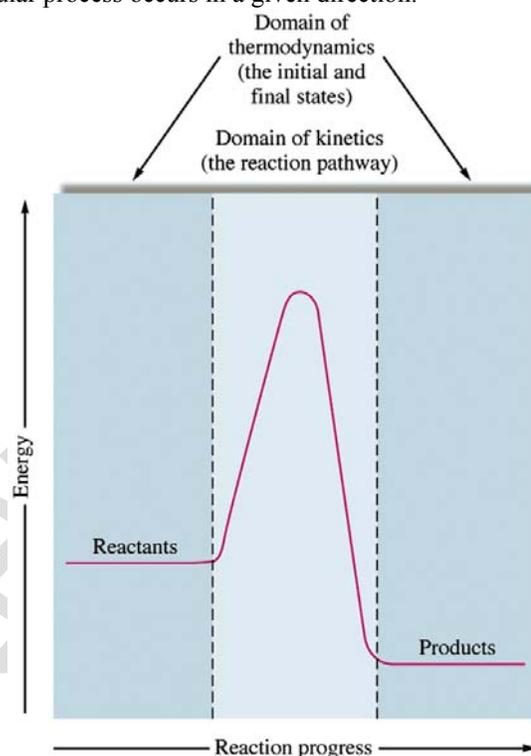


## Chapter 16 Outline – Spontaneity, Entropy, and Free Energy

The first law of thermodynamics is a statement of the law of conservation of energy: Energy can be neither created nor destroyed. The energy of the universe is constant. Although the first law of thermodynamics provides the means for accounting for energy, it gives no hint as to why a particular process occurs in a given direction.

### Spontaneous Processes and Entropy

- A process is said to be spontaneous if it occurs without outside intervention.
- Spontaneous processes may be fast or slow.
- Thermodynamics can tell us the direction in which a process will occur but can say nothing of the speed of the process.
- As you saw in chapter 12, the rate of a reaction depends on many factors, such as activation energy, temperature, concentration and catalyst, and we were able to explain these effects using a simple collision model.
- Chemical kinetics focuses on the pathway between reactants and products; thermodynamics considers only the initial and final states and does not require knowledge of the pathway between reactants and products.
- The characteristic common to all spontaneous processes is an increase in a property called **entropy**, denoted by the symbol **S**. The driving force for a spontaneous process is an increase in the entropy of the universe.
- Entropy can be viewed as a measure of the molecular randomness or disorder. The natural progression of things is from order to disorder, from low entropy to high entropy.
- Entropy is a thermodynamic function that describes the number of arrangements (positions and/or energy levels) that are available to a system existing in a given state.
- Nature spontaneously proceeds toward the states that have the highest probability of existing.
- Look at the example below in table 16.1. Note that for arrangements I and V, there is only one possible microstate for each. Arrangement III has six possible microstates and thus is the most probable. The probability of occurrence of a particular arrangement (state) depends on the number of ways (microstates) in which that arrangement can be achieved.
- This type of probability is called **positional probability** because it depends on the number of configurations in space (positional microstates) that yield a particular state.
- Positional entropy increases in going from solid to liquid to gas.



**TABLE 16.1** The Microstates That Give a Particular Arrangement (State)

Arrangement	Microstates
I	
II	
III	
IV	
V	

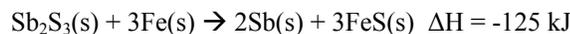
- Positional entropy is also very important in the formation of solutions. The entropy change associated with the mixing of two pure substances is expected to be positive. An increase in entropy is expected because there are many more microstates for the mixed condition than for the separated condition. This effect is due principally to the increased volume available to a given “particle” after mixing occurs.
- **You try:** For each of the following pairs, choose the substance with the higher positional entropy (per mole) at a given temperature.
  - A. Solid CO<sub>2</sub> and gaseous CO<sub>2</sub>
  - B. N<sub>2</sub> gas at 1 atm and N<sub>2</sub> gas at 1.0 x 10<sup>-2</sup> atm
- **You try:** Predict the sign of the entropy change for each of the following processes.
  - A. Solid sugar is added to water to form a solution.
  - B. Iodine vapor condenses on a cold surface to form crystals.

