Chem 1515.001-006
Problem Set \#15
Fall 2001

Name
TA's Name
$\longrightarrow$

ALL work must be shown in all problems for full credit. Due by 4:45 pm on Friday, December 7, 2001.

PS15.1. Using the table of thermodynamic values found in Appendix B in your textbook, calculate the $\Delta \mathrm{H}^{\circ}{ }_{\mathrm{rxn}}$ (standard enthalpy change) for each of the following reactions:
a) $2 \mathrm{C}_{6} \mathrm{H}_{6}(l)+15 \mathrm{O}_{2(g)} \rightarrow 12 \mathrm{CO}_{2(g)}+6 \mathrm{H}_{2} \mathrm{O}(l)$
b) $\mathrm{N}_{2}(g)+4 \mathrm{NH}_{3}(g) \rightarrow 3 \mathrm{~N}_{2} \mathrm{H}_{4}(l)$
c) $2 \mathrm{Na}(s)+2 \mathrm{H}_{2} \mathrm{O}(l) \rightarrow 2 \mathrm{NaOH}(a q)+\mathrm{H}_{2}(g)$

PS15.2. For each of the following pairs, indicate which substance you would expect to possess the larger standard entropy:

b) $1 \mathrm{~mol} \mathrm{NaNO}_{3}(\mathrm{aq})$ at $30^{\circ} \mathrm{C}$ or $1 \mathrm{~mol} \mathrm{NaNO}_{3}(s)$ at $30^{\circ} \mathrm{C}$.
c) $1 \mathrm{~mol}_{2}(g)$ at $10{ }^{\circ} \mathrm{C}$ and 1 atm or $1 \mathrm{~mol}_{2}(g)$ at $10{ }^{\circ} \mathrm{C}$ and 10 atm .
d) $1 \mathrm{~mol} \mathrm{He}(g)$ at $25^{\circ} \mathrm{C}$ and 1 atm or $1 \mathrm{~mol} \mathrm{~N}_{2} \mathrm{O}(g)$ at $25^{\circ} \mathrm{C}$ and 1 atm

PS15.3. Predict whether the entropy change in the system is positive or negative for each of the following processes: (Note: do not do any calculations.)
a) $2 \mathrm{Hg}(l)+\mathrm{O}_{2}(g) \rightarrow 2 \mathrm{HgO}(s)$
b) $\mathrm{CH}_{4}(g)+2 \mathrm{O}_{2}(g) \rightarrow \mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(l)$
c) $2 \mathrm{KClO}_{4(s)} \rightarrow 2 \mathrm{KClO}_{3}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g})$
d) $\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2(g)} \rightarrow 2 \mathrm{NO}(g)$

PS15.4. For each reaction below, use the table of thermodynamic values from Appendix B in your textbook to determine the values of $\Delta \mathrm{H}^{\circ}$ and $\Delta \mathrm{S}^{\circ}$.
a) $\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
b) $6 \mathrm{CO}_{2}(g)+6 \mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(s)+6 \mathrm{O}_{2}(g)$
c) $\mathrm{Br}_{2}(g) \rightarrow \mathrm{Br}_{2}(l)$
d) $2 \mathrm{H}_{2} \mathrm{O}_{2}(l) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(l)+\mathrm{O}_{2}(g)$
e) $\mathrm{HCl}_{(g)}+\mathrm{NH}_{3}(g) \rightarrow \mathrm{NH}_{4} \mathrm{Cl}_{( }(s)$

PS15.5. a) Calculate $\Delta \mathrm{G}^{\circ}$ for each of the reactions in problem PS15.4.
b) Which of the reactions in PS15.4 are spontaneous at 298 K ?
c) For each of the reactions listed in b), find the temperature above or below which the reaction becomes nonspontaneous.
d) Which of the reactions in PS15.4 are nonspontaneous at 298 K ?
e) For each of the reactions listed in d), find the temperature above or below which the reaction becomes spontaneous.

PS15.6. Ethanol could be synthesized using either of the following reactions;

$$
\begin{gathered}
\mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \\
\mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \xrightarrow{\rightarrow} \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}(l)+\mathrm{H}_{2}(\mathrm{~g})
\end{gathered}
$$

Using thermodynamics arguments which reaction is more feasible under standard conditions? Explain.

PS15.7. When liquid water is introduced into an evacuated vessel at $25^{\circ} \mathrm{C}$, some of the water vaporizes. Predict how the enthalpy, entropy, and free energy change in the system during this process. Explain the reasoning behind your predictions.

PS15.8. Under what conditions do enthalpy, entropy and free energy take on values of zero?

PS15.9. The enthalpy of combustion, $\Delta \mathrm{H}^{\circ}{ }_{\text {comb }}$, for oxalic acid, $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}_{4}(s)$, is - 246.05 $\mathrm{kJ} \cdot \mathrm{mol}^{-1}$ and

| Substance | $\Delta \mathrm{H}^{\circ}{ }^{\circ}\left(\frac{\mathrm{kJ}}{\mathrm{mol}}\right)$ | $\mathrm{S}^{\circ}\left(\frac{\mathrm{J}}{\mathrm{mol} \cdot \mathrm{K}}\right)$ |
| :--- | :---: | :---: |
| $\mathrm{C}_{(s)}$ | 0 | 5.69 |
| $\mathrm{CO}_{2(g)}$ | -393.5 | 213.6 |
| $\mathrm{H}_{2}(g)$ | 0 | 130.6 |
| $\mathrm{H}_{2} \mathrm{O}(l)$ | -285.8 | 69.96 |
| $\mathrm{O}_{2}(g)$ | 0 | 205 |
| $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}_{4(s)}$ | $?$ | 120.1 |

a) Write the balanced chemical equation that describes the combustion of one mole of oxalic acid.
b) Write the balanced chemical equation that describes the standard formation of oxalic acid.
c) Using the information given above and the equations in a) and b), calculate $\Delta \mathrm{H}_{\mathrm{f}}{ }^{\mathrm{C}}$ for oxalic acid.
d) Calculate $\Delta \mathrm{S}_{\mathrm{f}}^{\circ}$ for oxalic acid and $\Delta \mathrm{S}_{\mathrm{rxn}}^{\circ}$ for the combustion of one mole of oxalic acid.
e) Calculate $\Delta \mathrm{G}_{\mathrm{f}}^{\circ}$ for oxalic acid and $\Delta \mathrm{G}_{\mathrm{rxn}}^{\circ}$ for the combustion of one mole of oxalic acid.
f) Is the formation of oxalic acid from its elements spontaneous? Is the combustion of oxalic acid at $25^{\circ} \mathrm{C}$ spontaneous?

