \right) = \left( \frac{\Delta_{vap} H}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{(Clausius-Clapeyron equation)} \]

\[ Y/[L] = n/K - Y/K \quad \text{(Scatchard equation)} \]

\[ \log(f/(1-f)) = N \log[L] - \log K \quad \text{(Hill equation)} \]

\[ f = c - p + 2 \quad \text{(phase rule)} \]

A periodic table is provided on the last page of the exam.
Part 1. Write the letter of the answer which best satisfies each statement or question in the blank at the left. Please check your answers. Credit will only be given for the letter written in the blank (3 points each).

D
1. At equilibrium, \( \Delta G = \) (A) \( \Delta H \) (B) \(-T\Delta S\) (C) \(-RT\ln K\) (D) \(0\)

D
2. Which of the following is an extensive property?
   (A) chemical potential (B) molar enthalpy (C) mass density (D) entropy

D
3. The work done by an expanding ideal gas equals the heat absorbed by the gas from its surroundings if
   (A) the enthalpy of the ideal gas is the same before and after expansion
   (B) the pressure of the ideal gas is the same before and after expansion
   (C) the entropy change due to expansion of the gas is zero
   (D) the internal energy of the ideal gas is the same before and after expansion

A
4. The heat absorbed by an isolated system from its surroundings is
   (A) zero     (B) positive     (C) negative    (D) reversible

D
5. Consider the exothermic reaction \( A(g) <\rightarrow B(g) \) at equilibrium. To increase the concentration of \( B \), one can
   (A) raise pressure   (B) raise temperature   (C) lower pressure   (D) lower temperature

B
6. If the equilibrium constant, \( K \), is larger than the reaction quotient, \( Q \), this favors the formation of
   (A) reactants     (B) products   (C) both products and reactants (D) neither products nor reactants

D
7. Which of the following can we conclude about the reaction
   \[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]
   (A) \( \Delta H > 0 \)     (B) \( \Delta H < 0 \)     (C) \( \Delta S < 0 \)     (D) \( \Delta S > 0 \)

C
8. To measure the equilibrium constant for protein-ligand binding at constant pressure, one could use
   (A) a constant volume calorimeter   (B) a constant pressure calorimeter
   (C) equilibrium dialysis   (D) a mass spectrometer

B
9. For liquid \( \text{N}_2 \) in equilibrium with \( \text{N}_2 \) in the gas phase, how many independent intensive variables can be varied while maintaining a liquid-gas equilibrium?
   (A) 0     (B) 1     (C) 2    (D) 3

C
10. The third law of thermodynamics tells us that
   (A) energy is conserved     (B) the entropy of an isolated system increases
    (C) entropy is 0 when temperature is 0 K   (D) work is path dependent
Part II. Short answer: Answer the following in the space provided. (12 points each)

1. Consider the binding of a ligand, L, to a protein, P, with one binding site. If at equilibrium the concentrations of free ligand and bound ligand are $5.1 \times 10^{-6}$ M and $7.0 \times 10^{-7}$ M, respectively, and the total protein concentration is $1.3 \times 10^{-6}$ M, what is the value of the equilibrium constant for the dissociation of the protein-ligand complex, $K_d$?

$$[P] + [LP] = [P]_0 = 1.3 \times 10^{-6} \text{ M}$$

then $[P] = 1.3 \times 10^{-6} \text{ M} - 7.0 \times 10^{-7} \text{ M} = 6.0 \times 10^{-7} \text{ M}$

$$K_d = [P][L]/[LP] = (6.0 \times 10^{-7}\text{ M})(5.1 \times 10^{-6}\text{ M})/ 7.0 \times 10^{-7}\text{ M} = 4.4 \times 10^{-6}$$

2. It takes 171.4 J to raise the temperature of 32.7 g of $\text{H}_2\text{O}_2$ by 2.0°C. What is the molar heat capacity of $\text{H}_2\text{O}_2$?

