Chem 107 - Hughbanks
Exam 3, April 14, 2016

Name (Print) ____________________________ KEY ____________________________

UIN # ____________________________

Section 502
Exam 3, Version A

On the last page of this exam, you’ve been given a periodic table and some physical constants. You’ll probably want to tear that page off the to use during the exam – you don’t need to turn it in with the rest of the exam.

The exam contains 9 problems, with 8 numbered pages. You have the full 75 minutes to complete the exam. Please show ALL your work as clearly as possible – this will help us award you partial credit if appropriate. Even correct answers without supporting work may not receive credit. You may use an approved calculator for the exam, one without extensive programmable capabilities or the ability to store alphanumeric information. Print your name above, provide your UIN number, and sign the honor code statement below.

On my honor as an Aggie, I will neither give nor receive unauthorized assistance on this exam.

SIGNATURE: ____________________________
(1) (20 pts) For (a) – (e), fill in the blanks. (Please enter just one word in each blank. You may use the same word more than once if appropriate. 2 points for each blank.) BE SURE THAT YOU READ EACH STATEMENT VERY CAREFULLY.

(a) The calorimetry experiment performed at constant __PRESSURE__ would be a good way of measuring $\Delta H$ for a chemical reaction.

(b) A solid material with a modest, but nonzero, electronic energy band gap is likely to exhibit the electrical conductivity properties typical of a(n) ____ SEMICONDUCTOR _____.

(c) For a spontaneous solution-phase exothermic reaction at room temperature, we can’t know whether the change in ____ ENTROPY ____ of the system is positive or negative without more information.

(d) In graphite, each carbon atom is covalently bonded to ____THREE____ neighboring carbon atoms.

(e) At absolute zero (0 K), the standard molar ____ ENTROPY ____ of a defect-free crystal of a pure substance is zero.

For (f) – (j). Consider each of the following thermodynamic quantities, and decide whether it should be positive, negative, or zero. (Enter either +, −, or 0 in the blank. 2 points each.)

$\Delta S^\circ$ for a spontaneous endothermic reaction.

(g) $\Delta G^\circ$ for a spontaneous endothermic reaction.

(h) The heat of formation, $\Delta H_f^\circ$, of an element in its most stable form at room temperature and pressure.

(i) $\Delta H^\circ$ for the conversion of a gas to a liquid.

(j) $\Delta S^\circ$ for the conversion of a gas to a liquid.
(2) (a) (5 pts) The standard state of carbon is graphite, and diamond is another form of pure elemental carbon. Write a chemical equation for the formation reaction for diamond.

\[ \text{C (s, graphite)} \rightarrow \text{C (s, diamond)} \]

(b) (7 pts) The standard enthalpy changes for several reactions are shown below. Use any or all of these data to find the enthalpy of formation of diamond. Enter your answer in the blank below.

\[
\begin{align*}
\text{C (diamond) + O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -395.4 \text{ kJ} \\
2 \text{CO}_2(g) & \rightarrow 2 \text{CO (g) + O}_2(g) \quad \Delta H^\circ = 566.0 \text{ kJ} \\
\text{C (graphite) + O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -393.5 \text{ kJ} \\
2 \text{CO (g) } & \rightarrow \text{C (graphite) + CO}_2(g) \quad \Delta H^\circ = -172.5 \text{ kJ} \\
\text{C (graphite) + O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -393.5 \text{ kJ} \\
\text{CO}_2(g) & \rightarrow \text{C (diamond) + O}_2(g) \quad \Delta H^\circ = +395.4 \text{ kJ} \\
& \quad \Delta H^\circ = 1.9 \text{ kJ}
\end{align*}
\]

Ans. 2b_____________
(3) (6 pts) For which one of the following processes/reactions is $\Delta S$ largest? (Circle the correct answer.)

