Multiple Choice and Short Answer Problems.

1) The zwitterion form of the amino acid alanine is prevalent at pH = 7. Which of the following structures therefore represents the major species of alanine in neutral aqueous solution?

(A) \[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{H} \\
\text{H}_3\text{N}^+ \\
\text{C} \quad \text{C} \\
\text{H} \\
\text{O} \\
\end{array}
\]

(B) \[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{H} \\
\text{H}_2\text{N} \\
\text{C} \quad \text{C} \\
\text{H} \\
\text{O} \\
\end{array}
\]

(C) \[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{H} \\
\text{H}_3\text{N}^+ \\
\text{C} \quad \text{C} \\
\text{O} \\
\end{array}
\]

(D) \[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{H} \\
\text{H}_2\text{N} \\
\text{C} \quad \text{C} \\
\text{O} \\
\end{array}
\]

(5 points)

2) NaCl is added slowly to a solution that is 0.010M in Cu⁺, Ag⁺ and Au⁺. The K_{sp} values for the chloride salts are \(1.9 \times 10^{-7}\), \(1.6 \times 10^{-10}\) and \(2.0 \times 10^{-13}\) respectively. Which compound will precipitate first?

a) CuCl (s)

b) AgCl (s)

c) AuCl (s)

(5 points)
3) Consider the following reaction:

\[ \text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3 (g) + \text{Cl}_2 (g) \quad \Delta H = +93 \text{ kJ mol}^{-1} \]

Which of the following statements is FALSE:

(a) Addition of PCl₃ to the container will shift the equilibrium toward formation of more PCl₅
(b) An increase in temperature will shift the equilibrium toward formation of more PCl₃
(c) A decrease in the volume of the container will shift the equilibrium toward formation of more PCl₅
(d) Removal of PCl₅ from the container will shift the equilibrium toward the formation of more PCl₃
(e) None of the above

(5 points)

4) A concentration cell is constructed using two Ni electrodes with Ni²⁺ concentrations of 1.0 M and 1.00 x 10⁻⁴ M in the two half cells. The standard reduction potential \( \text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni} \) is -0.23 V. Calculate the potential of the cell at 25 °C.

(a) - 0.368 V
(b) + 0.132 V
(c) - 0.132 V
(d) + 0.118 V
(e) +0.0592 V

(10 points)
5) Circle each of the functional groups in the following molecules and identify by name each functional group you have circled.

Phentermine - the "Phen" in the Fen-Phen drug combination

Aspartame - the sweetener in Equal

(10 points)
6) Carefully read each of the following statements. Mark each one as true or false, and for each statement you mark as false, change the statement so that it becomes correct.

(a) For a process to be spontaneous ΔG must be positive. FALSE
(b) Aluminum has a lower first ionization energy than Magnesium TRUE
(c) The process $X(g) + e^- \rightarrow X^-(g)$ is exothermic TRUE
(d) The electronic configuration of Phosphorus is [Ne] 3s$^2$ 3p$^3$ and of Iron is [Ar] 3d$^6$ [Ar] 4s$^2$ 3d$^6$ FALSE
(e) Co$^{2+}$ and elemental Mn have the same number of $d$-electrons TRUE
(f) In a galvanic cell, electrons flow through the salt bridge to complete the circuit FALSE
(g) If heat flows from the system to surroundings, the entropy of the surroundings decreases FALSE
(h) The molecularity of an elementary reaction cannot be a fraction TRUE
(i) The standard entropy of 1.0 mole of water is lower than 1.0 mole of ice but higher than 1.0 mole of steam. FALSE
(k) In Organic chemistry an alkene has at least one triple bond FALSE

(15 points)
Long Answers. You must show all your working to receive full credit.

