

Chapter 18: Entropy and Free Energy18.2 & 18.3: Spontaneous Process & Entropy

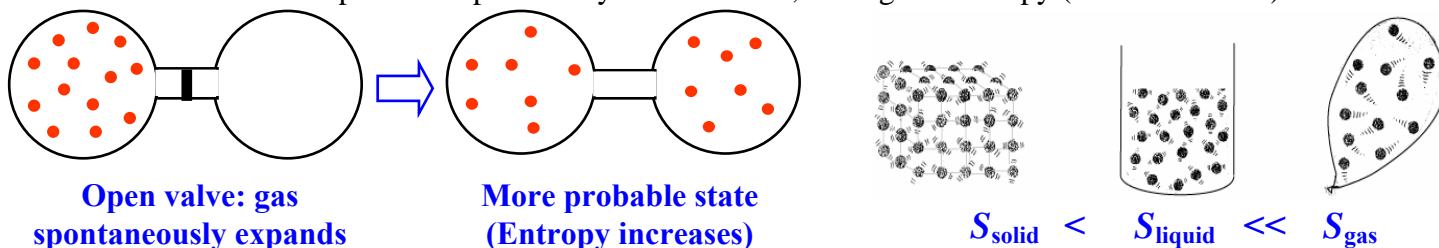
**Spontaneous Process:** - a thermodynamic process that happens without any external interventions.  
- it does NOT indicate the speed (kinetics) of the process.

**Entropy (S):** - a measure of the amount of disorder or randomness.  
- it mainly explains the number of molecular arrangement and the probabilities of molecular in any given arrangements.  
- **unlike enthalpy,  $S_{\text{elements}} \neq 0$ . All  $S > 0$ , however,  $\Delta S$  can be positive or negative.**  
- **the more positive the entropy becomes, the more spontaneous is the process.**  
- **most but NOT all exothermic reactions are spontaneous. Temperature of the surrounding is also an important factor.**

$$\Delta S = S_{\text{final}} - S_{\text{initial}} \text{ or } \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}$$

When  $\Delta S > 0$ , the process is Thermodynamically **Spontaneous**  
When  $\Delta S < 0$ , the process is Thermodynamically **Non-Spontaneous**

**Positional Probability:** - the probability of how the molecules are arranged in a given system.  
- the higher the positional probability for a set of arrangements, the higher the entropy it is for that set of arrangements.  
- the complete mixing of molecules to fill a given system produces the highest positional probability and therefore, the highest entropy (or random state).



**Example 1:** For the following process, determine whether it is spontaneous and predict the sign of  $\Delta S$ .

- the heat from the heat vent eventually warms up the room.
- diluting a salt solution.
- photosynthesis occurs naturally in plants

a. the heat from the heat vent eventually warms up the room.

(**Spontaneous,  $\Delta S > 0$ , temperature naturally goes from high to low to achieve thermodynamic equilibrium**)

b. diluting a salt solution.

(**Spontaneous,  $\Delta S > 0$ , diluted solution has more randomness and higher positional entropy than a concentrated state – volume has increased**)

c. photosynthesis occurs naturally in plants.

(**Non-Spontaneous,  $\Delta S < 0$ , even though photosynthesis occurred naturally, it does need an external intervention, namely sunlight energy to initiate the process - endothermic**)

Assignment

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18.4: The Second Law of Thermodynamics

**Second Law of Thermodynamics:** - states that all spontaneous processes involve an increase in entropy in the universe. Hence, the entropy in the universe is always increasing.  
 - when **evaluating Spontaneity**, we must **evaluate the sign of  $\Delta S$  of the UNIVERSE**, and not just  $\Delta S_{\text{sys}}$  or  $\Delta S_{\text{surr}}$ .

Second Law of Thermodynamics

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

When  $\Delta S_{\text{univ}} > 0$ , the process is **Thermodynamically Spontaneous**

When  $\Delta S_{\text{univ}} = 0$ , the **System is at Equilibrium** ( $\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$ )

When  $\Delta S_{\text{univ}} < 0$ , the process is **Thermodynamically Non-Spontaneous**

**Example 1:** The process of cleaning up a messy room of a teenager is a non-spontaneous process. However face with the threat of being grounded, most teenagers will clean up their room in a hurry. Rationalize this phenomenon using the second law of thermodynamics.

