REMOVE THIS PAGE PRIOR TO STARTING EXAM.
# ANSWER KEY

CHEMISTRY F1403    THIRD EXAM    12/8/99
PROFESSOR J. MORROW

PRINT NAME, LAST: _________________________
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I.D.#: _________________________

MAXIMUM POINT VALUE IS IN PARENTHESES

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<table>
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COLUMN TOTALS (MAXIMUM):

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EXAM TOTAL (205 pts) __________
OUT OF 100
1) Given the following table of thermodynamic data for the indicated species. All of the following species are in the gaseous state at 298 K.

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>( S^0 ) (J mol(^{-1}) K(^{-1}))</th>
<th>( \Delta H_f^0 ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>213.79</td>
<td>-393.51</td>
</tr>
<tr>
<td>NO(^-)</td>
<td>214.86</td>
<td>?</td>
</tr>
<tr>
<td>CO(_2)^-</td>
<td>218.70</td>
<td>-441.40</td>
</tr>
<tr>
<td>NO</td>
<td>210.76</td>
<td>90.29</td>
</tr>
</tbody>
</table>

For the following reaction, \( K_p = 2.189 \times 10^{-7} \)

\[
\text{CO}_2^- + \text{NO} \rightleftharpoons \text{CO}_2 + \text{NO}^- 
\]

Calculate \( \Delta G^0_{\text{rxn}} \) (in kJ) at 298 K for this reaction. (10 pts)

\[
\Delta G^0_{\text{rxn}} = -RT \ln K_p = -(8.314 \times 10^{-3})(298) \ln(2.189 \times 10^{-7}) = 38.00 \text{ kJ}
\]

\[
\Delta G^0_{\text{rxn}} = \boxed{38.00} \text{ kJ}
\]

2) Calculate \( \Delta H_f^0 \) (in kJ) for NO\(^-\) at 298 K for the reaction using the data from problem 1. (20 pts) SHOW WORK

\[
\text{T} \Delta S_{\text{rxn}} = (298)(214.86 + 213.79 - 218.70 - 210.76)(10^{-3}) = -0.241 \text{ kJ} \quad \text{ (FROM TABLE)}
\]

\[
\Delta H_{\text{rxn}} = (\Delta H_f^0 + (-393.51) - (-441.40) - (90.29)) = \Delta H_f^0 - 42.40 \text{ kJ} \quad \text{ (FROM TABLE)}
\]

\[
\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - \text{T} \Delta S_{\text{rxn}} \quad \therefore \quad 38.00 = \Delta H_f^0 - 42.40 \text{ kJ} - (-0.241)
\]

\[
\Delta H_f^0 = 80.2 \text{ kJ}
\]

\[
\Delta H_f^0 = \boxed{80.2} \text{ kJ}
\]
3) Using the ion-electron method, balance the following reaction under the conditions given. Show the balanced oxidation and reduction half reactions where indicated. Write your answers in the space provided.

\[ \text{C}_3\text{H}_4\text{O}_4 \ + \ \text{S}_2\text{O}_6^{2-} \longrightarrow \text{CH}_3\text{OH} \ + \ 2 \text{CO}_2(\text{g}) + \ \text{SO}_2(\text{g}) \ (\text{acidic}) \]

oxidation half reaction: (5 pts)
\[ \text{C}_3\text{H}_4\text{O}_4 \ + \ \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{OH} \ + \ 2 \text{CO}_2 \ + \ 2 \text{H}^+ + 2 \text{e}^- \]

reduction half reaction: (5 pts)
\[ 2 \text{e}^- + 4 \text{H}^+ + \text{S}_2\text{O}_6^{2-} \longrightarrow 2 \text{SO}_2 + 2 \text{H}_2\text{O} \]

ANSWER: (5 pts) Subscripts need NOT be shown in final answer.