Mol. wt. of $\text{H}_2\text{O}_2$ is 34.0 g mol$^{-1}$

$$q = n\bar{C}_p \Delta T$$

$$\bar{C}_p = (171.4 \text{ J})(34.0 \text{ g mol}^{-1})/(32.7 \text{ g})(2.0 \text{ K}) = 89.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

3. Consider the reaction,

$$\text{C}_{10}\text{H}_8(s) + 12\text{O}_2(g) \rightarrow 10\text{CO}_2(g) + 4\text{H}_2\text{O}(l), \quad \Delta H^\circ = -5153.0 \text{ kJ mol}^{-1}$$

If the standard molar enthalpies of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$, respectively, what is the standard molar enthalpy of formation of naphthalene ($\text{C}_{10}\text{H}_8$)?

$$-5153.0 \text{ kJ mol}^{-1} = (10(-393.5)+4(-285.8)) \text{ kJ mol}^{-1} - \Delta_f H^\circ (\text{C}_{10}\text{H}_8)$$

$$\Delta_f H^\circ (\text{C}_{10}\text{H}_8) = 74.8 \text{ kJ mol}^{-1}$$
Part III. Write your answer to the problems below in the space provided. Please show all work. Partial credit will be given based on work shown.

1. Consider the equilibrium of a protein in its native, N, and denatured, D, state

\[ \text{N} \rightleftharpoons \text{D} \]

Suppose that \( \Delta_r H^o = 418.0 \text{ kJ mol}^{-1} \) and \( \Delta_r S^o = 1.32 \text{ kJ K}^{-1} \text{mol}^{-1} \).

(a) What is \( \Delta_r G^o \) at \( T = 298 \text{ K} \)? (5 points)

\[
\Delta_r G^o = \Delta_r H^o - T \Delta_r S^o = (418.0 \text{ kJ mol}^{-1} - (298 \text{ K})(1.32 \text{ kJ K}^{-1} \text{mol}^{-1})) = 24.64 \text{ kJ mol}^{-1}
\]

(b) What is the equilibrium constant, \( K \), at \( T = 298 \text{ K} \)? (5 points)

\[
K = e^{-\Delta_r G^o / RT} = \exp(-24,640 \text{ J mol}^{-1}/(8.31451 \text{ J K}^{-1} \text{mol}^{-1})(298 \text{K})) = 4.8 \times 10^{-5}
\]

c) At what temperature is the concentration of \([N]\) equal to 10 times the concentration of \([D]\) at equilibrium? (7 points)

\[
K = [D]/[N] = 0.1 \text{ at what } T?
\]

Changes in \( K \) if \( T \) changes:

\[
\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^o}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]

We know that \( K = 4.8 \times 10^{-5} \) at \( T = 298 \text{ K} \). Then

\[
\ln\left(\frac{0.1}{4.8 \times 10^{-5}}\right) = \frac{418,000 \text{ J} / \text{mol}}{8.31451 \text{ J} / \text{molK}} \left(\frac{1}{298\text{K}} - \frac{1}{T}\right)
\]

\[
T = 312 \text{ K}
\]
2. (a) (14 points) Calculate $\Delta G^o$ for the reaction of two different forms of sulfur,
\[
S(\text{rhombic}) \leftrightarrow S(\text{monoclinic})
\]
at $T = 298$ K given that the standard molar entropy of the rhombic form of sulfur is $31.88$ J K$^{-1}$ mol$^{-1}$ and the standard molar entropy of the monoclinic form is $32.55$ J K$^{-1}$ mol$^{-1}$.

Also:
\[
\begin{align*}
S(\text{rhombic}) + O_2(g) & \rightarrow SO_2(g) \quad \Delta_r H^o = -296.1 \text{ kJ mol}^{-1} \\
S(\text{monoclinic}) + O_2(g) & \rightarrow SO_2(g) \quad \Delta_r H^o = -299.1 \text{ kJ mol}^{-1}
\end{align*}
\]

\[
\Delta_r S^o = (32.55 - 31.88) \text{ J K}^{-1} \text{ mol}^{-1} = 0.67 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[
\Delta_r H^o = (299.1 - 296.1) \text{ kJ mol}^{-1} = 3.0 \text{ kJ mol}^{-1}
\]

\[
\Delta_r G^o = (3.0 - 298(0.00067)) \text{ kJ mol}^{-1} = 2.8 \text{ kJ mol}^{-1}
\]

(b) Based on the information in part (a), what is the standard molar enthalpy of formation of SO$_2$(g), $\Delta_f H^o$(SO$_2$)? (Hint: One of the two forms of S in the reaction above is the most stable form of S.) (3 points)

Since S(rhombic) is the more stable form, its standard molar heat of formation $= 0$, as is the case for O$_2$, so the standard molar heat of reaction for the top reaction gives $\Delta_f H^o$(SO$_2$) = -296.1 kJ mol$^{-1}$