Name _____ **Chem 163 Section**: _____ **Team Number:** _____

ALE 21. Gibbs Free Energy

(Reference: 20.3 Sil*berberg 5th edition*)

At what temperature does the spontaneity of a reaction change?

The Model: The Definition of Free Energy

So far in our study of thermodynamics, we have seen that in order to determine if a reaction is spontaneous we must consider the entropy change (ΔS) and the enthalpy change (ΔH) associated with the reaction. An equation that describes the quantitative relationship between entropy and the enthalpy was developed by **J. Willard Gibbs**, a professor of mathematical physics at Yale in the nineteenth century. He defined a new quantity, now called the **Gibbs free energy (G),** a single quantity that combines both of these ideas (**eqn 1**).

$$G = H - TS \qquad \qquad (1)$$

Because enthalpy is a **state function** (*i.e.*, ΔH is the same between two states, regardless of the path taken getting from the initial to the final state) and entropy is a state function, *Gibbs Free Energy is a state function, too*.

Just as it was for enthalpies, we often cannot determine the absolute value of the amount of Gibbs free energy that a system has. But that is okay, because we are principally interested in how much work we can obtain from a spontaneous reaction.
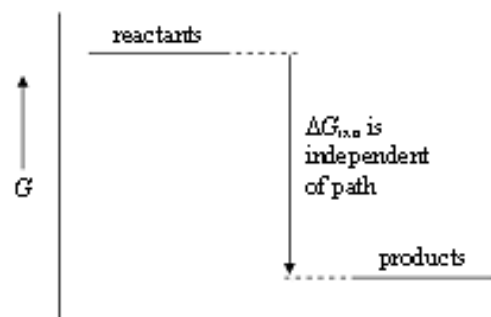
The maximum amount of non-expansion work obtainable is equal to ΔG_{rxn}, and the change in Gibbs free energy for a chemical reaction is something that can be determined.

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

- T is the temperature in Kelvin
- ΔH is $\Delta H_{reaction}$ (in Joules or kilojoules)
- ΔS is $\Delta S_{reaction}$ (in Joules or kilojoules)
- Note: $\Delta H_{reaction}$ and $\Delta S_{reaction}$ must either both be in J or both in kJ

Key Questions

1 a. Explain why the Gibbs free energy function (eqn **1**) is a state function.

b. Since enthalpy is a state function, the standard enthalpy change of a chemical reaction (ΔH_{rxn}^{o}) can be calculated from the standard heats of formation (ΔH_{f}^{o}) of the reactants and products. Likewise, since Gibbs free energy is a state function, there's a similar relationship that allows us calculate (ΔG_{rxn}^{o}) from tabulated values of standard molar Gibbs free energies of formation (ΔG_{f}^{o}). Write this relationship by completing the equation below.

$\Delta G_{rxn}^{o} =$

2. The absolute temperature is always positive. But the signs of ΔH_{rxn} and ΔS_{rxn} may be either negative or positive. Therefore, the sign of ΔG_{rxn} may be either positive or negative. Use **eqn 2, $\Delta G = \Delta H - T\Delta S$**, to complete the table by filling in each blank with a "<" or a ">", indicating what the sign of ΔG_{rxn} will be in each case.

	$\Delta H_{rxn} < 0$	$\Delta H_{rxn} > 0$
$\Delta S_{rxn} < 0$	ΔG_{rxn} ____ 0 at low T	ΔG_{rxn} ____ 0 at low T
	ΔG_{rxn} ____ 0 at high T	ΔG_{rxn} ____ 0 at high T
$\Delta S_{rxn} > 0$	ΔG_{rxn} ____ 0 at low T	ΔG_{rxn} ____ 0 at low T
	ΔG_{rxn} ____ 0 at high T	ΔG_{rxn} ____ 0 at high T

3 a. From the previous question and what we learned in the last ALE, it would seem that ΔG_{rxn} has to do with the spontaneity of a chemical reaction. Explain how the sign of ΔG_{rxn} can be used to tell whether a chemical reaction is spontaneous or not.

b. What does it mean if $\Delta G_{rxn} = 0$? (*Hint*: Recall that most chemical reactions are reversible.)

