EXAM 3
CH353 (51635) – Physical Chemistry I
Webb, Fall 2010
28 October 2010

Name:

You may use a 8.5 x 11 in sheet of paper for a crib sheet.

Always assume ideal gas unless directed otherwise.

Honor Code:

"The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community."

I certify that the work on this exam is entirely my own.

_________________________________________  ___________________________ 
Signature                                      Date
1. (18 points) Indicate whether the following statements are true or false.

a. True  
If one mole of an ideal gas is expanded reversibly and isothermally from 10 L to 20 L, \( \Delta S < 0 \). \( \nu_f > \nu_i \), \( \Delta S > 0 \). False

b. True  
When solid ice melts to liquid water, \( \Delta S_{sys} > 0 \) always. False

c. True  
Temperature is a natural variable of Gibbs free energy. False

d. True  
The chemical potential of a pure substance is equal to the molar Gibbs energy of that substance. False

e. True  
The Helmholtz free energy defines the minimum reversible work a system can perform. False

f. True  
For a non-ideal gas that is dominated by repulsive forces, internal pressure will be greater than zero always. False

2. (15 points) Prove that each of the following are true:

a. \( \frac{\partial S}{\partial U}_V = \frac{1}{T} \)
\[ dU = TdS - PDV \]
\[ (\frac{\partial U}{\partial S})_V = \frac{1}{T} \]
\[ (\frac{\partial S}{\partial U})_V = \frac{1}{T} \]

b. \( C_p = T \left( \frac{\partial S}{\partial T}_p \right) \)
\[ dS = dq/V \]
\[ dq = C_p dT \] (\text{const. } V)

\[ dS = C_p dT \]
\[ \Rightarrow T \left( \frac{\partial S}{\partial T}_p \right)_V = C_p \]

c. \( C_p - C_v = -T \left( \frac{\partial V}{\partial T}_p \right)^2 \left( \frac{\partial P}{\partial V}_T \right) \)
\[ dV = \left( \frac{\partial V}{\partial T}_p \right)_T dT + \left( \frac{\partial V}{\partial P}_T \right)_V dP \]
\[ dV \text{ is by } T \text{ at } dV = 0: \quad 0 = \left( \frac{\partial V}{\partial T}_p \right)_V \left( \frac{\partial P}{\partial V}_T \right)_V \]
\[ \text{rearranging: } \left( \frac{\partial P}{\partial V}_T \right)_V = -\left( \frac{\partial V}{\partial T}_p \right)_T \]
3. (18 points) Determine the effect of any change in volume on the internal energy of a gas that obeys the following equation of state:

\[ P(V_m - B) = RT \]

were \( B < 0 \) always.

\[
\left( \frac{\partial U}{\partial V} \right)_T = ?
\]

\[
dU = TdS - PdV
\]

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P
\]

\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V
\]

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \quad \quad P = \frac{RT}{V_m - B}
\]

\[
\left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{V_m - B}
\]

\[
\left( \frac{\partial U}{\partial V} \right)_T = \frac{TR}{V_m - B} - P = \frac{TR}{V_m - B} - \frac{TR}{V_m - B} = 0
\]

\[
\left( \frac{\partial U}{\partial V} \right)_T = 0
\]
4. (18 points) Determine the maximum amount of non-expansion work that can be obtained from a device in which the chemical reaction is the combustion of ethanol at 298 K.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$S_m^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$\rho$ (g mL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol (CH$_3$CH$_2$OH(l))</td>
<td>-278.7</td>
<td>160.7</td>
<td>0.8</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>-393.5</td>
<td>213.7</td>
<td>1.9 x 10$^3$</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>0</td>
<td>205.2</td>
<td>1.4 x 10$^3$</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>-241.8</td>
<td>188.8</td>
<td>0.4 x 10$^3$</td>
</tr>
</tbody>
</table>

$$w_{max, add} = \Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T \Delta S_{rxn}^\circ$$

$$CH_3COH + 3O_2 \rightarrow 3H_2O + 2CO_2$$

$$\Delta H_{rxn}^\circ = 2\Delta H^\circ(\text{O}_2) + 3\Delta H^\circ(\text{H}_2\text{O}_g) - \Delta H^\circ(\text{EtOH}) =$$

$$\Delta S_{rxn}^\circ = 2\Delta S^\circ(\text{O}_2) + 3\Delta S^\circ(\text{H}_2\text{O}) - \Delta S^\circ(\text{EtOH}) - 3\Delta S^\circ(\text{O}_2) =$$

$$\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - (298 K)(\Delta S_{rxn}^\circ) =$$
5. (18 points) A gas is expanded isothermally from 10 L to 20 L. Is the change in entropy of the gas greater if it is behaving as an ideal gas or a van der Waals gas?

\[
\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad / \quad AS = k_B \ln \left(\frac{V_T}{V_i}\right)
\]

**vdW:**
\[
P = \frac{RT}{V_n - b} - \frac{a}{V_n^2} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_n - b} \quad AS = k_B \ln \left(\frac{V_T - b}{V_i - b}\right)
\]

**Ideal:**
\[
P = \frac{RT}{V_n} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_n} \quad AS = k_B \ln \left(\frac{V_T}{V_i}\right)
\]

Because \(V_n - b < V_n\), \(\left(\frac{\partial P}{\partial T}\right)_V\) will be larger for a vdW gas than an ideal gas, and \(\left(\frac{\partial S}{\partial V}\right)_T \text{(vdW)}\) will be \(>\) \(\left(\frac{\partial S}{\partial V}\right)_T \text{(ideal)}\).

6. (13 points) Determine the change in Gibbs free energy when the pressure of hydrogen gas is increased isothermally and reversibly from 1.0 atm 100.0 atm at 298 K. Explicitly justify the sign of the change.

\[
dG = -SdT + VdP
\]

\[
P = nRT
\]

\[
dG = VdP = \frac{nRTdP}{P}
\]

\[
AG = nRT \ln \left(\frac{P_T}{P_i}\right) = 11410 \text{ J/mol}
\]

\(AG > 0\) because this is not spontaneous.