Chem 107 - Hughbanks
Exam 3A, Solutions

Name (Print) ____________________________

UIN # ____________________________

Section 503
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 11 problems, with 7 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) (6 pts) For a given reaction or a process such as a phase change, which of the following system state functions is equal to the heat transferred to the system in an experiment conducted in a coffee-cup calorimeter? (Put the letter of the correct answer in the blank provided.)

(A) \( \Delta H \)  (B) \(-\Delta H\)  (C) \(-\Delta G\)  (D) \(\Delta E\)  (E) \(\Delta G\)  (F) \(\Delta S\)

Ans. 1  \[A\]

(2) (6 pts) Which of the following substances will form intermolecular hydrogen bonds in the liquid state? If more than one substance is correct, put all the correct choices in the blank below.

(A) CH\(_3\)OH (methanol)  (B) HF  (C) CH\(_3\)OCH\(_3\)
(D) CH\(_3\)CO\(_2\)H (acetic acid)  (E) Br\(_2\)  (F) CH\(_4\)

Ans. 2  \[A, B, D\]

(3) (8 pts) 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 and the fraction of a container’s volume that gas molecules occupy. The van der Waals equation of state (for one mole of gas) is

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

Consider the following five substances:

(A) He  (B) H\(_2\)  (C) CO\(_2\)  (D) H\(_2\)O  (E) N\(_2\)

(a) Use the letters, A through E, to put these in order of increasing \(a\) values:

\[A < B < E < C < D\]

(b) Use the letters, A through E, to put these in order of increasing \(b\) values:

\[A < B < D < E < C\]
(4) (6 pts) For which one of the following processes/reactions is the difference between $\Delta H$ and $\Delta E$ largest? (Put the letter of the correct answer in the blank provided.)

(A) $\text{CaH}_2(s) + \text{O}_2(g) \rightarrow \text{CaO}(s) + \text{H}_2\text{O}(g)$
(B) $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(g)$
(C) $\text{I}_2(s) \rightarrow \text{I}_2(\ell)$
(D) $\text{C(diamond)} \rightarrow \text{C(graphite)}$
(E) $\text{CaO}(s) + \text{SiO}_2(s) \rightarrow \text{CaSiO}_3(s)$

Ans. 4___B___

(5) (7 pts) Phosphorus forms white crystals made of $\text{P}_4$ molecules. There are two forms of white crystalline phosphorus called “$\alpha$” and “$\beta$”. The difference between $\alpha$-$\text{P}_4$ and $\beta$-$\text{P}_4$ relates to the way the $\text{P}_4$ molecules pack together to form crystals. The $\alpha$ form is always obtained when liquid phosphorus freezes. However, at temperatures below $–77 ^\circ \text{C} (196 \text{ K})$, $\alpha$-$\text{P}_4$ crystals spontaneously change to $\beta$-$\text{P}_4$:

$$\alpha$-\text{P}_4 \xrightarrow{T < 196 \text{ K}} \beta$-\text{P}_4$

For the conversion of $\alpha$-$\text{P}_4$ to $\beta$-$\text{P}_4$, which of the following statements is true?

(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) $\Delta H > T\Delta S$, when $T < 196 \text{ K}$.

(Put the letter of the answer in the blank provided.)

Ans. 5___(b)___

(6) (9 pts) Which of the molecules below possess a dipole moment? Provide letters for all the correct answers in the space provided.

(A) $\text{NH}_3$ (B) $\text{CF}_4$ (C) $\text{SO}_2$

(D) $\text{F}_2\text{C}=\text{CF}_2$ (E) $\text{BrF}$ (F) $\text{CO}_2$

Ans. 6___A, C, E___
7) (8 pts) Fill in the blanks using terms selected from the list below. In each space provided, put in the letter corresponding to the best word or phrase. PLEASE, DO NOT ATTEMPT to put in the word or phrase since there is not enough space provided for that.

(A) The van der Waals equation of state for a non-ideal gas is \[ P + \frac{a}{V_m^2} \left( V_m - b \right) = RT. \] (Recall that \( V_m = V/n \), the volume per mole of gas). The parameter \( a \) accounts for \((e)\) and the parameter \( b \) accounts for \((g)\).

(B) If pure silicon is doped with a trace of boron, a \((n)\) semiconductor will be formed and a Lewis diagram showing the boron environment would have a \((d)\) formal charge on the boron atom.

(C) The second law of thermodynamics guarantees that for a spontaneous process, \((x)\) must be negative and \((t)\) must be positive.

(D) The NO molecule has \((i)\) unpaired electron(s). The highest occupied orbitals have \((o)\) character.