Question 7)

\((\text{HOCH}_2)_3\text{CNH}_2\), known as "TRIS", is often used as the basis for a buffer in biochemical studies. TRIS is an organic base with a \(K_b\) of \(1.19 \times 10^{-6}\).

\[
(\text{HOCH}_2)_3\text{CNH}_2 + \text{H}_2\text{O} \leftrightarrow (\text{HOCH}_2)_3\text{CNH}_3^+ + \text{OH}^-
\]

(a) Set up an equilibrium calculation for a weak base, and calculate the pH of a 0.5 mol L\(^{-1}\) solution of TRIS. Show your working.

\[
\begin{align*}
\text{I} & : 0.5 & 0 & 10^{-7} & 0 \\
\text{C} & : -x & x & & \\
\text{E} & : (0.5-x) & x & x & K_b = \frac{[\text{TRISH}^+][\text{OH}^-]}{[\text{TRIS}]} \\
\end{align*}
\]

\[
K_b = \frac{x^2}{(0.5-x)} = 1.19 \times 10^{-6}
\]

Approx. \(x \ll 0.5 \Rightarrow x^2 = (0.5)(1.19 \times 10^{-6})
\]

\[
\Rightarrow x = 7.71 \times 10^{-4}
\]

Check Approx. \(\frac{x}{0.5} = 0.15\%\) OK

\(\text{Conc.} = x = 7.71 \times 10^{-4} \Rightarrow \text{pOH} = 3.1 \Rightarrow \text{pH} = 14 - 3.1 = 10.9\)

(b) The conjugate acid to TRIS is usually written TRISH\(^+\). What is the pK\(a\) of TRISH\(^+\)?

\[
pK_a = 14.00 - pK_b
\]

\[
= 14.00 - 5.92 = 8.08
\]

\[
= -\log_{10} (1.15 \times 10^{-6})
\]
(c) A buffer is prepared by mixing 0.50 mol of TRIS and 0.25 mol of TRISH\(^+\) into 1 L of H\(_2\)O. Calculate the pH of the resulting buffer solution.

\[
\text{pH} = pK_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 8.08 + \log_{10}\left(\frac{0.5}{0.25}\right)
\]

\[\text{pH} = 8.38\]

(d) Often it is desirable to make a pH 7.0 buffer. Calculate the ratio of TRIS to TRISH\(^+\) for a pH 7.0 buffer.

\[
\text{pH} = pK_a + \log_{10}\left(\frac{[\text{TRIS}]}{[\text{TRISH}^+]}\right)
\]

For desired pH 7.0 buffer

\[
\log_{10}\left(\frac{[\text{TRIS}]}{[\text{TRISH}^+]}\right) = 7.0 - 8.08
\]

\[\quad = -1.08
\]

\[\Rightarrow \frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 0.08 \quad \text{to 1 sig fig.} \quad (30 \text{ points})\]
Question 8)

Cyanide is a good Lewis base and forms many complex ions with transition metal cations. For example, Co\(^{3+}\) forms a complex ion with CN\(^-\) according to following equilibrium:

\[
\text{Co}^{3+} + 6 \text{CN}^- \rightleftharpoons [\text{Co(CN)}_6]^{3-}
\]

(a) Write down the equilibrium constant expression that describes the formation of [Co(CN)_6]^{3-}:

\[
K = \frac{[\text{Co(CN)}_6]^{3-}}{[\text{Co}^{3+}][\text{CN}^-]^6}
\]

(b) Draw the structure (showing all atoms individually) of the 6-coordinate complex ion.

(c) What is the electronic configuration of cobalt in the cyanide complex ion?

\[
\text{Co}^{3+}: \quad [\text{Ar}] 3d^6
\]

(d) If the complex of Co\(^{3+}\) with ethylenediammine, [Co(en)]^{3+}, is known to be low spin, and the complex with chloride, [CoCl\(_2\)]^{3-}, known to be high spin, would you expect the [Co(CN)_6]^{3-} complex ion to be paramagnetic or diamagnetic? Explain.

\[
\text{CN}^- \text{ is a STRONG FIELD LIGAND (Spectrochem. Series)}
\]

\[
\text{OCTAHEDRAL FIELD} \quad \text{STRONGER THAN}
\]

\[
\text{en, so complex must be low spin}
\]

(20 points)
Question 9)

Formaldehyde is the simplest organic molecule with the aldehyde functional group. It has the following molecular structure:

![Molecular Structure of Formaldehyde]

(a) Identify the orbital hybridization of the carbon atom in formaldehyde and indicate approximate bond angles on the structure diagram above.

\[ \text{sp}^2 \]

(b) Formaldehyde can be produced by oxidation of a simple alcohol. Draw the molecular structure of this alcohol.