BAL EQ. \[ \text{C}_3\text{H}_4\text{O}_4 + \text{S}_2\text{O}_6^{2-} + 2 \text{H}^+ \longrightarrow \text{CH}_3\text{OH} + 2 \text{CO}_2 + 2\text{SO}_2 + \text{H}_2\text{O} \]

4) \[ \text{MnO}_4^- + \text{S}_2^- \longrightarrow \text{MnS}_2 + \text{S}^0 \ (\text{basic}) \]

oxidation half reaction: (5 pts)
\[ \text{S}_2^- \longrightarrow \text{S}^0 + 2 \text{e}^- \]

reduction half reaction: (5 pts)
\[ 3 \text{e}^- + 8 \text{H}^+ + \text{MnO}_4^- + 2 \text{S}^2- \longrightarrow \text{MnS}_2 + 4 \text{H}_2\text{O} \]

ANSWER: (5 pts) Subscripts need NOT be shown in final answer.

16 \text{H}^+ + 2 \text{MnO}_4^- + 7 \text{S}^2- \longrightarrow 2 \text{MnS}_2 + 3 \text{S}^0 + 8 \text{H}_2\text{O} \ (\text{ACIDIC})

8 \text{H}_2\text{O} + 2 \text{MnO}_4^- + 7 \text{S}^2- \longrightarrow 2 \text{MnS}_2 + 3 \text{S}^0 + 16 \text{OH}^-(\text{BASIC SOL'N})

5) The vapor pressure of water at 298 K is 0.03132 atm. The standard free energy of formation of H\(_2\)O\(_l\), \(\Delta G_f^o\), is -237.2 kJ/mol also at 298 K. Using this information, calculate the standard free energy of formation, \(\Delta G_f^o\) (in kJ), of H\(_2\)O\(_g\). BE CAREFUL USING THE DEFINITION OF EACH TERM! (20 pts) SHOW WORK

GIVEN: For the reaction, H\(_2\)O\(_l\) \(\rightleftharpoons\) H\(_2\)O\(_g\), \(\Delta G_{rxn} = -RT \ln P_{(atm)}\)

- a) -224.3
- b) -232.9
- c) -245.8
- d) -228.6

\[ \Delta G_{rxn} = \Delta G_{f(g)}^o - \Delta G_{f(l)}^o = -RT \ln P = -(8.314)(298)\ln(0.03132) \]
\[ \Delta G_{rxn} = \Delta G_{f(g)}^o + 8581 \ J/mol = 8581 \text{kJ/mol} \]
\[ \Delta G_{f(g)}^o = 8.581 - 237.2 = -228.6 \text{kJ/mol} \]

ANSWER IS: d

6) The equilibrium constant for the reaction
\[
\begin{align*}
\text{I}_2 & \quad + \quad \text{C}_5\text{H}_8 \quad \xleftrightarrow{\text{cyclopentene}} \quad \text{HI} & \quad + \quad \text{C}_5\text{H}_7\text{I} \quad \xleftrightarrow{\text{iodocyclopentene}} \\
\end{align*}
\]

was measured spectrophotometrically in the gas phase between 175°C and 415°C. The following equation was obeyed:

\[
\log_{10} K_p (\text{atm}) = -\frac{2611.4}{T} + 7.55
\]

Calculate \(\Delta H^0\) and \(\Delta S^0\) for this reaction (20 pts) SHOW WORK

a) \(\Delta H^0 = 25.0\) kJ  
   b) \(\Delta H^0 = 50.0\) kJ  
   c) \(\Delta H^0 = 21.7\) kJ  
   d) \(\Delta H^0 = 25.0\) kJ  
   e) \(\Delta H^0 = 50.0\) kJ  

\(\Delta S^0 = 78\) J  
\(\Delta S^0 = 145\) J  
\(\Delta S^0 = 63.0\) J  
\(\Delta S^0 = 145.0\) J  
\(\Delta S^0 = 63.0\) J  

\[
\begin{align*}
\ln K &= \frac{-\Delta G^0}{RT} \\
\log_{10} K &= -\frac{\Delta G^0}{2.303RT} = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \\
-\frac{\Delta H^0}{2.303RT} &= -\frac{2611.4}{T} \quad \text{AND} \quad \frac{\Delta S^0}{2.303R} = 7.55
\end{align*}
\]