### Entropy and the Second Law of Thermodynamics

- In any spontaneous process there is always an increase in the entropy of the universe. This is the second law of thermodynamics.
- Energy is conserved in the universe, but entropy is not. The entropy of the universe is increasing.
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- If  $\Delta S_{\text{univ}}$  is **positive**, the **entropy** of the universe **increases**, and the process is **spontaneous** in the direction written.
- If  $\Delta S_{\text{univ}}$  is **negative**, the **entropy** of the universe **decreases**, and the process is **spontaneous** in the **opposite** direction.
- If  $\Delta S_{\text{univ}}$  is **zero**, the process has no tendency to occur, and the system is at equilibrium.

### The Effect of Temperature on Spontaneity

- The entropy changes in the surroundings are primarily determined by heat flow. An exothermic process in the system increases the entropy of the surroundings, because the resulting energy flow increases the random motions in the surroundings. This means that exothermicity is an important driving force for spontaneity.
- In earlier chapters we saw that a system tends to undergo changes that lower its energy. You now can see the reason for this tendency. The energy it gives up is transferred to the surroundings, leading to an increase in entropy there.
- The sign  $\Delta S_{\text{surr}}$  depends on the direction of the heat flow. At constant temperature, an exothermic process increases the energy, motions and thus the entropy of the surroundings. Thus,  $\Delta S_{\text{surr}}$  is positive. The opposite is true for an endothermic process in a system at constant temperature.
- The significance of exothermicity as a driving force depends on the temperature at which the process occurs. That is, the magnitude of  $\Delta S_{\text{surr}}$  depends on the temperature at which heat is transferred.
- The impact of the transfer of a given quantity of energy as heat to or from the surroundings will be greater at lower temperatures.
- $\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$  The minus sign is necessary because the sign of  $\Delta H$  is determined with respect to the reaction system, and this equation expresses a property of the surroundings.
- **Example: Determining  $\Delta S_{\text{surr}}$ .** In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony to sulfide ores:



Calculate  $\Delta S_{\text{surr}}$  for this reaction at 25°C and 1 atm.

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

$$T = 25 + 273 = 298 \text{ K}$$

$$\Delta S_{\text{surr}} = -\frac{-125}{298}$$

$$\Delta S_{\text{surr}} = 0.419 \text{ kJ/K} = 419 \text{ J/K}$$

- You try: Carbon is used as the reducing agent for oxide ores:  

$$\text{Sb}_4\text{O}_6(\text{s}) + 6\text{C}(\text{s}) \rightarrow 4\text{Sb}(\text{s}) + 6\text{CO}(\text{g}) \quad \Delta H = 778 \text{ kJ}$$
 Calculate  $\Delta S_{\text{surr}}$  for this reaction at 25°C and 1 atm.
- We have seen that the spontaneity of a process is determined by the entropy change it produces in the universe. We have also seen that  $\Delta S_{\text{univ}}$  has two components,  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$ . The chart below summarizes how these values influence whether or not a reaction is spontaneous.

**TABLE 16.3** Interplay of  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  in Determining the Sign of  $\Delta S_{\text{univ}}$

Signs of Entropy Changes				Process Spontaneous?
$\Delta S_{\text{sys}}$	$\Delta S_{\text{surr}}$	$\Delta S_{\text{univ}}$		
+	+	+	Yes	
-	-	-	No (reaction will occur in opposite direction)	
+	-	?	Yes, if $\Delta S_{\text{sys}}$ has a larger magnitude than $\Delta S_{\text{surr}}$	
-	+	?	Yes, if $\Delta S_{\text{surr}}$ has a larger magnitude than $\Delta S_{\text{sys}}$	

### Free Energy

- Free energy**, symbolized by  $G$  is defined by the relationship:  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , where  $\Delta H^\circ$  is the change in enthalpy of the system,  $T$  is the Kelvin temperature, and  $\Delta S^\circ$  is the change in entropy of the system.
- A process at constant temperature and pressure is spontaneous in the direction in which the free energy decreases. ( $-\Delta G$  means  $+\Delta S_{\text{univ}}$ )
- Consider the following equation:  $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$   $\Delta H^\circ = 6.03 \times 10^3 \text{ J/mol}$  and  $\Delta S^\circ = 22.1 \text{ J/K mol}$  (Note: the superscript degrees symbol ( $^\circ$ ) symbol means all substances are in their standard states.) The table below outlines the calculation made for this reaction at -10°C, 0°C and 10°C.

