Chem. 1B Final Exam
March 20, 2002

Name: ____________________________
Last Name__________ First Name__________
Perm # ____________________________

First letter of your last name: ______

There are a total of six pages (19 problems) in the exam. All work must be shown on the exam. Show your method of calculation clearly. Correct answers not showing the work will not receive credit. Include the UNITS of all answers.

Notes written on one 8.5 X 11 inch page may be used. All other notes and books are not allowed.

The last page contains information that may be useful as well as a periodic table. You may remove the last page from the exam.

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1. Consider the following reaction mechanism:

\[
2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \quad \text{(fast equilibrium)} \\
\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad \text{(slow)} \\
\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad \text{(fast)}
\]

a) (2 pts) What is the overall reaction?
\[2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}\]

b) (2 pts) List the intermediate(s) in the reaction.
\[\text{N}_2\text{O}_2 \quad \text{N}_2\text{O}\]

c) (8 pts) Derive the rate law. Be sure to eliminate intermediates from your answer.
\[
\text{rate} = k_2 \left[ \frac{[\text{N}_2\text{O}_2][\text{H}_2]}{[\text{NO}]^2} \right] \\
K_1 = \frac{k_2}{k_{-1}} \\
[N_2O_2] = K_1[\text{NO}]^2
\]
\[
\text{rate} = k_2 K_1 [\text{NO}]^2 [\text{H}_2] \
\text{or rate} = k_{\text{obs}} [\text{NO}]^2 [\text{H}_2]
\]
d) (3 pts) If the concentration of NO is doubled, while the concentration of H\(_2\) is kept constant, how will this affect the rate of reaction?
\[2^2 = 4 \text{ rate increases by a factor of 4}\]

2. (6 pts) One mole of an ideal gas is heated from 25°C to 35°C under two different conditions. First, the gas is heated from 25°C to 35°C at constant volume then the gas is heated from 25°C to 35°C at constant pressure.

a) What is the heat absorbed at constant volume relative to the heat absorbed at constant pressure? Circle the answer.
\[q_v = q_p \quad q_v < q_p \quad q_v > q_p\]

b) What is the change in enthalpy relative to the change in energy for these processes? Circle the answer.
\[\Delta H = \Delta E \quad \Delta H < \Delta E \quad \Delta H > \Delta E\]

3. (8 pts) In a common car battery, six identical cells each carry out the following reaction.

\[
\text{Pb (s) + PbO}_2 + \text{HSO}_4^- + 2 \text{H}^+ \rightarrow 2 \text{PbSO}_4 + 2 \text{H}_2\text{O} \quad \theta = 2.04 \text{ V}
\]

Suppose that to start a car on a cold morning, 125 A is drawn for 15.0 seconds from this cell. How many grams of Pb (s) would be consumed? Circle the correct answer. NO WORK = NO CREDIT

a) 8.05 g
b) 2.01 g
c) 0.0180 g
d) 0.0360 g
e) 4.02 g
f) 1.01 g

\[
125 \frac{C}{\text{sec}} \left( 15 \text{ sec} \right) \left( \frac{1 \text{ mol e}^-}{96,485 \text{ C}} \right) = 0.0194 \text{ mol e}^-\]
\[
0.0194 \text{ mol e}^-\left( \frac{1 \text{ mol Pb}}{2 \text{ mol e}^-} \right) = 2.01 \text{ g}
\]
4. (4 pts) How many electrons are transferred in the following reaction?

\[ 6 \text{Ag} + 3 \text{HS}^- + 2 \text{CrO}_4^{2-} + 5 \text{H}_2\text{O} \rightarrow 3 \text{Ag}_2\text{S} + 2 \text{Cr(OH)}_3^- + 7 \text{OH}^- \]

\[ 6 e^- \]

5. (4 pts) For which of the following processes would \(\Delta S^\circ\) be expected to be most positive?