\(\Delta H^0 = 50.0\) kJ AND \(\Delta S^0 = 145\) J

(15 pts) ANSWER IS: b

7) If equal pressures (1 atm each) of I\(_2\) and cyclopentene (see question 6) are mixed at 300°C, what will be the equilibrium partial pressure of HI (in atm)? (10 pts) SHOW WORK

a) 0.21  
   b) 0.044  
   c) 0.46  
   d) 0.12  
   e) 0.34

\[
\begin{align*}
\log_{10} K_p (\text{atm}) &= -\frac{2611.4}{300} + 7.55 : \quad K_p = 0.0700 = \frac{x^2}{(1-x)^2} \\
x &= 0.209 \ \text{atm} = P_{\text{HI}} (= 0.21 \ \text{atm})
\end{align*}
\]

(15 pts) ANSWER IS: 0.21

8) If an ideal gas is expanded at constant temperature, then ; (10 pts)

a) \(\Delta E > 0\) and \(\Delta S > 0\)  
   b) \(\Delta E = 0\) and \(\Delta S = 0\)  
   c) \(\Delta E = 0\) and \(\Delta S < 0\)  
   d) \(\Delta E < 0\) and \(\Delta S > 0\)  
   e) \(\Delta E = 0\) and \(\Delta S > 0\)

ANSWER IS: e
9) If $\Delta G^0_f (\text{HI}_g) = 1.70 \text{ kJ}$ what is the equilibrium constant at 25°C for the reaction, $2 \text{ HI}_g \rightleftharpoons \text{ H}_2(g) + \text{ I}_2(s)$? (10 pts)

a) 3.9  

b) 2.0  

c) 0.69  

d) 0.50  

e) 0.25

ANSWER IS: a

10) For the reaction, $\text{ H}_2\text{O}(\ell) \rightleftharpoons \text{ H}_2\text{O}(g)$ at 100°C and 1 atm pressure, which of the following is true; (10 pts)

a) $\Delta H = 0$  

b) $\Delta S = 0$  

c) $\Delta H = \Delta E$  

d) $\Delta H = T\Delta S$  

e) $\Delta H = \Delta G$

ANSWER IS: d

11) For the gas phase decomposition, $\text{ PCl}_5(g) \rightleftharpoons \text{ PCl}_3(g) + \text{ Cl}_2(g)$ (10 pts)

a) $\Delta H < 0$ and $\Delta S < 0$  

b) $\Delta H > 0$ and $\Delta S > 0$  

c) $\Delta H > 0$ and $\Delta S < 0$  

d) $\Delta H < 0$ and $\Delta S > 0$  

e) $\Delta H = 0$ and $\Delta S > 0$

ANSWER IS: b

12) You are given four reactions along with their equilibrium constants and heats of reaction: (10 pts)

<table>
<thead>
<tr>
<th>REACTION</th>
<th>$K$</th>
<th>$\Delta H_{rxn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$K_1$</td>
<td>$\Delta H_1$</td>
</tr>
<tr>
<td>2.</td>
<td>$K_2$</td>
<td>$\Delta H_2$</td>
</tr>
<tr>
<td>3.</td>
<td>$K_3$</td>
<td>$\Delta H_3$</td>
</tr>
<tr>
<td>4.</td>
<td>$K_4$</td>
<td>$\Delta H_4$</td>
</tr>
</tbody>
</table>

You want to combine these four reactions to obtain a fifth reaction.

If for the fifth reaction, $K_5 = \frac{K_2K_3^2}{K_1K_4^2}$, then $\Delta H_5 =$

a) $\Delta H_2 + 2\Delta H_4 - \Delta H_1 - 3\Delta H_3$  

b) $\Delta H_2 + 3\Delta H_4 - \Delta H_1 - 2\Delta H_3$  

c) $\Delta H_1 + 2\Delta H_3 - \Delta H_2 - 3\Delta H_4$  

d) $3\Delta H_2 + \Delta H_4 - \Delta H_1 - 2\Delta H_3$

ANSWER IS: b

13) Correlate each of the curves in the figure with the appropriate reaction.  