**TABLE 16.4** Results of the Calculation of  $\Delta S_{\text{univ}}$  and  $\Delta G^\circ$  for the Process  $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$  at -10°C, 0°C, and 10°C\*

$T$ (°C)	$T$ (K)	$\Delta H^\circ$ (J/mol)	$\Delta S^\circ$ (J/K · mol)	$\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T}$ (J/K · mol)	$\Delta S_{\text{univ}} = \Delta S^\circ + \Delta S_{\text{surr}}$ (J/K · mol)	$T\Delta S^\circ$ (J/mol)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J/mol)
-10	263	$6.03 \times 10^3$	22.1	-22.9	-0.8	$5.81 \times 10^3$	$+2.2 \times 10^2$
0	273	$6.03 \times 10^3$	22.1	-22.1	0	$6.03 \times 10^3$	0
10	283	$6.03 \times 10^3$	22.1	-21.3	+0.8	$6.25 \times 10^3$	$-2.2 \times 10^2$

- The table below summarizes the various combinations of  $\Delta H$  and  $\Delta S$  for a process are the resulting dependence of spontaneity on temperature.

**TABLE 16.5** Various Possible Combinations of  $\Delta H$  and  $\Delta S$  for a Process and the Resulting Dependence of Spontaneity on Temperature

Case	Result
$\Delta S$ positive, $\Delta H$ negative	Spontaneous at all temperatures
$\Delta S$ positive, $\Delta H$ positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
$\Delta S$ negative, $\Delta H$ negative	Spontaneous at low temperatures (where exothermicity is dominant)
$\Delta S$ negative, $\Delta H$ positive	Process not spontaneous at <i>any</i> temperature (reverse process is spontaneous at <i>all</i> temperatures)

- **For example:** At what temperature is the following process spontaneous at 1 atm? What is the boiling point of liquid Br<sub>2</sub>?



**Solution:** The vaporization process will be spontaneous at all temperatures where  $\Delta G^\circ$  is negative. At the boiling point of Br<sub>2</sub>, the liquid and gas Br<sub>2</sub> are in equilibrium ( $\Delta G^\circ = 0$ ). To solve this problem, we use  $\Delta G^\circ = 0$ .

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

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T = \frac{31000}{93.0}$$

$$T = 333 \text{ K}$$

Above 333 K, the vaporization process is spontaneous; the opposite process occurs spontaneously below this temperature.

- **You try:** For mercury, the enthalpy of vaporization is 58.51 kJ/mol and the entropy of vaporization is 92.92 J/K mol. What is the normal boiling point of mercury?

### Entropy Changes in Chemical Reactions

- The second law of thermodynamics tells us that a process will be spontaneous if the entropy of the universe increases when the process occurs.
- However, the entropy changes in the system are determined by positional probability.
- Consider the following reaction:  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$   
Four reactant molecules become two product molecules, lowering the number of independent units in the system which leads to less positional disorder.
- In general, when a reaction involves gaseous molecules, the change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products.
- You try: Predict the sign of  $\Delta S^\circ$  for each of the following reactions.
  - a. The thermal decomposition of solid calcium carbonate:  
 $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
  - b. The oxidation of SO<sub>2</sub> in air:  
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
- The third law of thermodynamics is that the entropy of a perfect crystal at 0 K is zero.
- Because entropy is a state function of the system (it is not pathway dependent) the entropy change for a given chemical reaction can be calculated by taking the difference between the standard entropy values of products and those of the reactants.