Exercises

4. The standard heats of formation and entropies of diamond and graphite at 25 °C are given in the table to the right.

	ΔH_f^o (kJ/mol)	S° (J mol^{-1} K^{-1})
C(diamond)	1.9	2.4
C(graphite)	0	5.7

Calculate ΔH_{rxn}^o, ΔS_{rxn}^o and ΔG_{rxn}^o for the conversion of diamond to graphite (**eqn 3**) at 25 °C. Show your work using units and sig. figs. *Circle your answers*.

$$C(\text{diamond}) \rightarrow C(\text{graphite}) \qquad (3)$$

a. $\Delta H_{rxn}^o =$

b. $\Delta S_{rxn}^o =$

c. $\Delta G_{rxn}^o =$

d. What can you say about the slogan "a diamond is forever"?

5. Even at 25 °C, solid iodine sublimes. Gaseous iodine reacts with excess fluorine to form iodine pentafluoride according to the thermochemical **equation 4**.

$$I_2(g) + 5 F_2(g) \rightarrow 2 IF_5(g) \quad \Delta H° = -1743.1 \text{ kJ} \qquad (4)$$

The standard Gibbs free energies of formation and standard molar entropies of the reactants and products are provided in the table to the right From this information, determine the standard molar entropy of gaseous iodine at 25 °C.

	ΔG_f^o (kJ/mol)	$S°$ (J mol^{-1} K^{-1})
$I_2(g)$	19.4	???
$F_2(g)$	0	203.3
$IF_5(g)$	-771.6	334.5

(*Hint*: You will need to use the version of Hess's law for both ΔG_{rxn}^o and ΔS_{rxn}^o .)

Key Questions

6. Unless ΔH_{rxn} and ΔS_{rxn} have *different* signs, the spontaneity of a reaction is temperature dependent. The spontaneity of a chemical reaction changes when $\Delta G_{rxn} = 0$. Hence, if we know ΔH_{rxn} and ΔS_{rxn} we can use the following equation to determine the *approximate* temperature at which the spontaneity of a reaction changes (either from spontaneous to non-spontaneous, or from non-spontaneous to spontaneous).

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$$

Starting with the above equation, solve for T (in terms of ΔH_{rxn} and ΔS_{rxn}) when $\Delta G_{rxn} = 0$.

Exercises

7. The standard heats of formation and entropies of liquid water and water vapor at 25 °C are given in the following table to the right

	ΔH_f^o (kJ/mol)	$S°$ (J mol^{-1} K^{-1})
$H_2O(l)$	-285.8	69.9
$H_2O(g)$	-241.8	188.7

   a. From this data (which are valid at 25 °C), estimate the temperature at which water spontaneously boils at a pressure of 1 atm.

   b. Note that the value you calculated in part a is only an estimation. Briefly explain the source of error in the calculation.

For the next two Questions:
   Refer to thermodynamic data on pages A5 - A7 of Appendix B of your textbook.

8. The U.S. government now requires automobile fuels to contain a renewable component. The fermentation of glucose from corn to produce ethanol for addition to gasoline is a key process fulfilling this requirement:

$$C_6H_{12}O_{6\,(s)} \rightarrow 2\,C_2H_5OH_{(l)} + 2\,CO_{2(g)}$$
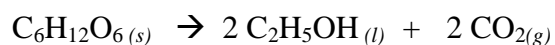
Calculate ΔH^o, ΔS^o and ΔG^o for the reaction at 25 °C. Is the spontaneity of the reaction dependent on temperature? *Explain*.

9. Consider the following combustion of butane gas:

$$C_4H_{10\ (g)} + 6.5\ O_{2\ (g)} \rightarrow 4\ CO_{2(g)} + 5\ H_2O_{\ (g)}$$
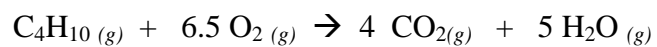
a.) Predict the signs of ΔS^o and ΔH^o. _Explain_

b.) Calculate ΔG^o by two different methods.
   Method #1: Using $\Delta G_f{}^o$

   Method #2: Using ΔS^o and ΔH^o

10. Is an endothermic reaction more likely to be spontaneous at higher temperatures or lower temperatures?
   Explain.