20 pts - 5 pts each answer
HINT: \( \ln K_p = -\frac{\Delta H}{RT} + \text{constant} \) (\( y = mx + b \)), and, \( \Delta G^o = -RT \ln K_p \)

\[
\begin{array}{c|c|c|c}
\text{Reaction} & \Delta G^o (kJ) & \Delta H^o (kJ) & \text{ANSWERS} \\
\hline
\text{I} & -16.4 & -41 & b \\
\text{II} & -9.8 & +20 & c \\
\text{III} & -14.8 & +20 & d \\
\text{IV} & -24.6 & -41 & a
\end{array}
\]

GIVEN THE FOLLOWING PISTON FOR USE IN QUESTIONS 14 and 15.

14) A 1.25 L sample of a gas is heated and expands against a constant pressure of 0.86 atm to a final volume of 3.75 L. Calculate the work done by this gas during the expansion in joules. THIS IS QUESTION 54 FROM YOUR TEXTBOOK.

(10 pts)

\[
W = -P_{ex}\Delta V = -(0.86)(3.75 - 1.25)(101.3)
\]

\[
W = -217.8 \text{ J}
\]

ANSWER IS: ______

15) The above piston contains 0.50 mol of an inert gas at an initial temperature of 300 K. An adiabatic expansion now occurs with the volume changing from 1.25 L to 3.75 L at a constant external pressure of 0.86 atm.
Calculate the final temperature, $T_f$ (in Kelvin), in the piston at the end of this expansion. Given: $C_{v,m} = 12.47 \frac{J}{\text{deg mol}}$. (15 pts)

$$\Delta E = nC_{v,m}\Delta T = W \quad \therefore \Delta T = \frac{W}{nC_{v,m}} = \frac{-217.8}{(0.5)(12.47)} = -34.9^\circ = -35^\circ$$

$$\therefore T_f = 265 \text{ K}$$

**ANSWER IS: 265 K**

16) 50.0 g of ice at 0°C are mixed with 40.0 g of liquid (water) at 0°C and an unknown mass of liquid (water) at 75°C. At equilibrium the final temperature of the entire system is 10°C. Calculate the starting mass of liquid at 75°C. (20 pts)

**SHOW WORK**

**GIVEN:** specific heat of liquid = 4.18 J/g·°C; heat of fusion = 333 J/g.

a) 15.0 g  b) 75.1 g  c) 25.5 g  d) 50.1 g  e) 30.2 g

\[ q_1 \quad + \quad q_2 \quad + \quad q_3 \quad + \quad q_4 = 0 \]

\[ (50)(333) + (50)(4.18)(10) + (40)(4.18)(10) + (m)(4.18)(-65) = 0 \]

\[ m = 75.1 \text{ g} \]

**ANSWER IS: b**
BOND ENTHALPIES (kJ/mole)

C-C 348, C=C 610, C≡C 835, C-Cl 339,
C-H 412, H-H 431, O-O 146, O=O 494,
C-O 358, C=O 745, C≡O 1070, O-H 463,
N-H 391, P-H 322, S-H 347, Se-H 276,
Te-H 239, N≡N 945, H-Cl 431, N-N 163,

Using the above table of bond enthalpies, calculate the heat of reaction, \( \Delta H_{\text{rxn}} \), for the gaseous reaction, (20 pts) SHOW WORK

\[
\text{H}_2\text{O}_2 \quad + \quad \text{C}_4\text{H}_6 \quad \longrightarrow \quad \text{C}_4\text{H}_6(\text{OH})_2
\]

where \( \text{C}_4\text{H}_6 \) is \( \text{CH}_3\text{CCCH}_3 \) (one triple bond) and cyclobutadiol (all single bonds) is,

\[
\begin{align*}
&\text{H} \quad \text{H} \\
&\big| \quad \big| \\
&\text{H-O-O-H} & \text{H - C - C + C - C - H} \\
&\text{H} \quad \text{H}
\end{align*}
\]

HINT: FIRST WRITE THE LEWIS STRUCTURE FOR EACH MOLECULE.