If we define the cleaning of the room as a system, then  $\Delta S_{\text{sys}} < 0$ . Similarly, the threat of being grounded by an outside source can be defined as the surrounding. In this case, the result of being grounded has a much lower entropy than the amount of entropy cleaning the room (they might be asked to clean the entire house and yard work). Or putting it in another way, the act of going out can be represented by  $\Delta S_{\text{surr}} \gg 0$  (teenagers can behave more randomly outside parental supervisions than being messy in their rooms). Since  $\Delta S_{\text{surr}} \gg |\Delta S_{\text{sys}}|$ , **most teenagers will clean their rooms due to the overall  $\Delta S_{\text{univ}} > 0$ .**

The Effect of Temperature on Spontaneity

**Entropy of the Surrounding** ( $\Delta S_{\text{surr}}$ ): depends on the  $\Delta S_{\text{sys}}$ ,  $\Delta H$  and the temperature of the surrounding.

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

$\Delta S_{\text{surr}}$  = Entropy of the Surrounding (kJ/K)

$\Delta H$  = Change in Enthalpy of the Process (kJ)       $T$  = Temperature (K)

When  $\Delta H < 0$ ,  $\Delta S_{\text{surr}} > 0$

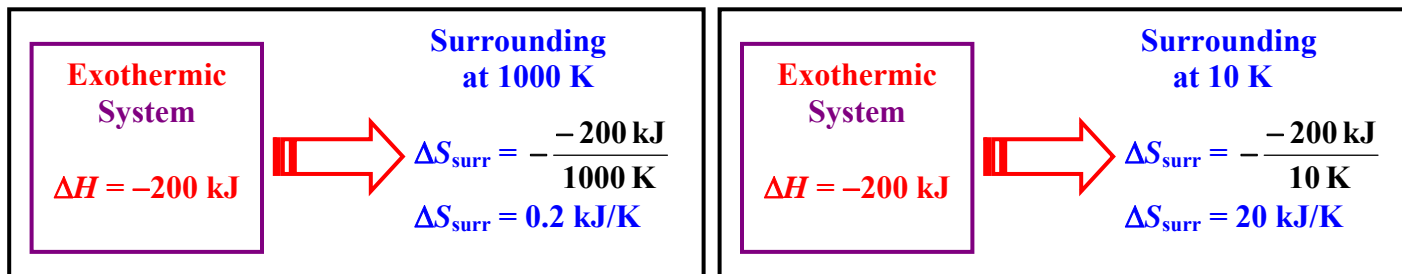
When  $\Delta H > 0$ ,  $\Delta S_{\text{surr}} < 0$

When  $T$  is Large,  $|\Delta S_{\text{surr}}|$  is Small

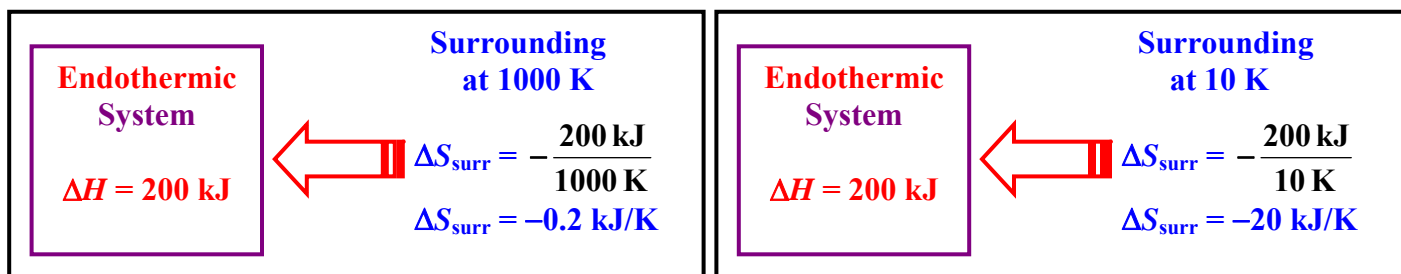
When  $T$  is small,  $|\Delta S_{\text{surr}}|$  is Large

1. System is Exothermic ( $\Delta H < 0$ ):  $-\Delta S_{\text{surr}} > 0$  (Surrounding's Randomness Increases – Less Order)

- a. And if **T is Large**, the amount of energy flows into the surrounding **cannot increase the randomness of the surrounding effectively**. Therefore,  $\Delta S_{\text{surr}} > 0$  but Small.
- b. And if **T is Small**, the amount of energy flows into the surrounding **increases the randomness of the surrounding significantly**. Therefore,  $\Delta S_{\text{surr}} > 0$  and Large.

