This exam is schedule for 75 minutes and I anticipate it to take the full time allotted. You are free to leave if you finish. In multiple part problems, points awarded will not be penalized for incorrect answer on previous parts, so simply **move on if you get stuck on one part**. If you need to, make up an answer for the previous part. Always neatly show work for partial credit.

1. Define the first and second laws of thermodynamics and explain what impact they have on the important concepts of thermodynamics that we have discussed in class.

- 2. Coal power plants are not 100% efficient; that is, not all of the energy produced from the combustion reaction results in usable energy.
 - a. The combustion of coal is shown below. Is this reaction endothermic or exothermic? Explain your choice.

 $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

- b. What happens to the rest of the energy?
- c. Clearly explain how this is related to thermodynamics.

3. $\Delta S_{vaporization} > \Delta S_{fusion}$; Explain why this statement is true.

4. Which direction does a reaction "shift" when Q > K. You must clearly explain your choice to receive full credit.

Reactants

Products

What is the sign of ΔG when Q < K ?

positive

negative

- 5. Explain why each of the following statements are false.
 - a. A spontaneous reaction occurs when energy is consumed by a system.
 - b. Liquid water has a formation enthalpy of zero ($\Delta H_f^0 = 0$).
 - c. Br₂ (*I*) has a standard molar entropy of zero ($S^0 = 0$)
 - d. Endothermic reactions are never spontaneous.
 - e. Equilibrium occurs when the concentration of products and reactants are equal.
- 6. Consider the following reactions. Which is most likely to have a **negative** Δ S? You must clearly explain your answer to receive credit.

$$CO_{2}(g) + H_{2}O(I) \rightleftharpoons H_{2}CO_{3}(aq) \qquad 2 C_{8}H_{18}(I) + 25 O_{2}(g) \rightleftharpoons 16 CO_{2}(g) + 18 H_{2}O(g)$$

7. The synthesis of NO occurs according to the following reaction where $Kc = 7.5 \times 10^{-9} M^{-1}$ at 1000 K.

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

- a. If 1 M of each gas is mixed together at 1000 K, would the synthesis of NO₂ be spontaneous?
- b. Determine Kc for this related reaction: $2 \text{ NO}_2(g) \rightleftharpoons \text{N}_2(g) + 2 \text{ O}_2(g)$
- c. Calculate Kp at 1000 K. Include the correct units.

8. Consider the following reaction:

 $6 \text{ HCl}(g) + 2 \text{ As}(s) \rightleftharpoons 2 \text{ AsCl}_3(I) + 3 \text{ H}_2(g)$

- a. For each of the following, determine if the equilibrium will shift. If so, determine if products or reactants will be formed.
 - i. Magnesium is added
 - ii. HCl is added.
 - iii. The volume of the flask is decreased.
- b. Using the information available at the back of the exam, calculate ΔG° and ΔH° .

ΔG° = _____

ΔH° = _____

- c. What is the equilibrium constant at 25 °C?
- d. Calculate ΔS°

e. Calculate ΔG if 0.4 atm of CO, 2.5 atm of CO₂, 14 g of S, and 0.98 atm of CS₂ are added to a reaction flask at 25 °C.

9. Consider the following reaction.

$$3 F_2(g) + N_2(g) \rightleftharpoons 2 NF_3(g)$$

a. 2 atm of F_2 and 1 atm of N_2 are combined in a sealed reaction flask at 100 °C. Once equilibrium has been reached, the pressure is the flask is 1.706 atm. Determine the equilibrium constant at this temperature.

- b. When the temperature is raised to 200 $^{\circ}$ C, the pressure of F₂ decreases to 0.01 atm.
 - i. Is this reaction endothermic or exothermic? Justify your selection.
 - ii. Optional (bonus): calculate ΔH .

10. Consider the two reaction coordinates below. Answer each of the following questions. If it is not possible to determine, say that. Partial credit will be considered if your answer is explained.



- a. Which reaction is spontaneous?
- b. Which reaction has a larger equilibrium constant?
- c. Which reaction has a larger rate constant?
- d. Which of these reactions is endothermic?
- e. Which reaction might have $\Delta H > 0$ and $\Delta S < 0$?

- 11. **Complete one of the problems on this page**. You can answer more for extra credit. Please use the next page to show your work if you need more space.
 - a. Determine the total pressure at equilibrium if 14 grams of carbon, 1.82 atm of H_2 , and 2.33 atm of CH₄ are added to a reaction flask at 500 °C.

 $C(s) + 2 H_2 (g) \rightleftharpoons CH_4 (g) \qquad \qquad Kp = 2690 \text{ atm}^{-1} \text{ at } 500 \text{ }^\circ C$

- b. Using the information in the table below, determine the heat capacity of solid CS_2 if 2.34 kJ of heat is released when 10 grams of liquid CS_2 is cooled from 46.3 °C to -150 °C.
- c. ΔS_{vap} of CS₂ is 86.55 J mol⁻¹ K⁻¹. Using the information in the table below, determine the boiling temperature.

Thermodynamic values for CS ₂												
T _b (°C)	T _m (°C)	ΔH_{fusion} (kJ/mol)	$\Delta H_{vaporization}$	C (solid)	C (liquid)	C (gas)						
			(kJ/mol)	J / (mol K)	J / (mol K)	J / (mol K)						
	-110.8	4.39	27.65		78.99	46.55						

d. 1368 kJ of heat is required to decompose 112.04 grams of CO (g). Noting that the bond enthalpy of a CO triple bond is 1072 kJ mol⁻¹, calculate the bond enthalpy of a CO double bond.

 $2 \text{ CO} (g) \rightleftharpoons C(s) + CO_2 (g)$

e. Incomplete combustion of natural gas produces carbon monoxide and water vapor (see unbalanced reaction below).

$$CH_4$$
 (g) + O_2 (g) \rightleftharpoons CO (g) + H_2O (g)

Determine ΔH° for this reaction from the data below:

 $CH_4 (g) + 2 O_2 (g) \rightleftharpoons CO_2 (g) + 2 H_2O (g) \qquad \Delta H^\circ = -802 \text{ kJ mol}^{-1}$ $2 CO (g) + O_2 (g) \rightleftharpoons 2 CO_2 (g) \qquad \Delta H^\circ = -566 \text{ kJ mol}^{-1}$

f. Using the information at the back of the exam, determine the temperature that is needed to make this reaction spontaneous.

 $6 \text{ HCl}(g) + 2 \text{ As}(s) \rightleftharpoons 2 \text{ AsCl}_3(s) + 3 \text{ H}_2(g)$

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	ΔH_f^0	ΔG_f^0
	kJ mol⁻¹	kJ mol⁻¹
AsCl₃ (I)	-305.2	-259.0
HCI (g)	-110.5	-137.2

Equations

Kp = Kc (RT) ^{∆ngas}	$x = \frac{-b \pm \sqrt{b^2 - 4}}{2a}$	tac	
$\Delta H = C_p \Delta T$	$ln\frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$	R = 0.08206 L atm mol ⁻¹ K ⁻¹	R = 8.314 J mol ⁻¹ K ⁻¹
$\Delta U = q + w$	$w = -p\Delta V$	$\Delta G = -T\Delta S_{universe}$	
$\Delta G = \Delta H - T \Delta S$	$\Delta G^0 = -RT lnK$	$\Delta G = \Delta G^{o} + RT lnQ$	