- For example: Calculate the  $\Delta S^\circ$  at 25°C for the reaction:  
 $2\text{NiS}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + 2\text{NiO}(\text{s})$

$$\Delta S^\circ_{\text{reaction}} = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

$$\Delta S^\circ_{\text{reaction}} = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

$$\Delta S^\circ_{\text{reaction}} = [2(248) + 2(38)] - [2(53) + 3(205)]$$

$$\Delta S^\circ_{\text{reaction}} = -149 \text{ J/K}$$

Substance	S°(J/K mol)
SO <sub>2</sub> (g)	248
NiO(s)	38
O <sub>2</sub> (g)	205
NiS(s)	53

- You try: Calculate the  $\Delta S^\circ$  at 25°C for the reaction:  
 $\text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{Al}(\text{s}) + 3\text{H}_2\text{O}(\text{g})$

Substance	S°(J/K mol)
Al <sub>2</sub> O <sub>3</sub> (s)	51
H <sub>2</sub> (g)	131
Al(s)	28
H <sub>2</sub> O(g)	189

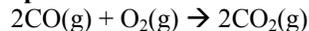
### Free Energy and Chemical Reactions

- The standard free energy change ( $\Delta G^\circ$ ), the change in free energy that will occur if the reactants in their standard states are converted to products in their standard states.
- Consider the following reaction:  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$   $\Delta G^\circ = -33.3 \text{ kJ}$
- The value of  $\Delta G^\circ$  tells us nothing about the rate of a reaction, only its eventual **equilibrium position**.
- The **more negative** the value of  $\Delta G^\circ$ , the further a reaction **will go to the right to reach equilibrium**.
- One way to calculate  $\Delta G^\circ$  is to use the following equation:  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- You try: Consider the reaction being carried out at  $25^\circ\text{C}$  and 1 atm:  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$   
Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  using the following data:

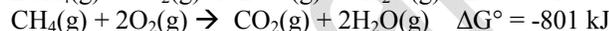
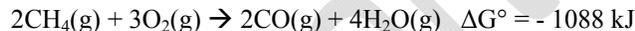
Substance	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/K mol)
$\text{SO}_2(\text{g})$	-297	248
$\text{SO}_3(\text{g})$	-396	257
$\text{O}_2(\text{g})$	0	205

- Another method for calculating  $\Delta G$  for a reaction takes advantage of the fact that, like enthalpy, free energy is a state function. Therefore we can use procedures for finding  $\Delta G^\circ$  that are similar to those for finding  $\Delta H$  using Hess's Law.

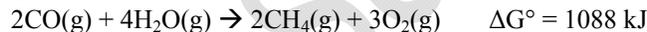
- For example:** Calculate  $\Delta G^\circ$  for the following reaction:



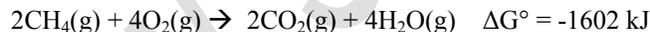
from:



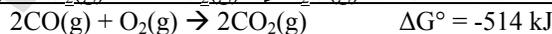
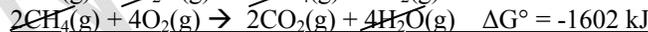
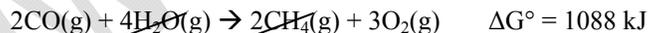
Flip the first reaction:



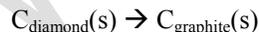
Double the second reaction:



Put together and add:



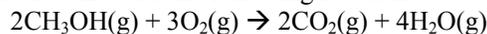
- You try.** Calculate  $\Delta G^\circ$  for the following reaction:



from:



- A third method for calculating free energy change for a reaction uses standard free energies of formation. The **standard free energy of formation** ( $\Delta G_f^\circ$ ) of a substance is defined as the change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states. The  $\Delta G_f^\circ = 0$  of any element in its standard state.
- $\Delta G^\circ = \sum n_p G_f^\circ \text{ products} - \sum n_r G_f^\circ \text{ reactants}$
- For example: Calculate  $\Delta G^\circ$  for the following reaction:



$$\Delta G^\circ = \sum n_p G_f^\circ \text{ products} - \sum n_r G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = [2(-394) + 4(-229)] - [2(-163) + 3(0)]$$