2. System is Endothermic ( $\Delta H > 0$ ):  $-\Delta S_{\text{surr}} < 0$  (Surrounding's Randomness Decreases – More Order)

- a. And if **T is Large**, the amount of energy flows from the surrounding **cannot decrease the randomness of the surrounding effectively**. Therefore,  $\Delta S_{\text{surr}} < 0$  but Small.
- b. And if **T is Small**, the amount of energy flows from the surrounding **decreases the randomness of the surrounding significantly**. Therefore,  $\Delta S_{\text{surr}} < 0$  and Large.



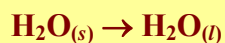
**Note:** The magnitude and the sign of  $\Delta S_{\text{surr}}$  alone CANNOT predict spontaneity. Spontaneity depends on  $\Delta S_{\text{univ}}$  and the magnitude and the sign of  $\Delta S_{\text{sys}}$  must also be taken into consideration.

**Example 2:** The molar heat of fusion for water is 6.01 kJ/mol. Determine the  $\Delta S_{\text{surr}}$  for the following phase change of  $\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$  at  $-20.0^\circ\text{C}$  and at  $10.0^\circ\text{C}$  under 1 atm.

$$\Delta H = 6.01 \text{ kJ/mol}$$

$$T_1 = -20.0^\circ\text{C} = 253.15 \text{ K}$$

$$T_2 = 10.0^\circ\text{C} = 283.15 \text{ K}$$



$$\Delta H = 6.01 \text{ kJ}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T_1} = -\frac{6.01 \text{ kJ}}{253.15 \text{ K}}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T_2} = -\frac{6.01 \text{ kJ}}{283.15 \text{ K}}$$

$$\Delta S_{\text{surr}} = ?$$

$$\Delta S_{\text{surr}} = -2.37 \times 10^{-2} \text{ kJ/K at } -20.0^\circ\text{C}$$

$$\Delta S_{\text{surr}} = -23.7 \text{ J/K at } -20.0^\circ\text{C}$$

$$\Delta S_{\text{surr}} = -2.12 \times 10^{-2} \text{ kJ/K at } 10.0^\circ\text{C}$$

$$\Delta S_{\text{surr}} = -21.2 \text{ J/K at } 10.0^\circ\text{C}$$

As predicted,  $\Delta S_{\text{surr}} < 0$  due to  $\Delta H > 0$  (Endothermic), and the magnitude of  $\Delta S_{\text{surr}}$  is Higher at low Temperature

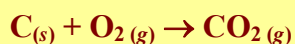
**Example 3:** The equation of  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} + 393.5 \text{ kJ}$  describes the combustion of carbon. What is the  $\Delta S_{\text{surr}}$  when the reaction happens at a barbecue at  $-40.0^\circ\text{C}$  in Anchorage, Alaska on a cold winter day compared to  $40^\circ\text{C}$  on a hot summer day at Phoenix, Arizona?

$$\Delta H = -393.5 \text{ kJ/mol}$$

$$T_1 = -40.0^\circ\text{C} = 233.15 \text{ K}$$

$$T_2 = 40.0^\circ\text{C} = 313.15 \text{ K}$$

$$\Delta S_{\text{surr}} = ?$$



$$\Delta H = -393.5 \text{ kJ}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T_1} = -\frac{-393.5 \text{ kJ}}{233.15 \text{ K}}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T_2} = -\frac{-393.5 \text{ kJ}}{313.15 \text{ K}}$$

$$\Delta S_{\text{surr}} = 1.69 \text{ kJ/K at } -40.0^\circ\text{C}$$

$$\Delta S_{\text{surr}} = 1.26 \text{ kJ/K at } 40.0^\circ\text{C}$$

As predicted,  $\Delta S_{\text{surr}} > 0$  due to  $\Delta H < 0$  (Exothermic), and the magnitude of  $\Delta S_{\text{surr}}$  is Higher at low Temperature.

**Third Law of Thermodynamics:** - states that at **0 K (absolute zero)**, the **entropy is 0** for a perfect crystal (perfect order – no randomness).

**General Guidelines for Entropy of System ( $S_{\text{sys}}$  or  $S^\circ$ ):**

- $S^\circ$  INCREASES when Matters change from Solid to Liquid and from Liquid to Gas.**
- $S^\circ$  INCREASES with more Gaseous Molecules or Aqueous Ions (more molecules mean more possible configurations and positional probabilities).**
- $S^\circ$  INCREASES with Higher Internal Temperature.** Temperature is the average kinetic energy of particles. The higher the temperature, the faster they move (more Translation Motion), resulting in more randomness.
- $S^\circ$  INCREASES with the Complexity of the Molecule.** The more bonds a molecule has, the more different ways it can rotate and vibrate its bonds (Rotational and Vibration Motions).