(A) $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$

(B) $\text{HNC}(g) \rightarrow \text{HCN}(g)$

(C) $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(\ell)$

(D) $\text{C(s, diamond)} \rightarrow \text{C(s, graphite)}$

(E) $\text{CaO}(s) + \text{SiO}_2(s) \rightarrow \text{CaSiO}_3(s)$

(4) (10 points) What will be the final temperature of a well-stirred mixture made from equal masses of the following: water at 25.0 °C, benzene at 40.0 °C, and iron at 95.0 °C? None of these substances are miscible (they don’t form a solution, i.e., there is complete heat transfer, but they remain as separate substances).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat, $c$ (J g$^{-1}$ K$^{-1}$)</th>
<th>Molar Heat Capacity, $C_P$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe(s)}$</td>
<td>0.444</td>
<td>24.8</td>
</tr>
<tr>
<td>$\text{H}_2\text{O(ℓ), water}$</td>
<td>4.184</td>
<td>75.3</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_6(\ell), benzene}$</td>
<td>1.74</td>
<td>136</td>
</tr>
</tbody>
</table>

$q_{\text{Fe}} + q_{\text{H}_2\text{O}} + q_{\text{benzene}} = 0$

$m_{\text{Fe}}c_{\text{Fe}}\Delta T + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}\Delta T + m_{\text{benzene}}c_{\text{benzene}}\Delta T = 0$

$(1.0 \text{ g})(0.444 \text{ J} \text{g}^{-1}\text{K}^{-1})\Delta T_{\text{Fe}} + (1.0 \text{ g})(4.184 \text{ J} \text{g}^{-1}\text{K}^{-1})\Delta T_{\text{H}_2\text{O}} + (1.0 \text{ g})(1.74 \text{ J} \text{g}^{-1}\text{K}^{-1})\Delta T_{\text{benzene}} = 0$

$0.444\Delta T_{\text{Fe}} + 4.184\Delta T_{\text{H}_2\text{O}} + 1.74\Delta T_{\text{benzene}} = 0$

$0.444(T_f - 368.15 \text{ K}) + 4.184(T_f - 298.15 \text{ K}) + 1.74(T_f - 313.15 \text{ K}) = 0$  

$0.444T_f - 163.39 + 4.184T_f - 1246.83 + 1.74T_f - 544.62 = 0$

$T_f = \frac{163.39 + 1246.83 + 544.62}{0.444 + 4.184 + 1.74} = \frac{1954.84}{6.368} = 306.98 = 307 \text{ K}$

$T_f = 306.98 \text{ K} = 34.0 \text{ °C}$
5) (10 points) In lecture, we used the van der Waals equation of state to introduce the corrections to ideal-gas law behavior due to the effects of attractive intermolecular forces (parameter $a$) and the fraction of a container’s volume that gas molecules exclude other gas molecules from occupying (parameter $b$). Using the notation $V_m = V/n$ (the volume per mole of gas), the van der Waals equation of state is

$$\left( P + \frac{a}{V_m^2} \right)(V_m - b) = RT. $$

The following table, adapted from your text and lecture notes, is incomplete. There are five missing boiling points $T_b$ (20.3, 90.2, 112, 293, 373) and five missing substances (He, Ar, HF, NH$_3$, H$_2$). **In the blanks below, fill in the missing data.** To do this, choose from lists of missing boiling points and missing substances (given again below the table).

<table>
<thead>
<tr>
<th>Gas</th>
<th>$a$ (atm L$^2$ mol$^{-2}$)</th>
<th>$b$ (L mol$^{-1}$)</th>
<th>$T_b$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, CH$_4$</td>
<td>2.253</td>
<td>0.04278</td>
<td>112</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.2444</td>
<td>0.02661</td>
<td>20.3</td>
</tr>
<tr>
<td>Sulfur dioxide, SO$_2$</td>
<td>6.714</td>
<td>0.05636</td>
<td>263</td>
</tr>
<tr>
<td>HF</td>
<td>9.433</td>
<td>0.0739</td>
<td>293</td>
</tr>
<tr>
<td>Nitrogen, N$_2$</td>
<td>1.390</td>
<td>0.03913</td>
<td>77.4</td>
</tr>
<tr>
<td>He</td>
<td>0.034</td>
<td>0.0237</td>
<td>4.2</td>
</tr>
<tr>
<td>Water, H$_2$O</td>
<td>5.464</td>
<td>0.03049</td>
<td>373</td>
</tr>
<tr>
<td>Oxygen, O$_2$</td>
<td>1.360</td>
<td>0.03183</td>
<td>90.2</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>4.170</td>
<td>0.03707</td>
<td>240</td>
</tr>
<tr>
<td>Ar</td>
<td>1.345</td>
<td>0.03219</td>
<td>87.3</td>
</tr>
<tr>
<td>Carbon dioxide, CO$_2$</td>
<td>3.592</td>
<td>0.04267</td>
<td>195 \footnotesize{(sublimes)}</td>
</tr>
</tbody>
</table>


Missing substances: He, Ar, H$_2$, HF, NH$_3$. 


