$\qquad$

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.

$$
\mathrm{C}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}_{2}(\mathrm{~g})
$$

b. What happens to the rest of the energy?
c. Clearly explain how this is related to thermodynamics.
3. $\Delta \mathrm{S}_{\text {vaporization }}>\Delta \mathrm{S}_{\text {fusion }}$; Explain why this statement is true.
4. Which direction does a reaction "shift" when $\mathrm{Q}>\mathrm{K}$. You must clearly explain your choice to receive full credit.

Reactants
Products
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 $\left(\Delta H_{f}^{0}=0\right)$.
c. $\mathrm{Br}_{2}(I)$ has a standard molar entropy of zero $\left(S^{0}=0\right)$
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 $\Delta \mathrm{S}$ ? You must clearly explain your answer to receive credit.

$$
\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq}) \quad 2 \mathrm{C}_{8} \mathrm{H}_{18}(\mathrm{I})+25 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 16 \mathrm{CO}_{2}(\mathrm{~g})+18 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

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

$$
\mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})
$$

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

$$
6 \mathrm{HCl}(\mathrm{~g})+2 \mathrm{As}(\mathrm{~s}) \rightleftharpoons 2 \mathrm{AsCl}_{3}(\mathrm{l})+3 \mathrm{H}_{2}(\mathrm{~g})
$$

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 $\Delta \mathrm{G}^{\circ}$ and $\Delta \mathrm{H}^{\circ}$.

$$
\begin{aligned}
& \Delta \mathrm{G}^{\circ}= \\
& \Delta \mathrm{H}^{\circ}=
\end{aligned}
$$

c. What is the equilibrium constant at $25^{\circ} \mathrm{C}$ ?
d. Calculate $\Delta \mathrm{S}^{\circ}$
e. Calculate $\Delta \mathrm{G}$ if 0.4 atm of $\mathrm{CO}, 2.5 \mathrm{~atm}$ of $\mathrm{CO}_{2}, 14 \mathrm{~g}$ of S , and 0.98 atm of $\mathrm{CS}_{2}$ are added to a reaction flask at $25^{\circ} \mathrm{C}$.
9. Consider the following reaction.

$$
3 \mathrm{~F}_{2}(\mathrm{~g})+\mathrm{N}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NF}_{3}(\mathrm{~g})
$$

a. 2 atm of $\mathrm{F}_{2}$ and 1 atm of $\mathrm{N}_{2}$ are combined in a sealed reaction flask at $100^{\circ} \mathrm{C}$. 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 $200^{\circ} \mathrm{C}$, the pressure of $\mathrm{F}_{2}$ decreases to 0.01 atm .
i. Is this reaction endothermic or exothermic? Justify your selection.
ii. Optional (bonus): calculate $\Delta \mathrm{H}$.
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 $\Delta \mathrm{H}>0$ and $\Delta \mathrm{S}<0$ ?
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 $\mathrm{H}_{2}$, and 2.33 atm of $\mathrm{CH}_{4}$ are added to a reaction flask at $500^{\circ} \mathrm{C}$.

$$
\mathrm{C}(\mathrm{~s})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{4}(\mathrm{~g}) \quad \mathrm{Kp}=2690 \mathrm{~atm}^{-1} \text { at } 500^{\circ} \mathrm{C}
$$

b. Using the information in the table below, determine the heat capacity of solid $\mathrm{CS}_{2}$ if 2.34 kJ of heat is released when 10 grams of liquid $\mathrm{CS}_{2}$ is cooled from $46.3^{\circ} \mathrm{C}$ to $-150^{\circ} \mathrm{C}$.
c. $\Delta \mathrm{S}_{\text {vap }}$ of $\mathrm{CS}_{2}$ is $86.55 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$. Using the information in the table below, determine the boiling temperature.

| Thermodynamic values for $\mathrm{CS}_{2}$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{T}_{\mathrm{b}}\left({ }^{\circ} \mathrm{C}\right)$ | Tm ( ${ }^{\circ} \mathrm{C}$ ) | $\Delta \mathrm{H}_{\text {fusion }}(\mathrm{kJ} / \mathrm{mol})$ | $\Delta \mathrm{H}_{\text {vaporization }}$ | C (solid) | C (liquid) | C (gas) |
|  |  |  | (kJ/mol) | $\mathrm{J} /(\mathrm{mol} \mathrm{K})$ | $\mathrm{J} /$ (mol K) | $\mathrm{J} /$ (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 $\mathrm{CO}(\mathrm{g})$. Noting that the bond enthalpy of a CO triple bond is $1072 \mathrm{~kJ} \mathrm{~mol}^{-1}$, calculate the bond enthalpy of a CO double bond.

$$
2 \mathrm{CO}(\mathrm{~g}) \rightleftharpoons \mathrm{C}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g})
$$

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

$$
\mathrm{CH}_{4}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

Determine $\Delta \mathrm{H}^{\circ}$ for this reaction from the data below:

$$
\begin{array}{ll}
\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) & \Delta \mathrm{H}^{\circ}=-802 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
2 \mathrm{CO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{H}^{\circ}=-566 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{array}
$$

f. Using the information at the back of the exam, determine the temperature that is needed to make this reaction spontaneous.
$6 \mathrm{HCl}(\mathrm{g})+2 \mathrm{As}(\mathrm{s}) \rightleftharpoons 2 \mathrm{AsCl}_{3}(\mathrm{~s})+3 \mathrm{H}_{2}(\mathrm{~g})$

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|  | $\Delta \boldsymbol{H}_{\boldsymbol{f}}^{\mathbf{0}}$ <br> kJ mol | $\Delta \boldsymbol{G}_{\boldsymbol{f}}^{\mathbf{0}}$ <br> kJ mol |
| :---: | :---: | :---: |
| $\mathrm{AsCl}_{3}(\mathrm{l})$ | -305.2 | -259.0 |
| $\mathrm{HCl}(\mathrm{g})$ | -110.5 | -137.2 |

## Equations

| $\Delta G=\Delta H-T \Delta S$ | $\Delta G^{0}=-R T \ln K$ | $\Delta G=\Delta G^{o}+R T \ln Q$ |
| :--- | :--- | :--- |
| $\Delta U=q+w$ | $w=-p \Delta V$ | $\Delta G=-T \Delta S_{\text {universe }}$ |
| $\Delta H=C_{p} \Delta T$ | $\ln \frac{K_{2}}{K_{1}}=\frac{\Delta H}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)$ | $\mathrm{R}=0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ |
| $\mathrm{Kp}=\mathrm{Kc}(\mathrm{RT})^{\Delta \mathrm{ngas}}$ | $x=\frac{-b \pm \sqrt{b^{2}-4 a c}}{2 a}$ |  |