(Check out animation at <http://wine1.sb.fsu.edu/chm1046/notes/Thermody/MolBasis/MolBasis.htm>)

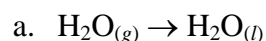
$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$\Delta S^\circ$  = Standard Change in Entropy of a System

$\sum S^\circ_{\text{products}}$  = Total Standard Entropy of all Products

$\sum S^\circ_{\text{reactants}}$  = Total Standard Entropy of all Reactants

**Example 4:** Predict the sign of  $\Delta S^\circ$  for each reaction below. Then, calculate the  $\Delta S^\circ$  at  $25.0^\circ\text{C}$  and 1 atm using the given values.



$$S^\circ (H_2O_{(g)}) = 189 \text{ J/(K} \cdot \text{mol)}$$

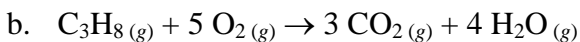
$$S^\circ (H_2O_{(l)}) = 70 \text{ J/(K} \cdot \text{mol)}$$

This is a phase change from gas to liquid,  $\Delta S^\circ < 0$ .

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = (1 \text{ mol})(70 \text{ J/(K} \cdot \text{mol)}) - (1 \text{ mol})(189 \text{ J/(K} \cdot \text{mol)})$$

$$\Delta S^\circ = -119 \text{ J/K (per mole of steam changed to water)}$$



$$S^\circ(\text{C}_3\text{H}_8(g)) = 270 \text{ J/(K} \cdot \text{mol)}$$

$$S^\circ(\text{O}_2(g)) = 205 \text{ J/(K} \cdot \text{mol)}$$

$$S^\circ(\text{CO}_2(g)) = 214 \text{ J/(K} \cdot \text{mol)}$$

$$S^\circ(\text{H}_2\text{O}(g)) = 189 \text{ J/(K} \cdot \text{mol)}$$

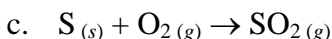
Since there are more moles of gaseous products,  $\Delta S^\circ > 0$ .

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(3 \text{ mol})(214 \text{ J/(K} \cdot \text{mol)}) + (4 \text{ mol})(189 \text{ J/(K} \cdot \text{mol)})] - [(1 \text{ mol})(270 \text{ J/(K} \cdot \text{mol)}) + (5 \text{ mol})(205 \text{ J/(K} \cdot \text{mol)})]$$

$$\Delta S^\circ = [1398 \text{ J/K}] - [1295 \text{ J/K}]$$

$$\Delta S^\circ = 103 \text{ J/K (per mole of propane burned)}$$



$$S^\circ(\text{S}(s)) = 33 \text{ J/(K} \cdot \text{mol)}$$

$$S^\circ(\text{O}_2(g)) = 205 \text{ J/(K} \cdot \text{mol)}$$

$$S^\circ(\text{SO}_2(g)) = 248 \text{ J/(K} \cdot \text{mol)}$$

There is the same number of moles of gaseous chemicals on both sides of the equation. However,  $\text{SO}_2(g)$  has more bonds than  $\text{O}_2(g)$ . Hence  $\Delta S^\circ > 0$ .

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(1 \text{ mol})(248 \text{ J/(K} \cdot \text{mol)})] - [(1 \text{ mol})(205 \text{ J/(K} \cdot \text{mol)}) + (1 \text{ mol})(33 \text{ J/(K} \cdot \text{mol)})]$$

$$\Delta S^\circ = [248 \text{ J/K}] - [238 \text{ J/K}]$$

$$\Delta S^\circ = 10 \text{ J/K (per mole of SO}_2(g) \text{ formed)}$$

### Assignment

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## 18.5: Gibbs Free Energy

**Free Energy (G):** - the amount of energy related to the entropy of the universe accounting for the

dependency of a constant temperature  $\left(\Delta S_{\text{univ}} = -\frac{\Delta G}{T}\right)$  or  $\Delta G = -\Delta S_{\text{univ}}T$ .

- also known as Gibbs Free Energy named after Willard Gibbs.

- like enthalpy,  $G_{\text{elements}} = 0$ .