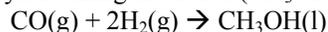
$$\Delta G^\circ = -1378 \text{ kJ}$$

Substance	$\Delta G_f^\circ$ (kJ/mol)
CH <sub>3</sub> OH(g)	-163
O <sub>2</sub> (g)	0
CO <sub>2</sub> (g)	-394
H <sub>2</sub> O(g)	-229

### The Dependence of Free Energy on Pressure

- The equilibrium position represents the lowest free energy value available to a particular reaction system.
- $\Delta G = \Delta G^\circ + RT \ln(Q)$  where Q is the reaction quotient (from law of mass action), T is the Kelvin temperature, R is the ideal gas law constant and is equal to 8.3145 J/K mol,  $\Delta G^\circ$  is the free energy change for the reaction with all reactants and products at a pressure of 1 atm and  $\Delta G$  is the free energy change for the reaction for the specified pressures of reactants and products.
- Example: Calculating  $\Delta G$  at a Different Pressure**

One method for synthesizing methanol (CH<sub>3</sub>OH) involves reacting carbon monoxide and hydrogen gases.



Calculate  $\Delta G$  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.

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

In order to calculate  $\Delta G^\circ$  you need to use the standard free energies of formation (they can be found in Appendix 4 of your text book and at [www.sartep.com](http://www.sartep.com) under thermodynamic data on the tools menu)

$$\Delta G^\circ = \sum n_p G_f^\circ \text{ products} - \sum n_r G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum(-166) - \sum(-137) + 0$$

$$\Delta G^\circ = -29 \text{ kJ or } -2.9 \times 10^4 \text{ J}$$

Substance	$\Delta G_f^\circ$ (kJ/mol)
CO	-137
H <sub>2</sub>	0
CH <sub>3</sub> OH	-166

To calculate  $Q = \frac{1}{(P_{\text{CO}})(P_{\text{H}_2})^2} = \frac{1}{(5.0)(3.0)^2} = 2.2 \times 10^{-2}$

Note CH<sub>3</sub>OH is not used because it is a liquid.

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

$$\Delta G = (-2.9 \times 10^4 \text{ J/mol}) + (8.3145 \text{ J/K mol})(298 \text{ K}) \ln(2.2 \times 10^{-2})$$

$$\Delta G = -38 \text{ kJ/mol}$$

Note that  $\Delta G$  is more negative than  $\Delta G^\circ$ , implying that the reaction is more spontaneous at reactant pressures greater than 1 atm.

- You try: Calculate  $\Delta G$  for the reaction:  $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  for these conditions:  
 $T = 298 \text{ K}$ ,  $P_{\text{NO}} = 1.00 \times 10^{-6} \text{ atm}$ ,  $P_{\text{O}_3} = 2.00 \times 10^{-6} \text{ atm}$ ,  $P_{\text{NO}_2} = 1.00 \times 10^{-7} \text{ atm}$ ,  $P_{\text{O}_2} = 1.00 \times 10^{-3} \text{ atm}$

Substance	$\Delta G_f^\circ$ (kJ/mol)
NO	87
O <sub>3</sub>	163
NO <sub>2</sub>	52
O <sub>2</sub>	0

### The Meaning of $\Delta G^\circ$ for a Chemical Reaction

- The system can achieve the lowest possible free energy by going to equilibrium, not by going to completion.
- Although the value of  $\Delta G^\circ$  for a given reaction system tells us whether the products or reactants are favored under a given set of conditions, it does not mean that the system will proceed to pure products (if  $\Delta G^\circ$  is negative) or remain at pure reactants (if  $\Delta G^\circ$  is positive). Instead, the system will spontaneously go to the equilibrium position, the lowest possible free energy available to it.