![Molecular Structures of Alcohol]

(c) If formaldehyde is further oxidized under strongly oxidizing conditions (acidic KMnO₄), a carboxylic acid is formed. Draw the structure of the carboxylic acid product and identify on your drawing the hydrogen that is normally lost when this molecule acts as an Bronsted-Lowry acid.

![Molecular Structure of Formic Acid]

(20 points)
Question 10) Consider the following two half cell reactions and their standard reduction potentials:

\[ \text{PbSO}_4 (s) + 2e^- \rightarrow \text{Pb} (s) + \text{SO}_4^{2-} (aq) \quad E^0 = -0.35 \text{V} \]

\[ \text{Pb}^{2+} (aq) + 2e^- \rightarrow \text{Pb} (s) \quad E^0 = -0.13 \text{V} \]

(a) Combine the two half cells and their reactions to write down an overall full reaction that is spontaneous at standard conditions. What is the full cell voltage, \( E_{\text{cell}}^{\circ} \)?

\[
\begin{align*}
Pb^{2+} + 2e^- & \rightarrow Pb \quad E^0 = +0.35 \\
Pb + SO_4^{2-} & \rightarrow PbSO_4 + 2e^- \quad E^0 = -0.13 \\
\hline
Pb^{2+} + SO_4^{2-} & \rightarrow PbSO_4 \\
E_{\text{cell}}^{\circ} = 0.22 \quad \text{SPONTANEOUS POSITIVE}
\end{align*}
\]

(b) Using the overall full cell voltage, calculate \( \Delta G^0 \) for the spontaneous reaction you wrote down for part (a).

\[
\Delta G^0 = -nF E^0 = -2(96,485)(0.22) = -42 \text{ kJ mol}^{-1}
\]

(c) Use your answer to calculate the solubility product, \( K_{sp} \), for \( \text{PbSO}_4 \) at 25°C?

\[
RT \ln K_{sp} = -\Delta G^0
\]

\[
\Rightarrow \quad K_{sp} = e^{-\Delta G^0/RT} = e^{\frac{-42,453}{(8.314)(298)}}
\]

\[
K_{sp} = 3.6 \times 10^{-8}
\]

(25 points)
Question 11)

A mixture of liquid dinitrogen tetroxide $\text{N}_2\text{O}_4$ and liquid monomethyl hydrazine, is used as the fuel for the NASA space shuttle. The reaction is

$$5 \text{ N}_2\text{O}_4 \,(l) + 4 \text{ N}_2\text{H}_3\text{CH}_3 \,(l) \rightarrow 12 \text{ H}_2\text{O} \,(g) + 9 \text{ N}_2 \,(g) + 4 \text{ CO}_2 \,(g)$$

(a) Write the expression for the equilibrium constant, $K_p$, for this reaction. What are the units for this $K_p$?

$$K_p = \frac{P_{\text{H}_2\text{O}}}{{P_{\text{N}_2}}^9 \cdot P_{\text{CO}_2}^4}$$

**Units are ATm$^{-2}$**

(b) Is $\Delta S_{\text{system}}$ likely to be positive, negative or zero for this reaction? Why?

Thee are (i) large number of gaseous products, zero gas molecules on reactant side

(ii) large increase in number of species on product side

**LARGE INCREASE IN SYSTEM ENTROPY**

$$\Delta S_{\text{system}} = \text{ positive}$$
(c) Using the following standard free energy of formation data, calculate $\Delta G^\circ$ for the reaction.