(a) n-type  
(b) p-type  
(c) positive  
(d) negative  
(e) intermolecular forces  
(f) Coulomb repulsions  
(g) molecular volume  
(h) zero  
(i) one  
(j) two  
(k) three  
(l) four  
(m) σ-bonding  
(n) σ-antibonding  
(o) π-antibonding  
(p) π-bonding  
(q) nonbonding  
(r) ΔS_sys  
(s) ΔS_surr  
(t) ΔS_univ  
(u) ΔH_sys  
(v) ΔH_surr  
(w) ΔH_univ  
(x) ΔG_sys  
(y) ΔG_surr  
(z) ΔG_univ
Questions 8-10 – show all work (50 pts)

(8) (13 pts) A material for use in an electronics application is prepared by doping germanium (Ge) with arsenic (As).

(a) (6 pts) Draw a schematic energy diagram for this material (use shading to indicate filled energy levels).

See Lecture Notes or the text

(b) (4 pts) Provide a vertical axis label for your diagram and label the valence band, conduction band, and the band gap.

(c) (3 pts) Circle the phrase that best describes this material?

- insulator
- metal
- n-type semiconductor
- p-type semiconductor
- positively-charged solid
- negatively-charged solid
(9) (11 pts) Nitrogen, N₂, is one of the top chemicals produced in industry. The nitrogen phase diagram is shown below. ΔHₘₚ(N₂) and ΔHᵥₚ(N₂) are the respective enthalpy changes for melting and boiling one mole of N₂ at 1.0 atm pressure.

![Nitrogen phase diagram](image)

**Important information:**

\[
\Delta H_{\text{fus}}(N₂) = 0.721 \text{ kJ/mol} \quad \quad \Delta H_{\text{vap}}(N₂) = 5.565 \text{ kJ/mol}
\]

\[S°(N₂) = 191.61 \text{ J/mol•K} \]

(a) (3 pts) What phases of matter (gas, liquid, solid) are stable in regions A, B, and C (fill in the blanks)

A: ____ solid ____ B: ____ liquid ____ C: ____ gas ____

(b) (8 pts) From the information given, calculate ΔSₘₚ(N₂) and ΔSᵥₚ(N₂) for P = 1.0 atm.

Both melting and boiling are processes involving equilibrium: N₂(s) ⇌ N₂(l) ; N₂(l) ⇌ N₂(g). For both then, \( \Delta G = \Delta H - T\Delta S = 0 \Rightarrow \Delta H_{\text{fus}} = T\Delta S_{\text{fus}} \quad \Delta H_{\text{vap}} = T\Delta S_{\text{vap}} \) Thus,

\[
\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} = \frac{721 \text{ J/mol}}{63.14 \text{ K}} = 11.4 \text{ J/mol•K} \quad \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} = \frac{5565 \text{ J/mol}}{77.36 \text{ K}} = 71.9 \text{ J/mol•K}
\]
(10) (16 pts) Using the thermodynamic data given, estimate the temperature range over which each of the following two reactions is spontaneous. Show your work and clearly circle your answer.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta G^\circ ) (kJ mol(^{-1}))</th>
<th>( S^\circ ) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(s)</td>
<td>28.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlCl(_3)(s)</td>
<td>-704.2</td>
<td>-628.9</td>
<td>110.7</td>
</tr>
<tr>
<td>Cl(_2)(g)</td>
<td></td>
<td></td>
<td>223.0</td>
</tr>
<tr>
<td>H(_2)(g)</td>
<td></td>
<td></td>
<td>130.6</td>
</tr>
<tr>
<td>H(_2)O(g)</td>
<td>-241.8</td>
<td>-228.6</td>
<td>188.7</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>-285.8</td>
<td>-237.2</td>
<td>69.91</td>
</tr>
<tr>
<td>NH(_3)(g)</td>
<td>-46.11</td>
<td>-16.55</td>
<td>192.3</td>
</tr>
<tr>
<td>NO(g)</td>
<td>90.25</td>
<td>86.57</td>
<td>210.7</td>
</tr>
<tr>
<td>NOCl(g)</td>
<td>52.59</td>
<td>66.36</td>
<td>264</td>
</tr>
<tr>
<td>P(g)</td>
<td>5.4</td>
<td>13</td>
<td>163.1</td>
</tr>
<tr>
<td>PH(_3)(g)</td>
<td></td>
<td></td>
<td>210.1</td>
</tr>
</tbody>
</table>

(a) \( 2 \text{ Al(s)} + 3 \text{ Cl}_2(g) \rightarrow 2 \text{ AlCl}_3(s) \)

\[
\Delta H^\circ = (2 \text{ mol})(-704.2 \text{ kJ mol}^{-1}) = -1408.4 \text{ kJ}
\]

\[
\Delta S^\circ = 2 \times 110.7 - 3 \times 223.0 - 2 \times 28.3 = -504.2 \text{ J K}^{-1}
\]

\( \Delta G \) is dominated by \( \Delta H \) at low T, and since \( \Delta H < 0 \), the reaction is spontaneous at low T. Since \( \Delta S < 0 \), \( \Delta G \) will increase until \( \Delta G = 0 \). The temp. at which that will occur is estimated as

\[
\Delta G \equiv \Delta H^\circ - T \Delta S^\circ = 0 \quad T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{1408.4}{0.5042} = 2793 \text{ K}
\]

Above about 2800 K, the reaction is not spontaneous.

