

Free Energy and Chemical Reactions

- Solving ΔG° Using Hess's Law.
- Using the following data (at 25° C)
 - $C_{\text{diamond}}(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta G^\circ = -397 \text{ kJ}$
 - $C_{\text{graphite}}(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta G^\circ = -394 \text{ kJ}$
- Calculate ΔG° for the reaction

$$C_{\text{diamond}}(s) \rightarrow C_{\text{graphite}}(s)$$

Free Energy and Chemical Reactions

- Calculating ΔG° as a State Function.
- Standard Free Energy of Formation (ΔG_f°).
- $\Delta G^\circ = \sum n_p \Delta G_f^\circ \text{ products} - \sum n_r \Delta G_f^\circ \text{ reactants}$
- Methanol is a high-octane fuel used in high-performance racing engines. Calculate ΔG° for the reaction

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

Substance	ΔG_f° (kJ/mol)
$CH_3OH(g)$	-163
$O_2(g)$	0
$CO_2(g)$	-394
$H_2O(g)$	-229

Free Energy and Chemical Reactions

A chemical engineer wants to determine the feasibility of making ethanol (C_2H_5OH) by reacting water with the ethylene (C_2H_4) according to the equation



Is the reaction spontaneous under standard conditions?

$\Delta G_f^\circ(C_2H_5OH(l)) = -175 \text{ kJ/mol}$
$\Delta G_f^\circ(H_2O(l)) = -237 \text{ kJ/mol}$
$\Delta G_f^\circ(C_2H_4(g)) = 68 \text{ kJ/mol}$

The Dependence of Free Energy on Pressure

- The equilibrium position represents the lowest free energy value available to a particular reaction.
- Free energy changes throughout the course of a reaction because it is pressure and concentration dependent.
- For any 1 mole of a gas at a given temperature
 - $S_{\text{large } V} > S_{\text{small } V}$ or $S_{\text{low } P} > S_{\text{high } P}$

Free Energy and Equilibrium

- For standard conditions at equilibrium
 - $\Delta G^\circ = -RT \ln(K)$
 - This is on the equations sheet**
 - ΔG° is the free energy at standard conditions, T is the Kelvin temperature, R is the ideal gas constant 8.31 J/mol K, and K is an equilibrium constant (from the previous unit)
 - Note- R gives you a value in J, not kJ.**
 - We learned 8.31 kPa L / mol K last year. From pressure volume work, a L kPa = J

Equilibrium and Free Energy

- The reaction for the synthesis of ammonia is:
 - $N_2 + 3 H_2 \rightarrow 2 NH_3$
- Calculate the equilibrium constant for this reaction at 25°C.

	H_f° (kJ/mol)	S_f° (J/mol)
N_2	0	192
H_2	0	131
NH_3	-46	193

Free Energy and Equilibrium

- LeChâtelier's is about reactions being at equilibrium, then switching to be thermodynamically favored in one direction or the other in certain conditions (switching the sign of ΔG).
- For standard conditions
 - $\Delta G^\circ = -RT \ln(K)$
- However ΔG changes at nonstandard conditions
 - $\Delta G = \Delta G^\circ + RT \ln(Q)$
- The difference between ΔG , and ΔG° is the 2nd one is at standard conditions. The first is not.

The Dependence of Free Energy on Pressure

- One method for synthesizing methanol (CH_3OH) involves reacting carbon monoxide and hydrogen gases:
 - $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$
- Calculate ΔG at 25° C for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol.

$\Delta G_f^\circ(CH_3OH(l)) = -166 \text{ kJ}$
$\Delta G_f^\circ(H_2(g)) = 0$
$\Delta G_f^\circ(CO(g)) = -137 \text{ kJ}$

The Meaning of ΔG for a Chemical Reaction

- A system achieves the lowest magnitude of free energy possible by going to **equilibrium**, not by going to completion.
- Spontaneous reactions do not go to completion, shift all the way over to products from reactants, but instead to equilibrium
- At equilibrium $\Delta G = 0$

Free Energy and Equilibrium

- The equilibrium point occurs at the lowest value of free energy available to the reaction.
- Recall the following:
 - If $K > Q$, then the reaction as written proceeds to the right.
 - If $K < Q$, then the reaction as written proceeds to the left.
 - If $K = Q$, then the reaction as written is at equilibrium, and there is no net reaction in either direction.