a) \(2 \text{N}_2\text{O}_5\text{(g)} \rightarrow 4 \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}\)

b) \(\text{H}_2\text{O}\text{(l)} \rightarrow \text{H}_2\text{O}\text{(s)}\)

c) \(\text{NH}_3\text{(g)} + \text{HCl}\text{(g)} \rightarrow \text{NH}_4\text{Cl}\text{(g)}\)

d) \(\text{N}_2\text{O}_4\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)}\)

e) \(4 \text{ClO}_2\text{(g)} \rightarrow 2 \text{Cl}_2\text{O}\text{(g)} + 3 \text{O}_2\text{(g)}\)

6. (4 pts) At constant pressure, the following reaction is exothermic. \(2 \text{NO}_2\text{(g)} \rightarrow \text{N}_2\text{O}_4\text{(g)} + \text{heat}\)

In the direction written, the reaction is

a) always spontaneous.

b) spontaneous at high temperatures

c) spontaneous at low temperatures

d) never spontaneous.

\[ \Delta H < 0 \]
\[ \Delta S < 0 \]
\[ \Delta G = \Delta H - T\Delta S \]

7. (10 pts) Answer the following question using the data given below:

<table>
<thead>
<tr>
<th>Half Reaction</th>
<th>(E^\circ) (V)</th>
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<tbody>
<tr>
<td>(\text{Co}^{2+} + 2 e^- \rightarrow \text{Co}\text{(s)})</td>
<td>-0.28</td>
</tr>
<tr>
<td>(\text{Ni}^{2+} + 2 e^- \rightarrow \text{Ni}\text{(s)})</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

A piece of cobalt is placed in 0.25 M \(\text{Ni(NO}_3\text{)}_2\). Calculate the concentrations of \(\text{Co}^{2+}\) and \(\text{Ni}^{2+}\) at equilibrium, at 25°C.

\[
\begin{align*}
\text{Co(s)} & \rightarrow \text{Co}^{2+} + 2\text{e}^- + 0.28 \\
\text{Ni}^{2+} + 2\text{e}^- & \rightarrow \text{Ni}\text{(s)} - 0.23 \\
\text{Ni}^{2+} + \text{Co}\text{(s)} & \rightarrow \text{Co}^{2+} + \text{Ni}\text{(s)} + 0.05\text{V}
\end{align*}
\]

Initial concentration

| at equilib. | \(0.25 - x\) |

\[K = e^{nF E^\circ / RT} = e^{2(96485} \text{ C mol}^{-1}(0.05 V) / (8.315 \text{ K mol}^{-1})} = 49.11\]

\[K = \frac{[\text{Co}^{2+}]}{[\text{Ni}^{2+}]} = \frac{x}{0.25 - x} = 49.11\]

\[x = 0.245 \text{ M}\]

\[\text{[Co}^{2+}] = 0.245 \text{ M}\]

\[\text{[Ni}^{2+}] = 0.005 \text{ M}\]
8. (6 pts) Write the reactions that correspond to the following enthalpy changes:
   a) \( \Delta H^\circ_f \) for solid iron(III) oxide.
   \[
   2 \text{ Fe (s)} + \frac{3}{2} \text{ O}_2 (g) \rightarrow \text{ Fe}_2 \text{O}_3
   \]
   b) \( \Delta H^\circ_f \) for D-ribose, \( \text{C}_5\text{H}_{10}\text{O}_5 \).
   \[
   5 \text{ C (s)} + 5 \text{ H}_2 (g) + \frac{5}{2} \text{ O}_2 (g) \rightarrow \text{ C}_5\text{H}_{10}\text{O}_5
   \]

9. Using the following data:

   \[
   \begin{array}{ll}
   \text{H}_2\text{S (g)} & -35 \\
   \text{SO}_2 (g) & -300 \\
   \text{H}_2\text{O (g)} & -225 \\
   \text{S (s)} & 0 \\
   \end{array}
   \]

   a) (6 pts) Calculate \( \Delta G^\circ \) for the following reaction at 298 K:
   \[
   2 \text{ H}_2\text{S (g)} + \text{ SO}_2 (g) \rightleftharpoons 3 \text{ S (s)} + 2 \text{ H}_2\text{O (g)}.
   \]
   \[
   \Delta G^\circ = \left[3(0) + 2(-225)\right] - \left[2(-35) + (-300)\right]
   \]
   \[
   \Delta G^\circ = -80 \text{ kJ}
   \]

   b) (6 pts) Predict the sign of \( \Delta H \) and \( \Delta S \). Circle the answer.
   \[
   \begin{array}{c}
   \Delta S > 0 \\
   \Delta H = 0 \\
   \end{array}
   \]

   c) (3 pts) Will the reaction be more spontaneous at higher or lower temperature? Circle the answer.
   Higher T