### Free Energy and Equilibrium

- When the components of a given chemical reaction are mixed, they will proceed, rapidly or slowly, depending on the kinetics of the process, to the equilibrium position. In Chapter 13 we defined the equilibrium position as the point at which the forward and reverse reaction rates are equal. In this chapter we look at equilibrium from a thermodynamic point of view, and we find that the equilibrium point occurs at the lowest value of energy available to the reaction system.
- Consider the following hypothetical reaction:  $A(g) \rightleftharpoons B(g)$  where 1.0 mole of gaseous A is initially placed in a reaction vessel at a pressure of 2.0 atm.
  - As A changes to B, the free energy of A ( $G_A$ ) will decrease because  $P_A$  is decreasing.
  - The free energy of B ( $G_B$ ) will increase because  $P_B$  is increasing.
  - The reaction will proceed as long as the total free energy of the system decreases (as long as  $G_B$  is less than  $G_A$ ).
  - At some point the pressures of A and B reach equilibrium which makes  $G_A$  equal to  $G_B$ . At this point the system has reached equilibrium.
  - Since  $G_A = G_B$ ,  $\Delta G^\circ$  is zero for A changing to B. The system has reached minimum free energy.
  - There is no longer a driving force to change A to B or B to A, so the system remains at this position.
  - In Summary: when substances undergo a chemical reaction, the reaction proceeds to the minimum free energy (equilibrium), which corresponds to the point where:  $G_{\text{products}} = G_{\text{reactants}}$  OR  $\Delta G^\circ = G_{\text{products}} - G_{\text{reactants}} = 0$
- At equilibrium,  $\Delta G = 0$  and  $Q = K$  (equilibrium constant) so:
  - $\Delta G = \Delta G^\circ + RT \ln(Q)$
  - so:  $0 = \Delta G^\circ + RT \ln(K)$
  - or:  $\Delta G^\circ = -RT \ln(K)$
- If  $\Delta G^\circ = 0$ . The system is at equilibrium and  $K = 1$ .
- If  $\Delta G^\circ < 0$ . The system will adjust to the right and  $K$  will be greater than 1.
- If  $\Delta G^\circ > 0$ . The system will adjust to the left and  $K$  will be less than 1.

- **Example: Free Energy and Equilibrium**

The overall reaction for the corrosion(rusting) of iron by oxygen is:



Using the following data, calculate the equilibrium constant for this reaction at 25°C.

Substance	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/K mol)
$\text{Fe}_2\text{O}_3(s)$	-826	90
$\text{Fe}(s)$	0	27
$\text{O}_2(g)$	0	205

The equation to use is  $\Delta G^\circ = -RT \ln(K)$  but first you need to get  $\Delta G^\circ$  using the given data.

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= \sum H_f^\circ \text{ products} - \sum H_f^\circ \text{ reactants} \\ \Delta H^\circ_{\text{reaction}} &= 2(-826) - 0 \\ \Delta H^\circ_{\text{reaction}} &= -1652 \text{ kJ or } -1.652 \times 10^6 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{\text{reaction}} &= \sum n_p S^\circ \text{ products} - \sum n_r S^\circ \text{ reactants} \\ \Delta S^\circ_{\text{reaction}} &= [2(90)] - [4(27) + 3(205)] \\ \Delta S^\circ_{\text{reaction}} &= -543 \text{ J/K}\end{aligned}$$

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

$$\Delta G^\circ = (-1.652 \times 10^6 \text{ J}) - (298 \text{ K})(-543 \text{ J/K})$$

$$\Delta G^\circ = -1.490 \times 10^6 \text{ J}$$

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

$$-1.490 \times 10^6 \text{ J} = -(8.3145 \text{ J/K mol})(298 \text{ K}) \ln(K)$$

$$\ln(K) = 601$$

$$K = e^{601}$$

This is a very large equilibrium constant. The rusting of iron is clearly very favorable from a thermodynamic point of view. The reaction shifts equilibrium position is far to the right in the reaction:  $4\text{Fe}(s) + 3\text{O}_2(g) \rightleftharpoons 2\text{Fe}_2\text{O}_3(s)$