(6) (10 points) Methylhydrazine (CH₆N₂) and N₂O₄ can be used as a hypergolic rocket fuel, which means the mixture ignites immediately when the two reactants come into contact. An equation for the reaction is shown below, along with some related thermochemical data.

4 CH₆N₂(l) + 5 N₂O₄(l) → 4 CO₂(g) + 12 H₂O(g) + 9 N₂(g)

<table>
<thead>
<tr>
<th>Compound</th>
<th>CH₆N₂(l)</th>
<th>N₂O₄(l)</th>
<th>CO₂(g)</th>
<th>H₂O(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH°, kJ mol⁻¹</td>
<td>54.14</td>
<td>-19.56</td>
<td>-393.5</td>
<td>-241.818</td>
</tr>
</tbody>
</table>

Use the information given above as needed to find the amount of heat released when 2.5 kg of CH₆N₂ reacts with excess N₂O₄ according to the equation above.

\[
\Delta H_{rxn} = \sum \Delta H°_{products} - \sum \Delta H°_{reactants}
\]

\[
\Delta H°_{rxn} = n_{CO_2} \Delta H°(CO_2) + n_{H_2O} \Delta H°(H_2O) - n_{N_2O_4} \Delta H°(N_2O_4) - n_{CH_6N_2} \Delta H°(CH_6N_2)
\]

\[
\Delta H°_{rxn} = 4(-393.5) + 12(-241.818) - 4(54.14) - 5(-19.56)
\]

\[
\Delta H°_{rxn} = -1574.0 - 2901.8 - 97.8 - 216.56 = -4594.58 \text{ kJ}
\]

Molar mass CH₆N₂ = 12.00 g/mol + 6(1.008 g/mol) + 2(14.01 g/mol) = 46.07 g/mol

Moles of CH₆N₂ = \[
\frac{2500 \text{ g}}{46.07 \text{ g mol}^{-1}} = 54.27 \text{ mol}
\]

\[
\Delta H°_{rxn} = \frac{54.27}{4} (-4594.58 \text{ kJ})
\]

\[
\Delta H°_{rxn} = 62337 \text{ kJ}
\]
(7) (10 points) For the reaction between methane and chlorine shown below, \( \Delta H^\circ = -305.2 \text{ kJ} \).

\[
\text{CH}_4(\text{g}) + 3 \text{Cl}_2(\text{g}) \rightarrow \text{CHCl}_3(\text{g}) + 3 \text{HCl}(\text{g})
\]

Use the data in the table below to estimate the average C–Cl bond energy.

<table>
<thead>
<tr>
<th>Type of bond</th>
<th>Average bond energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td>413</td>
</tr>
<tr>
<td>Cl–Cl</td>
<td>243</td>
</tr>
<tr>
<td>H–Cl</td>
<td>432</td>
</tr>
</tbody>
</table>

\[
\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ (\text{bonds breaking}) - \Sigma \Delta H^\circ (\text{bonds forming})
\]

\[
3(\Delta H^\circ_{\text{C-H}}) + 3(\Delta H^\circ_{\text{Cl-Cl}}) - 3(\Delta H^\circ_{\text{C-Cl}}) - 3(\Delta H^\circ_{\text{H-Cl}}) = -305.2 \text{ kJ}
\]

\[
3(413) + 3(243) - 3(\Delta H^\circ_{\text{C-Cl}}) - 3(432) = -305.2 \text{ kJ}
\]

\[
1239 \text{ kJ} + 729 \text{ kJ} - 3(\Delta H^\circ_{\text{C-Cl}}) - 1296 \text{ kJ} = -305.2 \text{ kJ}
\]

\[
3\left(\Delta H^\circ_{\text{C-Cl}}\right) = 977.2 \text{ kJ}
\]

\[
\Delta H^\circ_{\text{C-Cl}} = 326 \text{ kJ}
\]
(8) (7 points) Draw an energy band diagram appropriate for boron-doped silicon. In your drawing be sure to