10. (8 pts) The standard enthalpy of combustion of ethene gas, \( \text{C}_2\text{H}_4 (g) \), is \(-1410 \text{ kJ/mol} \) at 298 K. Given the following enthalpies of formation, calculate \( \Delta H^\circ_f \) for \( \text{C}_2\text{H}_4 (g) \).

   \[
   \begin{array}{ll}
   \text{H}_2\text{O (l)} & -285.9 \\
   \text{CO}_2 (g) & -393.5 \\
   \end{array}
   \]

   \[
   \text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \]

   \[
   x \quad 0 \quad 2(-393.5) \quad 2(-285.9) 
   \]

   \[
   2(-393.5) + 2(-285.9) - \Delta H^\circ_f (\text{C}_2\text{H}_4) = -1410
   \]

   \[
   \boxed{\Delta H^\circ_f (\text{C}_2\text{H}_4) = +51.2 \text{ kJ/mol}}
   \]
11. (16 pts) Circle the formula that best fits each of the following descriptions:

a) greatest electronegativity
   \[ \text{H} \quad \text{P} \quad \boxed{\text{N}} \quad \text{B} \]

b) smallest first ionization energy
   \[ \text{S} \quad \boxed{\text{Na}} \quad \text{Mg} \quad \text{P} \]

c) smallest radius
   \[ \text{O} \quad \boxed{\text{N}^+} \quad \text{O}^- \]

d) largest ionic radius
   \[ \text{Cl}^- \quad \text{Ca}^{2+} \quad \boxed{\text{S}^2} \quad \text{K}^+ \]

e) longest CO bond length
   \[ \text{CO}_2 \quad \boxed{\text{CO}_3^{2-}} \quad \text{CO} \]

f) an excited state electron configuration
   \[ 1s^22s^22p^4 \quad [\text{Ar}]4s^33d^44p^1 \quad [\text{Ar}]4s^33d^1 \]

g) most polar bond
   \[ \text{C} - \text{O} \quad \text{O} - \text{Cl} \quad \boxed{\text{H} - \text{Cl}} \]

h) longest bond length
   \[ \text{O}_2 \quad \boxed{\text{N}_2} \quad \boxed{\text{Cl}_2} \quad \text{CO} \]

12. (6 pts) Write the electronic configuration and indicate the number of unpaired electrons for each of the following species.

<table>
<thead>
<tr>
<th>Electronic Configuration</th>
<th>Number of Unpaired Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) N ( [\text{He}]2s^22p^3 )</td>
<td>3</td>
</tr>
<tr>
<td>b) P(^-) ( [\text{Ne}]3s^23p^4 )</td>
<td>2</td>
</tr>
<tr>
<td>c) Se ( [\text{Ar}]4s^23d^{10}4p^4 )</td>
<td>2</td>
</tr>
</tbody>
</table>

13. a) (6 pts) **Draw the Lewis structures**, all three resonance forms, for the cyanate ion, OCN\(^-\). Carbon is the central atom.

\[
\begin{align*}
\text{[O=C=\text{N}]^-} & \quad \text{[O=\text{C}-\text{N}]^-} \quad \text{[O-C=\text{N}]^-}
\end{align*}
\]

b) (6 pts) **Assign formal charges on each of the atoms in all three resonance structures.**

\[
\begin{align*}
\text{O} & \quad \text{C} & \quad \text{N} & \quad \text{O} \quad \text{C} - \text{N} & \quad \text{O} \quad \text{C} \equiv \text{N} \quad \text{O} \\
0 & \quad 0 & \quad -1 & \quad +1 & \quad 0 & \quad -2 & \quad -1 & \quad 0 & \quad 0
\end{align*}
\]

c) (4 pts) **Based on the assigned formal charges, which of the resonance structures is least favored.**

\[
\text{O} \equiv \text{C} - \text{N} \]
14. Consider the following reaction. \( A \rightarrow B \) This reaction is exothermic, \( \Delta H^\circ = -62 \text{ kJ/mol} \), and the activation energy, \( E_a \), is 16 kJ/mol.
   
