**Chem 102H**  
**Exam 1 - Spring 2005**

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**PHYSICAL CONSTANTS/CONVERSION FACTORS**

- Speed of light = $3.00 \times 10^8$ m/s
- Planck's constant = $6.63 \times 10^{-34}$ J·s
- Avogadro's Number = $6.02 \times 10^{23}$
- Electron charge = $1.602 \times 10^{-19}$ C
- Faraday's constant = $96487$ C mol$^{-1}$ (e–)
- Mass of e = 0.00055 amu
- Mass of p = 1.0073 amu
- Mass of n = 1.0087 amu
- Mass of p = 1.0086 amu
- Mass of n = 1.0087 amu
- Mass of e = 1.0086 amu
- Mass of p = 1.0087 amu
- Mass of n = 1.0087 amu
- Mass of e = 1.0073 amu

**Pauling Electronegativity**

- **Atomic molar mass (Atomic weight)**

- **Lanthanide series**

- **Actinide series**

- *Mass of p = 1.0086 amu*
- *Mass of n = 1.0087 amu*
- *Mass of e = 1.0073 amu*

- *1.00 atm = 760 torr*
- *1 inch = 2.54 cm*
- *1 Å = 1.0 Å*
- *1.00 lb = 454 g*
- *1.6749*
Read questions carefully - some questions may provide information not needed to answer the question

(1) (8 pts) Choose the process below for which $\Delta H$ and $\Delta U$ are the most different. Assuming that one mole of the first “reactant” is involved, calculate $\Delta H - \Delta U$. (Give the correct letter, and then compute the value of $\Delta H - \Delta U$. If you don’t know how to get $\Delta H - \Delta U$, give a short explanation for your choice to receive partial credit. No credit for guessing and providing no explanation.)

(a) C(s, graphite) + O$_2$(g) → CO$_2$(g)
(b) CaO(s) + CO$_2$(g) → CaCO$_3$(s)
(c) NaCl(s) + excess H$_2$O(ℓ) → Na$^+$aq + Cl$^-$aq  (salt dissolves in water)
(d) H$_2$O(ℓ) → H$_2$O(s)  (water freezes to ice)

(2) (10 points) For each of the following thermodynamic properties, decide whether the value should be positive, negative, or zero. (Please answer by writing ‘+’, ‘-‘, or ‘0’ in the blank to the left of each one.) (2 pts. each)

_____ (a) $\Delta H^0_f$ for Cl$_2$(g)
_____ (b) $S^0$ for F$_2$(g)
_____ (c) $\Delta S^0$ for the evaporation of liquid methanol ( CH$_3$OH(l) → CH$_3$OH(g) )
_____ (d) $\Delta G$ for the combustion of propane: C$_3$H$_8$(g) + 5 O$_2$(g) → 3 CO$_2$(g) + 4 H$_2$O(ℓ)
_____ (e) $\Delta H$ for the combination of 2 oxygen atoms: O(g) + O(g) → O$_2$ (g)

(3) (6 points) For a process carried out at constant pressure, the heat measured in a calorimetry experiment, $q_p$, is related to $\Delta X$, where “$X$” is a state function. What is “$X$”?

(4) (7 points) Heat capacities measured at constant volume and constant pressure are respectively referred to as $C_V$ and $C_p$. Which of these is generally larger than the other? (Explain why in one or two sentences.) For full credit, give an expression for the difference between the two for one mole of a gas that behaves ideally.
(5) (6 points) All the isomeric pentanes (C₅H₁₂; A, B, C) with the structures shown below are liquids at room temperature. Put them in order of increasing entropy, S°.

A: n-pentane

C: neopentane

B: isopentane

(6) (8 points) Phosphorus forms white crystals made of P₄ molecules. There are two forms of white crystalline phosphorus called “α” and “β”. The difference between α-P₄ and β-P₄ relates to the way the P₄ molecules pack together to form crystals. The α form is always obtained when liquid phosphorus freezes. However, at temperatures below -77 °C (196 K), α-P₄ crystals spontaneously change to β-P₄:

$$\text{α-P₄} \rightarrow \text{β-P₄}$$

For the conversion of α-P₄ to β-P₄ (the equation shown) give the signs of ΔH and ΔS and briefly explain the behavior of ΔG as a function of temperature:

(7) (10 points). The flash point of a flammable substance is determined by its vapor pressure. The flash point of methanol (CH₃OH) is 13.0 °C, its normal boiling point is 64.7 °C. The enthalpy of vaporization, ΔHᵥap, for methanol is 39.35 kJ/mol. What is the vapor pressure of methanol at its flash point?
(8) (15 pts) Silicon nitride, \( \text{Si}_3\text{N}_4(\text{s}) \) is a ceramic compound with excellent strength and corrosion resistance, making it attractive for applications such as turbine blades. To evaluate the possibility of economically producing this ceramic, an engineering team must know its standard enthalpy of formation. Unfortunately, they are unable to locate a tabulated value. Elemental silicon is a solid at room temperature and pressure.