Relating

$$\Delta G^\circ = -RT \ln(K)$$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

- I could combine the two equations and get
- $\Delta G = RT \ln(Q) - RT \ln(K)$
- Note if $K > Q$ then ΔG is negative. The reaction is spontaneous and shifts to the right.
- if $K < Q$ then ΔG is positive. The reaction is spontaneous in the opposite direction or shifts to the left.

Another derivation of the same equation

- $\Delta G^\circ = -RT \ln(K)$
- In the learning objectives for the AP test, they mention an equation determined by solving the above for K .
- In which case, you get:
 - $K = e^{-\Delta G^\circ / (RT)}$
- This derivation is not on the equations sheet, you are not likely to need it.

Free Energy and Work

- For a spontaneous reaction, ΔG is the maximum work obtainable from the system.

$$w_{\max} = \Delta G$$
- For a nonspontaneous process, ΔG is the minimum work that must be done to the system to make a change happen.
- For $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$, ΔG_{sys} is the portion of the total energy change that does the work.
 - $T\Delta S_{\text{sys}}$ is given off as heat and is not usable.

Work

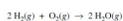
- In the real world, some free energy is always changed to heat and is unusable, or wasted. Therefore, no process is 100% efficient.
- 1. A spontaneous reaction will occur and can do work on the surroundings.
- 2. A nonspontaneous reaction will not occur unless the surroundings do work on it.
- 3. A reaction at equilibrium can no longer do work.

Review

- ΔH Enthalpy; negative is exothermic, positive is endothermic
- ΔS Entropy (Do NOT use spontaneity to determine); look for complexity of molecules or phases. Positive is increasing disorder (s \rightarrow l \rightarrow g, breaking larger molecules apart etc.), negative is decreasing disorder
- ΔG Gibbs Free Energy; negative means the equation is spontaneous, positive is not.
- $\Delta G = \Delta H - T\Delta S$

Questions from a previous test

29. Which of the following processes involves the greatest increase in entropy?
- $\text{SO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
 - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
 - $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 - $\text{C}_2\text{H}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
 - $\text{MgSO}_4(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{SO}_2(\text{g})$



52. For the reaction represented above at 25°C, what are the signs of ΔH° , ΔS° , and ΔG° ?

	ΔH°	ΔS°	ΔG°
(A)	+	+	+
(B)	+	+	-
(C)	+	-	-
(D)	-	-	-
(E)	-	-	+

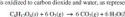
Free Response

2011 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

1. Answer the following questions about glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, an important biochemical energy source.

(a) Write the empirical formula of glucose.

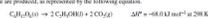
In many equations, glucose is oxidized to carbon dioxide and water, as represented by the following equation.



A 2.50 g sample of glucose and an excess of $\text{O}_2(\text{g})$ were placed in a calorimeter. After the reaction was initiated and proceeded to completion, the total heat released by the reaction was calculated to be 70.8 kJ.

(b) Calculate the value of ΔH° in kJ mol^{-1} for the combustion of glucose.

(c) When oxygen is not available, glucose can be oxidized by fermentation. In that process, ethanol and carbon dioxide are produced, as represented by the following equation.



The value of the equilibrium constant, K_p , for the reaction at 298 K is 8.9×10^5 .

(d) Calculate the value of the standard free-energy change, ΔG° , for the reaction at 298 K. Include units with your answer.

(e) Calculate the value of the standard entropy change, ΔS° , in $\text{J K}^{-1} \text{mol}^{-1}$, for the reaction at 298 K.

(f) Indicate whether the equilibrium constant for the fermentation reaction increases, decreases, or remains the same if the temperature is increased. Justify your answer.

(g) Using your answer for part (b) and the information provided in part (c), calculate the value of ΔH° for the following reaction.