a) (6 pts) Draw a potential energy profile for this reaction. Your diagram should show the reactants, products, transition state \([X]^*\), \( E_a \) and \( \Delta H^\circ \).

\[ \begin{align*}
E_a \quad \Delta H \quad \text{Reaction Coordinate}
\end{align*} \]

\[ \begin{align*}
\text{Energy}
\end{align*} \]

b) (4 pts) What is the activation energy for the reverse reaction, \( B \rightarrow A \)?

\[ \text{reverse} \quad E_a = 62 + 16 = 78 \text{ kJ/mol} \]

15. (10 pts) The activation energy for the decomposition of hydrogen peroxide is 35 kJ/mol.

\[ \begin{align*}
2 \text{H}_2\text{O}_2 \text{(l)} &\rightarrow 2 \text{H}_2\text{O(l)} + \text{O}_2 \text{(g)}
\end{align*} \]

When this reaction is catalyzed by the enzyme catalase, the activation energy is 7.0 kJ/mol. Calculate the temperature that would cause the decomposition reaction without the catalyst to proceed as rapidly as the enzyme-catalyzed decomposition at 20°C. Assume the frequency factor \( A \) to be the same in both cases.

\[ k = A e^{- \frac{E_a}{RT}} \]

\[ A e^{- \frac{35 \text{ kJ/mol}}{RT}} = A e^{- \frac{7 \text{ kJ/mol}}{R(293 \text{K})}} \]

\[ -\frac{35 \text{ kJ/mol}}{RT} = -\frac{7 \text{ kJ/mol}}{R(293 \text{K})} \]

\[ T = 1465 \text{K} \]
16. (6 pts) Balance the following oxidation-reduction reaction in acidic solution, using the half-reaction method.

\[ \text{ClO}_3^- + \text{Fe}^{2+} \rightarrow \text{Cl}^- + \text{Fe}^{3+} \]

In the balanced equation, what is the stoichiometric coefficient in front of \(\text{Fe}^{2+}\)? Circle the correct answer.

\[ 6\text{H}^+ + 6\text{e}^- + \text{ClO}_3^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} \]

\[ 6(\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 1\text{e}^-) \]

\[ 6\text{H}^+ + \text{ClO}_3^- + 6\text{Fe}^{2+} \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} + 6\text{Fe}^{3+} \]

17. For the decomposition of dimethyl ether, \((\text{CH}_3)_2\text{O}\), the first-order rate constant is \(3.4 \times 10^{-4} \text{ s}^{-1}\) at 450°C.

\((\text{CH}_3)_2\text{O} (\text{g}) \rightarrow \text{CH}_4 (\text{g}) + \text{H}_2 (\text{g}) + \text{CO (g)}\)

The reaction is carried out in a constant-volume flask. Initially only dimethyl ether is present and the pressure is 0.30 atm.

a) (10 pts) What is the pressure of dimethyl ether after 9.0 minutes? Assume ideal gas behavior.

\[ \ln [A] = -kt + \ln [A]_0 \]

or \[ \frac{[A]}{[A]_0} = e^{-kt} \]

\[ \frac{P_{/RT}}{0.30/RT} = e^{-(3.4 \times 10^{-4} \text{ s}^{-1})(5405)} \]

\[ \frac{P}{0.30} = 0.832 \]

\[ P = 0.25 \text{ atm} \]

b) (6 pts) What is the total pressure after 9.0 minutes? Assume ideal gas behavior.

\[ 0.3 - 0.25 = 0.05 \text{ atm of reactants converted to products} \]

\[ \frac{1 \text{ mol reactant}}{3 \text{ moles product}} \]

\[ 3(0.05) = 0.15 \text{ atm products} \]

\[ P_{\text{total}} = 0.25 + 0.15 = 0.40 \text{ atm} \]