BONDS BROKEN (+) 

\[
\begin{align*}
2 \text{ H-O} & \quad 2(463) \\
2 \text{ C-C} & \quad 2(348) \\
6 \text{ C-H} & \quad 6(412) \\
1 \text{ O-O} & \quad 1(146) \\
1 \text{ C+C} & \quad 1(835)
\end{align*}
\]

\[
+ 5075 \text{ kJ}
\]

BONDS FORMED (-)

\[
\begin{align*}
2 \text{ H-O} & \quad 2(-463) \\
2 \text{ C-O} & \quad 2(-358) \\
6 \text{ C-H} & \quad 6(-412) \\
4 \text{ C-C} & \quad 4(-348)
\end{align*}
\]

\[
- 5506 \text{ kJ}
\]

ANSWER IS: -431 kJ

18) Use the following data,

1. \( \text{Fe}_2\text{O}_3(\text{S}) + 3 \text{ CO}(\text{g}) \longrightarrow 2 \text{ Fe}(\text{S}) + 3\text{CO}_2(\text{g}) \quad \Delta H^\circ(\text{kJ}) \quad -30.0 \)
2. \[3 \text{Fe}_2\text{O}_3(S) + \text{CO}_2(g) \rightarrow 2 \text{Fe}_3\text{O}_4(S) + \text{CO}_2(g)\] \[\Delta H_{\text{rxn}} = -57.0 \text{kJ}\]

3. \[\text{Fe}_3\text{O}_4(S) + \text{CO}(g) \rightarrow 3 \text{FeO}(S) + \text{CO}_2(g)\] \[\Delta H_{\text{rxn}} = +42.0 \text{kJ}\]

to determine the heat of reaction, \(\Delta H_{\text{rxn}}^o\), for the reduction of ferrous oxide by carbon monoxide according to:

\[
\text{FeO}_2(S) + \text{CO}_2(g) \rightarrow \text{Fe}(S) + \text{CO}_2(g)
\]

\[
\begin{align*}
\text{a)} & -6.0 \text{kJ} & \text{b)} & +27.0 \text{kJ} & \text{c)} & +6.0 \text{kJ} & \text{d)} & -27.0 \text{kJ} \\
\text{e)} & -19.5 \text{kJ} & \text{f)} & +19.5 \text{kJ} & \text{g)} & +3.0 \text{kJ} & \text{h)} & -3.0 \text{kJ}
\end{align*}
\]

\[
\frac{1}{3}(-3) \quad \text{FeO}_2(S) + \frac{1}{3} \text{CO}_2(g) \rightarrow \frac{1}{3} \text{Fe}_3\text{O}_4(S) + \frac{1}{3} \text{CO}_2(g) \quad \frac{1}{3}(-42.0)
\]

\[
\frac{1}{2}(1) \quad \frac{1}{2} \text{Fe}_2\text{O}_3(S) + \frac{3}{2} \text{CO}_2(g) \rightarrow \text{Fe}(S) + \frac{3}{2} \text{CO}_2(g) \quad \frac{1}{2}(-30.0)
\]

\[
\frac{1}{6}(-2) \quad \frac{1}{3} \text{Fe}_3\text{O}_4(S) + \frac{1}{6} \text{CO}_2(g) \rightarrow \frac{1}{2} \text{Fe}_2\text{O}_3(S) + \frac{1}{6} \text{CO}_2(g) \quad \frac{1}{6}(+57.0)
\]

\[
\text{FeO}_2(S) + \text{CO}_2(g) \rightarrow \text{Fe}(S) + \text{CO}_2(g) \quad \Delta H_{\text{rxn}}^o = -19.5 \text{kJ}
\]

\text{ANSWER IS: e}