- when  $\Delta S_{\text{univ}} > 0$ ,  $\Delta G < 0$ , **the process is thermodynamically spontaneous.**

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

( $\Delta S_{\text{sys}} = \Delta S^\circ$  - standard entropy at constant temperature and pressure)

$$\left(-\frac{\Delta G}{T}\right) = \Delta S^\circ + \left(-\frac{\Delta H^\circ}{T}\right)$$

(Substitute  $\Delta S_{\text{univ}}$  with  $-\frac{\Delta G}{T}$  and  $\Delta S_{\text{surr}}$  with  $-\frac{\Delta H^\circ}{T}$ )

$$T\left(-\frac{\Delta G}{T}\right) = T\Delta S^\circ + T\left(-\frac{\Delta H^\circ}{T}\right)$$

(Multiply each term by T)

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

(Simplify and rearrange to  $\Delta G = \Delta H^\circ - T\Delta S^\circ$ )

**Gibbs Free Energy**

$$\Delta S_{\text{univ}} = -\frac{\Delta G}{T} \quad \text{or} \quad \Delta G = -\Delta S_{\text{univ}}T$$

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

$\Delta G$  = Free Energy of the Universe (kJ/mol or J/mol)

$\Delta H$  = Enthalpy of the System (kJ/mol or J/mol)       $T$  = Temperature (K)

$\Delta S^\circ$  = Standard Entropy the System (kJ/(K • mol) or J/(K • mol)]

When  $\Delta S_{\text{univ}} > 0$ ,  $\Delta G < 0$ , the process is **Thermodynamically Spontaneous**

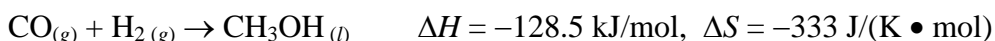
When  $\Delta S_{\text{univ}} = 0$ ,  $\Delta G = 0$ , the System is at **Equilibrium** ( $\Delta H^\circ = T\Delta S^\circ$ )

When  $\Delta S_{\text{univ}} < 0$ ,  $\Delta G > 0$ , the process is **Thermodynamically Non-Spontaneous**

**Cases for Spontaneity ( $\Delta G < 0$ )**

$\Delta H^\circ$	$\Delta S^\circ$	Thermodynamic Spontaneity ( $\Delta G$ )
+ (Endothermic)	+ (More Random - Less Order)	Spontaneous at <b>High T</b>
+ (Endothermic)	- (Less Random - More Order)	Always Non-Spontaneous ( $\Delta G > 0$ )
- (Exothermic)	+ (More Random - Less Order)	Always Spontaneous ( $\Delta G < 0$ )
- (Exothermic)	- (Less Random - More Order)	Spontaneous at <b>Low T</b>

**Example 1:** Together, carbon monoxide gas from incomplete combustion along with hydrogen gas is known as syngas. This is because the reaction of  $\text{CO}_{(g)}$  and  $\text{H}_{2(g)}$  produced liquid methanol, which is commonly used in the production of fibres and plastic, as well as light fuel. The production of methanol from syngas also produces energy that can be used for generating power.



- Determine whether the reaction is spontaneous at  $30.0^\circ\text{C}$ .
- Calculate the temperature at which the reaction will be at thermodynamic equilibrium.
- Comment on the spontaneity of this reaction if the temperature is above and below this equilibrium temperature.

a.

$$\Delta H = -128.5 \text{ kJ/mol}$$

$$\Delta S = -333 \text{ J/(K} \cdot \text{mol)} = -0.333 \text{ kJ/(K} \cdot \text{mol)}$$

$$T = 30.0^\circ\text{C} = 303.15 \text{ K}$$

$\Delta G = ?$

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

$$\Delta G = (-128 \text{ kJ/mol}) - (303.15 \text{ K})(-0.333 \text{ kJ/(K} \cdot \text{mol)})$$

$$\Delta G = -27.1 \text{ kJ/mol at } 30.0^\circ\text{C}$$

Since  $\Delta G < 0$ , the reaction is **Spontaneous**

b.

$$\Delta G = \Delta H^\circ - T\Delta S^\circ \quad 0 = \Delta H^\circ - T\Delta S^\circ \text{ at equilibrium}$$

$$\Delta G = 0 \text{ at equilibrium}$$

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

$$\Delta H = -128.5 \text{ kJ/mol}$$

$$\Delta S = -0.333 \text{ kJ/(K} \cdot \text{mol)}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-128 \text{ kJ/mol}}{-0.333 \text{ kJ/(K} \cdot \text{mol)}} = 384.384 \text{ K}$$