(a) (5 pts) Suppose the team decides to try to measure \( \Delta H^\circ_f (\text{Si}_3\text{N}_4(\text{s})) \) directly by calorimetry. What reaction would they need to carry out? (Please write a balanced equation for the reaction.)

(b) (10 pts) Despite many attempts, the engineers are unable to get the reaction above to take place. Finally, a helpful chemist points out that the direct measurement the engineers are attempting is not feasible. However, the chemist is able to accurately measure \( \Delta H^\circ \) for the reaction shown below. What additional data will be required to calculate the correct value of \( \Delta H^\circ_f \) for silicon nitride? (There are in principle any number of valid answers. Please try to choose the simplest one, which should rely on data that might be found in a table in the back of your book.) Write an expression giving the desired \( \Delta H^\circ_f \) in terms of the data you propose to use.

\[
3 \text{CO}_2(\text{g}) + \text{Si}_3\text{N}_4(\text{s}) \rightarrow 3 \text{SiO}_2(\text{g}) + 2 \text{N}_2(\text{g}) + 3 \text{C(\text{s, graphite})}
\]
(9) (15 pts) Consider the following facts when answering the questions given below:

(I) \( \text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s) \quad \Delta H^\circ = -176 \text{ kJ/mol} \quad |\Delta S^\circ| = 285 \text{ J/mol-K} \)

(II) Both NaCl and NH\(_4\)Cl are solid, white powders under standard conditions.

(III) The melting point of NaCl is approx. 800 °C. At atmospheric pressure, NH\(_4\)Cl does not form a liquid at any temperature.

(IV) Both NaCl and NH\(_4\)Cl are very soluble in water and separation of the two salts can not be achieved by exploiting differences in solubility.

(a) (5 pts) What is the sign of \( \Delta S^\circ \)? (briefly explain your answer).

(b) (10 pts) Suppose you have a sample in which NaCl and NH\(_4\)Cl are intimately mixed. Use the thermodynamic and other chemical information given to devise a simple method for removing the NH\(_4\)Cl from NaCl to obtain pure NaCl. Your answer should be concise (no more than a few sentences), but you should be clear in explaining why your method will work. (Answers which are unclear and difficult to understand will be given no credit.)
(10) (15 points) Nitrogen, N₂, is one of the top chemicals produced in industry. The nitrogen phase diagram is shown below. \( \Delta H_{\text{fus}}(N_2) \) and \( \Delta H_{\text{vap}}(N_2) \) are the respective enthalpy changes for melting and boiling one mole of N₂ at 1.0 atm pressure.

<table>
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(a) (3 pts) What phases of matter (gas, liquid, solid) are stable in regions A, B, and C?

(b) (5 pts) From the information given above and/or on the diagram, calculate \( S_{\text{fus}}(N_2) \) and \( S_{\text{vap}}(N_2) \).

(c) (7 pts) Estimate the heat absorbed (\( \Delta H \)) in warming one mole of N₂ gas from the boiling point to 298 K. Assume that the heat capacity (\( C_p \)) of N₂ gas is constant over this range and that vibrational contributions to N₂ can be ignored.

Important information:

\[
\Delta H_{\text{fus}}(N_2) = 0.721 \text{ kJ/mol} \quad \Delta H_{\text{vap}}(N_2) = 5.565 \text{ kJ/mol} \quad S^0(N_2) = 191.61 \text{ J/mol} \cdot \text{K}
\]
BONUS! (10 pts)

(d) (5 pts) Use the same heat capacity estimate you used in part (c) to estimate the entropy change for the process (An integral formula must be used.):

\[ \text{N}_2(\text{g}, \text{bp}) \rightarrow \text{N}_2(\text{g}, 298.15 \text{ K}) \]

(The experimental value is \( \Delta S = 40.12 \text{ J/mol} \cdot \text{K} \); your task is to show that a simple approximation is pretty good.)

(e) (5 pts) The heat capacity (\( C_p \)) for liquid nitrogen is approximately 56.5 J mol\(^{-1}\) K\(^{-1}\) over the entire liquid range (m.p. \( < \) T \( < \) b.p.). Using this information and information given in the problem or used in earlier parts of the problem, compute the entropy of solid \( \text{N}_2 \), just below the melting point.