ChemQuest 55

Free Energy

Name: _____

Date: _____

Hour: _____

Information: Free Energy

So far in our study of thermodynamics, we have seen that in order to determine if a reaction is spontaneous we must examine the entropy change (ΔS) and the enthalpy change (ΔH) associated with the reaction. A single quantity that combines both of these ideas is called the Gibbs Free Energy, which is given the symbol G. The change in free energy is related to the change in ethalpy for a reaction and the change in entropy for a reaction according to the following equation:

$$\Delta G = \Delta H - T\Delta S$$

- T is the temperature in units of 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 Joules or both kilojoules

Recall the following table:

Reaction	sign of $\Delta H_{reaction}$	Sign of $\Delta S_{reaction}$	Sign of $\Delta S_{surroundings}$	Sign of $\Delta S_{universe}$	Spontaneous?
#1 exothermic, entropy increase	-	+	+	+	yes
#2 endothermic, entropy increase	+	+	-	+ or -	depends
#3 exothermic, entropy decrease	-	-	+	+ or -	depends
#4 endothermic, entropy decrease	+	-	-	-	no

Critical Thinking Questions

1. What units must ΔS have if it is to be used in the above equation for free energy?
   ΔS must have units of kJ/K because T is in units of Kelvin and ΔH is in units of kJ.

2. For a spontaneous reaction, what is the sign of ΔG—positive or negative?
   Negative

3. For a nonspontaneous reaction, what is the sign of ΔG—positive or negative?
   Positive

4. In the table above, under "Spontaneous" for reactions #2 and #3 it says, "depends". What does this mean? In other words, what does the spontaneity depend on in reaction #2 and reaction #3?
   It depends on the magnitude of ΔS and ΔH. ΔG must be a negative value.

5. You have seen that $\Delta H_{reaction}$ can be calculated by the following:
   $\Delta H_{reaction}$ = [sum of ΔH_f of products] – [sum of ΔH_f of reactants]
   The ΔS and ΔG for reactions can be calculated in the same way using values from a table of standard values. Use the information in a table of standard values and the following balanced equation to prove that ΔG = ΔH - TΔS. Pay special attention to units and note that each value in the table was determined at 25°C (298 K).

	$CaCO_3$ (s)	→	CaO (s)	+	CO_2 (g)	
ΔH =	-1206.9 kJ		-635.1 kJ		-393.5 kJ	ΔH_{rxn} = 178.3 kJ
ΔS =	92.9 J		38.2 J		213.7 J	ΔS_{rxn} = 159 J
ΔG =	-1128.8 kJ		-603.5 kJ		-394.4 kJ	ΔG_{rxn} = 130.9 kJ

   proof

   ΔG = ΔH - TΔS = 178.3 – 298(0.159) = 130.9 kJ

6. Is the reaction from question 5 spontaneous at 25°C? Explain.
   No, ΔG is a positive number.

7. By varying the temperature, is it possible to change the spontaneity of the reaction from question 5? Explain.
   Yes, if the temperature is large enough then TΔS would be larger than ΔH and ΔG would therefore be negative.

Information: Coupling Reactions

Sometimes in industry we need to carry out nonspontaneous reactions. An example of a nonspontaneous reaction is isolating iron from iron ore. The equation and free energy are given below:

$$2\ Fe_2O_3\ (g) \rightarrow 4\ Fe\ (s) + 3\ O_2\ (g)\ ;\ \Delta G = 1487\ kJ$$

To get this reaction to proceed spontaneously, you can "couple" it with another reaction. One such reaction would be the conversion of carbon monoxide to carbon dioxide. This equation and its free energy is given below:

$$6\ CO\ (g) + 3\ O_2\ (g) \rightarrow 6\ CO_2\ (g)\ ;\ \Delta G = -1543\ kJ$$

By "coupling" the reactions, we essentially carry out both reactions at the same time and use the spontaneous reaction to drive the nonspontaneous one. The overall ΔG for the process then becomes -56 kJ (found by adding -1543 + 1487). The overall final balanced equation is then:

$$2\ Fe_2O_3\ (g) + 6\ CO\ (g) \rightarrow 4\ Fe\ (s) + 6\ CO_2\ (g)\ ;\ \Delta G = -56\ kJ$$

Critical Thinking Questions

8. In the overall final balanced equation above, why isn't O_2 written?
   O_2 appears on both sides of the reaction so it is produced and then used up so there is no need to write it in the overall equation.

9. Consider the following reaction to obtain pure aluminum from aluminum ore:

   $$Al_2O_3\,(s) + 2\,Fe\,(s) \rightarrow Fe_2O_3\,(s)\ 2\,Al\,(s)$$

   Which of the following two reactions would prove beneficial when coupled with the above reaction?

   a) $CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$
   OR
   b) $2\,CH_3OH\,(l) + 3\,O_2\,(g) \rightarrow 2\,CO_2\,(g) + 4\,H_2O\,(l)$

   First, calculate the ΔG value for the aluminum reaction:

   $$Al_2O_3\,(s) + 2\,Fe\,(s) \rightarrow Fe_2O_3\,(s)\ 2\,Al\,(s);\ \ \Delta G = 838\ kJ$$

   We need to find out which reaction (a or b) has a ΔG greater than -838 kJ so that when the reactions are added, the overall reaction will have a negative ΔG and be spontaneous.

   a. $CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g);\ \Delta G = -800.8\ kJ$

   b. $2\,CH_3OH\,(l) + 3\,O_2\,(g) \rightarrow 2\,CO_2\,(g) + 4\,H_2O\,(l);\ \Delta G = -1404.9\ kJ$

   Reaction b should be coupled with the aluminum ore reaction so that the overall ΔG will be negative.

10. Given your answer to question 9, write the overall equation (after coupling) and calculate the ΔG for this overall reaction.

$$Al_2O_3\,(s) + 2\,Fe\,(s) + 2\,CH_3OH\,(l) + 3\,O_2\,(g) \rightarrow Fe_2O_3\,(s)\ 2\,Al\,(s) + 2\,CO_2\,(g) + 4\,H_2O\,(l)$$

$\Delta G = 838 + (-1404.9) =$ **-566.9 kJ**

Skill Practice 55

Free Energy Practice

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1. Given the following reaction, calculate ΔH and ΔS.

$$2\ CH_3OH\ (l)\ +\ 3\ O_2\ (g)\ \rightarrow\ 2\ CO_2\ (g)\ +\ 4\ H_2O\ (l)$$

$\Delta H = -1453.2$ kJ
$\Delta S = -161.84$ kJ

2. Given your answers to question 1 and the fact that this reaction takes place at 25°C, calculate ΔG.

-1404.9 kJ

3. A certain reaction is nonspontaneous at room temperature and spontaneous at high temperatures. What are the signs of ΔS and ΔH?

ΔH = positive
ΔS = positive

4. Calculate ΔG for each of the following reactions. Indicate whether each reaction is spontaneous or not.

A) $C_2H_2\ (g)\ +\ 2\ H_2\ (g)\ \rightarrow\ C_2H_6\ (g)$

-241.86 kJ; spontaneous

B) $CS_2\ (l)\ +\ 3\ O_2\ (g)\ \rightarrow\ CO_2\ (g)\ +\ 2\ SO_2\ (g)$

-1058.4 kJ; spontaneous

C) $N_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2\ NO\ (g)$

173.2 kJ; nonspontaneous