- Draw and label the vertical axis
- Label the valence and conduction bands
- Show filled energy levels as ‘shaded’, leave unfilled energy levels ‘un-shaded’.
- Show the effect of the boron-doping on the band filling.
- Pure silicon absorbs light at wavelength of 1139 nm (and shorter). Using this information, quantitatively label your energy band diagram in an appropriate way.
- Write a sentence indicating whether this material is p-doped or n-doped.

**The material is p-doped. Boron-doping creates holes in the valence band.**
(9) (15 points) Of all metals, mercury has the lowest melting point and is a liquid at room temperature. Mercury has a low, but not completely negligible vapor pressure at room temperature (~0.002 torr) and it can pose some danger when people are chronically exposed to it in poorly ventilated areas.

(a) (10 pts) Use the table below to calculate estimates for the melting and boiling points, \( T_m \) and \( T_b \), of mercury in °C.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_f^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta G_f^\circ ) (kJ mol(^{-1}))</th>
<th>( S^\circ ) (J mol(^{-1}) K(^{-1}))</th>
<th>( C_p^\circ ) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(s)</td>
<td>-2.295</td>
<td>0.605</td>
<td>66.30</td>
<td>28.48</td>
</tr>
<tr>
<td>Hg(l)</td>
<td>0</td>
<td></td>
<td>76.03</td>
<td>27.98</td>
</tr>
<tr>
<td>Hg(g)</td>
<td>61.32</td>
<td>31.82</td>
<td>174.96</td>
<td>20.79</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\Delta H_{298} &= \Delta H_f^\circ_{g,as} - \Delta H_f^\circ_{l,liquid} \\
\Delta H_{298} &= 61.31 - 0 = 61.32 \text{ kJ mol}^{-1} = 62320 \text{ J mol}^{-1} \\
\Delta S_{298} &= 174.96 - 76.03 = 98.93 \text{ J mol}^{-1} \text{ K}^{-1} \\
\Delta G_{298} &= \Delta H_{298} - T_b \Delta S_{298} = 0 \\
\Delta H_{298} &= T_b \Delta S_{298} \\
T_b &= \frac{\Delta H_{298}}{\Delta S_{298}} = \frac{62320 \text{ J mol}^{-1}}{98.93 \text{ J mol}^{-1} \text{ K}^{-1}} = 620 \text{ K} \\
T_b &= 620 \text{ K} = 346.85 \text{ °C} \\
T_b &= 346.85 \text{ °C}
\end{align*}
\]

\[
\begin{align*}
\Delta H_{298} &= 0 - (-2.295) = 2.295 \text{ kJ mol}^{-1} = 2295 \text{ J mol}^{-1} \\
\Delta S_{298} &= 76.03 - 66.03 = 9.73 \text{ J mol}^{-1} \text{ K}^{-1} \\
\Delta H_{298} &= T_m \Delta S_{298} \\
T_m &= \frac{\Delta H_{298}}{\Delta S_{298}} = \frac{2295 \text{ J mol}^{-1}}{9.73 \text{ J mol}^{-1} \text{ K}^{-1}} = 235 \text{ K} \\
T_m &= 235 \text{ K} = -38.15 \text{ °C} \\
T_m &= -38.15 \text{ °C}
\end{align*}
\]

(b) (5 pts) Explain why these are just estimates and indicate which you think is the best estimate, \( T_m \) or \( T_b \). A one- or two-sentence explanation is all that is necessary.

These calculations assume that \( \Delta H^\circ \) and \( \Delta S^\circ \) (which are values for \( \Delta H \) and \( \Delta S \) at 298 K) don’t change very much at other temperatures. That assumption is best when the temperature isn’t too far from 298 K. The estimated melting point, \( T_m \), is much closer to 298 K than the estimated boiling point, \( T_b \), so \( T_m \) is the better estimate.