$\Delta G^\circ$ : 
- $\text{N}_2\text{O}_4$ (l) $\quad 97 \text{ kJ mol}^{-1}$
- $\text{N}_2\text{H}_5\text{CH}_3$ (l) $\quad 180 \text{ kJ mol}^{-1}$
- $\text{N}_2$ (g) $\quad 0 \text{ kJ mol}^{-1}$
- $\text{H}_2\text{O}$ (g) $\quad -229 \text{ kJ mol}^{-1}$
- $\text{CO}_2$ (g) $\quad -394 \text{ kJ mol}^{-1}$

\[
\begin{align*}
\Delta G^\circ_{\text{reaction}} &= 12(-229) + 9(0) + 4(-384) - (5(97) + 4(180)) \\
&= -4324 -1205 \\
&= -5529 \text{ kJ per mole of reaction}
\end{align*}
\]

HUGE!!

(d) By calculating the value of $K_p$ for this reaction using your result from part (c), show that even at 5000 Kelvin, the reaction essentially goes to completion. Show your working.

\[
\begin{align*}
\text{RTL} \ln K_p &= -\Delta G^\circ \\
K_p &= \exp\left(-\frac{\Delta G^\circ}{RT}\right) \\
&= \exp\left(-\frac{-5529,000 \text{ J mol}^{-1}}{(5000 \text{ K})(8.314 \text{ J K}^{-1}\text{mol}^{-1})}\right) \\
&= 5.8 \times 10^{57} \\
\text{Very large, } \Rightarrow \text{ reaction equilibrium is far to R.H.S.}
\end{align*}
\]

(25 points)
Question 12)

For the reaction \[ \text{H}_2 (g) + \text{I}_2 (g) \rightarrow 2 \text{HI} (g) \]
the rate law is:

\[-\frac{\Delta [\text{H}_2]}{\Delta t} = k \left[ \text{H}_2 \right] [\text{I}_2].\]

The value for the rate constant \( k \) is \( 2.45 \times 10^{-4} \) at 302°C and 0.950 at 508°C.

(a) What is the overall order of the reaction and what are the correct units for \( k \)?

Overall order = 2

\( k \) has units \( \text{mol}^{-1} \text{ L s}^{-1} \)

(b) Calculate the values of the activation energy \( E_a \) and the prefactor \( A \) in the Arrhenius Law for this reaction. Make sure to include appropriate units in your answer.

\[ \ln k = \ln A - \frac{E_A}{RT} \quad \text{Assume } A \text{ is constant} \]

\[ \ln k_1 = \ln A - \frac{E_A}{RT_1}, \quad \ln k_2 = \ln A - \frac{E_A}{RT_2} \]

\[ \ln k_1 - \ln k_2 = -\frac{E_A}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

\[ \ln \left( \frac{k_1}{k_2} \right) = -\frac{E_A}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

Substituting values and temps

\[ E_A = \frac{(8.314)(8.263)}{4.59 \times 10^{-4}} = +150 \text{ kJ mol}^{-1} \]

Using rate at 302°C to solve for \( A \)

\[ \ln A = \ln k + \frac{E_A}{RT} \]

\[ = -8.314 + \frac{150,000}{(8.314)(575)} = 23.01 \]

\[ A = e^{23.01} = 9.87 \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1} \]
(c) The reaction between hydrogen and iodine is endothermic ($\Delta H^\circ = +52 \text{ kJ mol}^{-1}$). Draw a diagram showing the energy along reaction profile from reactants to products for this reaction carefully labeling your diagram and indicating the activation energy calculated in part (b).

![Diagram of reaction profile]

(d) Calculate the value of the rate constant $k$ at 375 °C. Show your working.

Using value of $A$ and $E_a$ calculated in (b)

$$k = A \exp \left( \frac{-E_a}{RT} \right) = 9.87 \times 10^9 \exp \left( \frac{-150,000}{18.314 \times 648} \right)$$

At 375°C, $k = 8.35 \times 10^{-3}$ mol$^{-1}$ L s$^{-1}$

(30 points)