### Free Energy and Work

- It has been shown that at constant temperature and pressure, the sign of the change in free energy tells us whether a given process is spontaneous. This is very useful because it prevents us from wasting effort on a process that has no inherent tendency to occur.
- The maximum possible useful work obtainable from a process at constant temperature is equal to the change in free energy.  $W_{\max} = \Delta G$
- $\Delta G$  for a spontaneous process represents the energy that is free to do useful work. On the other hand, for a process that is not spontaneous, the value of  $\Delta G$  tells us the minimum amount of work that must be expended to make the process occur.
- The amount of work actually obtained from a spontaneous process is actually less than the maximum possible amount.
- A current flowing through a wire causes frictional heating, and the greater the current, the greater the heat. The heat represents wasted energy. Wasted energy can be minimized by running very low currents through the circuit.
- Achieving the maximum work available from a spontaneous process can occur only via a hypothetical pathway. Any real pathway wastes energy.
- In the near future (now?) the energy crisis will increase in severity. The crisis is not one of supply; the first law of thermodynamics tells us that the universe contains a constant supply of energy. The problem is the availability of useful energy. As we use energy, we degrade its usefulness.

I have the space, so try this old AP Free Response Question from 1983 – 9 points



Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
CO(g)	-110.5	-137.3	+197.9
CH <sub>3</sub> OH(l)	-238.6	-166.2	+126.8

The data in the table above were determined at 25°C.

- Calculate  $\Delta G^\circ$  for the reaction above at 25°C.
- Calculate  $K_{\text{eq}}$  for the reaction above at 25°C.
- Calculate  $\Delta S^\circ$  for the reaction above at 25°C.
- In the table above, there are no data for H<sub>2</sub>. What are the values of  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$ , and of the absolute entropy,  $S^\circ$ , for H<sub>2</sub> at 25°C?

The Answer: 1983 AP Free Response

a) two points

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ prod} - \sum \Delta G_f^\circ \text{ react}$$

$$\Delta G^\circ = -166.2 - (-137.3 + 2(0))$$

$$\Delta G^\circ = -28.9 \text{ kJ/mol}$$

b) two points

$$\Delta G^\circ = -RT \ln K \text{ (or } -2.3 RT \log K)$$

$$-28.9 = -(8.31 \times 10^{-3})(298) \ln K$$

$$\ln K = 11.67$$

$$K = 1.17 \times 10^5$$

c) two points

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

$$-28,900 = -128,100 - 298\Delta S^\circ$$

$$\Delta S^\circ = -99,200 / 298 = -333 \text{ J / mol-K}$$

d) three points

$$\Delta H_f^\circ (\text{H}_2) = 0 \text{ and } \Delta G_f^\circ (\text{H}_2) = 0$$

$$\Delta S^\circ = \sum S^\circ \text{ prod} - \sum S^\circ \text{ react}$$

$$-333 \text{ J / mol-K} = 126.8 \text{ J / mol-K} - 197.9 \text{ J / mol-K} - 2 S^\circ (\text{H}_2)$$

$$S^\circ = 131 \text{ J / mol-K}$$

### Important Formulas

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

At equilibrium (melting point and boiling point),  $\Delta G^\circ = 0$ ;  $\Delta H^\circ = T\Delta S^\circ$

$\Delta H^\circ$  &  $\Delta S^\circ$  will be given in terms of fusion (melting) or vaporization (boiling)

$$\text{For chemical reactions: } \Delta H^\circ_{\text{reaction}} = \sum n_p H^\circ_{\text{products}} - \sum n_r H^\circ_{\text{reactants}}$$

$$\text{For chemical reactions: } \Delta S^\circ_{\text{reaction}} = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

$$\text{For chemical reactions: } \Delta G^\circ = \sum n_p G_f^\circ_{\text{products}} - \sum n_r G_f^\circ_{\text{reactants}}$$

$$\text{For reactions involving pressure: } \Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\text{For chemical reactions at equilibrium, } \Delta G = 0 \text{ \& } Q = K; \Delta G^\circ = -RT \ln(K)$$