(b) \( 2 \text{ NOCl(g)} \rightarrow 2 \text{ NO(g)} + \text{ Cl}_2(g) \)

\[
\Delta H^\circ = (2 \text{ mol})(90.25 \text{ kJ mol}^{-1}) - (2 \text{ mol})(52.59 \text{ kJ mol}^{-1}) = +75.32 \text{ kJ}
\]

\[
\Delta S^\circ = 2 \times 210.7 + 1 \times 223.0 - 2 \times 264 = +116.4 \text{ J K}^{-1}
\]

\( \Delta G \) is dominated by \( \Delta H \) at low T, and since \( \Delta H > 0 \), the reaction is not spontaneous at low T. Since \( \Delta S > 0 \), \( \Delta G \) will decrease with increasing T until \( \Delta G = 0 \). The temp. at which that will occur is estimated as

\[
\Delta G \equiv \Delta H^\circ - T \Delta S^\circ = 0 \quad T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{75.32}{0.1164} = 647 \text{ K}
\]

Above about 650 K, the reaction becomes spontaneous.
(11) (10 pts) A piece of titanium metal with a mass of 23.96 g is heated in boiling water to 99.5 °C then dropped into a coffee cup calorimeter containing 86.4 g of water at 21.7 °C. When thermal equilibrium is reached, the final temperature is 24.3 °C. Neglect the effect of the calorimeter constant. (The specific heat capacity of water is 4.184 J g⁻¹ K⁻¹). Calculate the molar heat capacity of titanium.

For the titanium, \( \Delta T = -75.2 \) K ; for the water, \( \Delta T = +2.6 \) K

\[
-q_{Ti} = q_{H_2O}
\]

\[
-m_{Ti}c_{Ti}\Delta T_{Ti} = m_{H_2O}c_{H_2O}\Delta T_{H_2O}
\]

\[
c_{Ti} = -(m_{H_2O}c_{H_2O}\Delta T_{H_2O})/(m_{Ti}\Delta T_{Ti}) = -(86.4 \text{ g})(4.184 \text{ J g}^{-1} \text{ K}^{-1})(2.6 \text{ K})/(23.96 \text{ g})(-75.2 \text{ K})
\]

specific heat capacity of Ti = \( c_{Ti} = 0.522 \text{ J g}^{-1} \text{ K}^{-1} \)

The molar heat capacity is \((47.88 \text{ g mol}^{-1})(0.522 \text{ J g}^{-1} \text{ K}^{-1}) = 24.98 \text{ J mol}^{-1} \text{ K}^{-1}\)
### Physical Constants/Conversion Factors

- **Mass of p = 1.0070 amu**
- **1 kg = 1.6749 × 10⁻²⁷ kg**
- **Mass of e = 0.00055 amu**
- **Mass of d = 1.0036 amu**
- **1.00 amu = 2.23 kg**
- **1.00 atm = 760 torr**
- **1.00 lb = 554 grain**
- **1.00 ft = 30.5 cm**
- **1.00 in = 2.54 cm**
- **1.00 in ³ = 1.64 cm³**
- **1.00 ft³ = 1.728 cm³**
- **Avogadro's number = 6.023 × 10²³**
- **Speed of light = 3.00 × 10⁸ m/s**

### Madelung Constants

- **Madelung constant for NaCl = 0.951**
- **Madelung constant for KCl = 0.956**
- **Madelung constant for NaF = 0.959**
- **Madelung constant for KBr = 0.962**
- **Madelung constant for CsI = 0.965**

### Physical Properties

- **Density of water at 4°C = 1.000 g/cm³**
- **Density of ice at 4°C = 0.917 g/cm³**
- **Density of air at 0°C and 1 atm = 0.001225 g/cm³**
- **Density of hydrogen at 0°C and 1 atm = 0.08988 g/cm³**
- **Density of helium at 0°C and 1 atm = 0.1785 g/cm³**

### Conversion Factors

- **1 inch = 2.54 cm**
- **1 foot = 0.3048 m**
- **1 yard = 0.9144 m**
- **1 mile = 1.6093 km**
- **1 gallon = 3.785 liters**
- **1 liter = 0.001 cubic meter**

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**Note:** The image includes a periodic table and some physical properties, but the main focus is on the conversion factors and physical constants.