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:

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

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

\[ H = U + PV \]

\[ \Delta_G = \Delta G^o + RT \ln Q \]

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

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

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

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

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

* 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 (3 points each).

B 1. At equilibrium, $\Delta_r H = \text{(A)} \Delta_r G \text{ (B)} T \Delta_r S \text{ (C)} -T \Delta_r S \text{ (D)} -\Delta_r G$

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

A 3. For the isothermal, reversible expansion of a gas, $w$ is equal to
   (A) $-T\Delta S$  (B) $\Delta U$  (C) $-\Delta V$  (D) $p$

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

B 5. Consider the endothermic reaction $A(g) \rightleftharpoons 2B(g)$ at equilibrium.
   To increase the concentration of $A$ at equilibrium, I can increase
   (A) temperature (B) pressure (C) volume (D) work

D 6. If the reaction quotient, $Q$, is equal to equilibrium constant, $K$, then
   (A) product will form as equilibrium is approached
   (B) reactant will form as equilibrium is approached
   (C) both reactant and product will form as equilibrium is approached
   (D) the reaction is at equilibrium

B 7. For the reaction $H_2O(l) \rightarrow H_2(g) + (1/2)O_2(g)$, $\Delta_r H^\circ = 285.8 \text{ kJ mol}^{-1}$, we
   can conclude that $\Delta_r G^\circ$ is
   (A) greater than 285.8 kJ mol$^{-1}$  (B) less than 285.8 kJ mol$^{-1}$
   (C) equal to 285.8 kJ mol$^{-1}$  (D) zero

B 8. In an equilibrium dialysis experiment, 
   (A) ligand molecules cannot pass through the membrane 
   (B) protein molecules cannot pass through the membrane 
   (C) both protein and ligand pass through the membrane 
   (D) the membrane separates protein from ligand at equilibrium

C 9. At the solid-vapor equilibrium of CO$_2$ the number of independent intensive properties that can be varied while maintaining these phases at equilibrium is
   (A) $-1$  (B) $0$  (C) $1$  (D) $2$

B 10. The second 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. The equilibrium is \( L + P \rightleftharpoons PL \). The fraction of all protein molecules that have a ligand bound to them is 0.5 at equilibrium and the concentration of free ligand is \( 2.0 \times 10^{-3} \) M. What is \( K_a \), the equilibrium constant for association of L and P to form PL?

\[
Y = 0.5, \ [L] = 2.0 \times 10^{-3} \ M
\]

\[
\frac{Y}{[L]} = \frac{1-Y}{K_d}
\]

\[
\frac{0.5}{2.0 \times 10^{-3}} = \frac{0.5}{K_d}
\]

\[
K_a = \frac{1}{K_d} = 5.0 \times 10^2
\]

2. An air bubble is 24 feet below the surface of the sea. The pressure exerted by 33 ft of seawater is equivalent to 1 atm pressure. By what factor will the volume of the air bubble expand when it reaches the surface?

\[
P_1 = \text{atmospheric pressure} + \text{pressure exerted by 36 ft of seawater}
\]

\[
= 1.0 \text{ atm} + (24 \text{ ft})(1 \text{ atm}/33 \text{ ft}) = 1.7 \text{ atm}
\]

At constant \( n \) and \( T \), \( P_1 V_1 = P_2 V_2 \), so that the ratio between the volume of the diver’s lungs at 36 ft under the surface and that at the surface is

\[
\frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{1.7 \text{ atm}}{1.0 \text{ atm}} = 1.7
\]

3. Consider the reaction \( \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \)

At \( T=960 \) K, \( K = 0.534 \) while at \( T=1260 \) K, \( K = 1.571 \). What is the enthalpy of reaction, assuming that it is independent of temperature?

\[
\ln \left( \frac{1.571}{0.534} \right) = \left( \Delta_r H^\circ/8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right)(1/960 \text{ K} - 1/1260 \text{ K})
\]

\[
\Delta_r H^\circ = 3.62 \times 10^4 \text{ J mol}^{-1}
\]
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. (17 points each)

1. Consider the following reaction, a step in glycolysis,
   \[
glucose + HPO_4^{2-} \rightarrow glucose-6-phosphate + H_2O \quad \Delta r G^o = 13.4 \text{ kJ mol}^{-1}
   \]

   (a) Calculate \(\Delta r G\) for the following concentrations: [glucose] = 4.5 \times 10^{-2} \text{ M}, [HPO_4^{2-}] = 2.7 \times 10^{-3} \text{ M} and [glucose-6-phosphate] = 1.6 \times 10^{-4} \text{ M}. (7 points)

   \[
   \Delta r G = \Delta r G^o + RT \ln Q = \Delta r G^o + RT \ln[\text{glucose-6-phosphate}]/[\text{glucose}][HPO_4^{2-}]
   \]

   \[
   = 13.4 \times 10^3 \text{ J mol}^{-1} + \(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln((1.6 \times 10^{-4})/(4.5 \times 10^{-2})(2.7 \times 10^{-3}))
   \]

   \[
   = 14.1 \text{ kJ mol}^{-1} > 0.
   \]

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

   \[
   \Delta r G^o = -RT \ln K = 13.4 \times 10^3 \text{ J mol}^{-1} = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln K
   \]

   \[
   K = 4.48 \times 10^{-3}
   \]

   (c) For what values of \(Q\) will the reaction occur spontaneously? (5 points)

   The reaction occurs spontaneously as long as \(Q < K\), or as long as \(Q < 4.48 \times 10^{-3}\).
2. (a) (9 points) Calculate the standard molar enthalpy of formation for diamond, given

\[
\begin{align*}
\text{C(diamond)} + \text{O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H^o = -395.4 \text{ kJ mol}^{-1} \\
\text{C(graphite)} + \text{O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H^o = -393.5 \text{ kJ mol}^{-1}
\end{align*}
\]

\[
\text{C(graphite) } \rightarrow \text{ C(diamond)} \quad \Delta H^o = 1.9 \text{ kJ mol}^{-1}
\]

Since \(\Delta f H^o(\text{graphite}) = 0\), \(\Delta f H^o(\text{diamond}) = 1.9 \text{ kJ mol}^{-1}\)

(b) (8 points) Given that the standard molar entropies of diamond and graphite are 2.4 J K\(^{-1}\) mol\(^{-1}\) and 5.7 J K\(^{-1}\) mol\(^{-1}\), respectively, calculate \(\Delta r G^o\) for the reaction \(\text{C(diamond) } \rightarrow \text{ C(graphite)}\) at 298 K.

\[
\Delta r G^o = \Delta r H^o - T \Delta r S^o
\]

\[
\Delta r S^o = \overline{S^o}(\text{graphite}) - \overline{S^o}(\text{diamond}) = (5.7 - 2.4) \text{ J K}^{-1} \text{ mol}^{-1} = 3.3 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[
\Delta r G^o = -1.9 \text{ kJ mol}^{-1} - (298 \text{ K})(3.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) = -2.9 \text{ kJ mol}^{-1}
\]

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