$T = ?$

$$T_{\text{eq}} = 111^\circ\text{C}$$

- At  $T > 111^\circ\text{C}$ ,  $\Delta G > 0$  because  $-T\Delta S$  term will be **dominant** (bigger magnitude than  $\Delta H^\circ$ ). The reaction will be **Non-Spontaneous**.  
At  $T < 111^\circ\text{C}$ ,  $\Delta G < 0$  because  $\Delta H^\circ$  term will be **dominant** (bigger magnitude than  $-T\Delta S$ ). The reaction will be **Spontaneous**.

**Example 2:** The molar heat of vaporization and its corresponding molar change in entropy of methanol is 35.2 kJ/mol and 104 J/(K • mol) respectively at 1 atm. Determine the theoretical boiling point of methanol. What is the % error if an experimental result of 66.4°C was reported?

$$\begin{aligned} \Delta G &= 0 \text{ at boiling point} & \text{CH}_3\text{OH}_{(l)} &\rightarrow \text{CH}_3\text{OH}_{(g)} & \Delta H &= 35.2 \text{ kJ/mol}, \Delta S = 104 \text{ J/(K} \cdot \text{mol)} \\ \Delta H &= 35.2 \text{ kJ/mol} & \Delta G &= \Delta H^\circ - T\Delta S^\circ & 0 &= \Delta H^\circ - T\Delta S^\circ \text{ at equilibrium} \\ \Delta S &= 104 \text{ J/(K} \cdot \text{mol)} & T\Delta S^\circ &= \Delta H^\circ \\ \Delta S &= 0.104 \text{ kJ/(K} \cdot \text{mol)} & T &= \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{35.2 \text{ kJ/mol}}{0.104 \text{ kJ/(K} \cdot \text{mol)}} = 338.4615 \text{ K} \\ T &= ? \end{aligned}$$

$$\text{Theoretical } T_b = 65.3^\circ\text{C}$$

$$\% \text{ error} = \frac{|\text{Theoretical} - \text{Experimental}|}{\text{Theoretical}} \times 100\% = \frac{|65.3^\circ\text{C} - 66.4^\circ\text{C}|}{65.3^\circ\text{C}} \times 100\%$$

$$\% \text{ error} = 1.68\%$$

### Gibbs Free Energy and Chemical Reactions

#### Free Energy of a Chemical Reaction

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{or} \quad \Delta G^\circ = \Sigma G^\circ_{\text{products}} - \Sigma G^\circ_{\text{reactants}}$$

$\Delta G^\circ$  = Standard Change in Free Energy of a System

$\Sigma G^\circ_{\text{products}}$  = Total Standard Free Energy of all Products

$\Sigma G^\circ_{\text{reactants}}$  = Total Standard Free Energy of all Reactants

**Example 3:** Given that  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$  has a  $\Delta H = -484 \text{ kJ}$  and  $\Delta S = -89.0 \text{ J/K}$ , determine the free energy for  $\Delta G^\circ$  of the given chemical equation at 25.0°C.

$$\begin{aligned} \Delta H &= -484 \text{ kJ} & 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) &\rightarrow 2 \text{H}_2\text{O}(\text{g}) & \Delta H &= -484 \text{ kJ} \\ \Delta S &= -89.0 \text{ J/K} = -0.0890 \text{ kJ/K} & \Delta G &= \Delta H^\circ - T\Delta S^\circ = (-484 \text{ kJ}) - (298.15 \text{ K})(-0.089 \text{ kJ/K}) \\ T &= 25.0^\circ\text{C} = 298.15 \text{ K} \\ \Delta G &= ? & \Delta G &= -457 \text{ kJ at } 25.0^\circ\text{C} \\ & & \text{Since } \Delta G < 0, & \text{the reaction is Spontaneous} \end{aligned}$$

**Example 4:** Given that  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$  has the following thermodynamic values, determine  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  of the given chemical equation at 25.0°C. At what temperature will the formation of ammonia at equilibrium?

Chemicals	$H^\circ$ (kJ/mol)	$S^\circ$ [J/(K • mol)]
$\text{N}_2(\text{g})$	0	192
$\text{H}_2(\text{g})$	0	131
$\text{NH}_3(\text{g})$	-46	193

$$\Delta H^\circ = \Sigma H^\circ_{\text{products}} - \Sigma H^\circ_{\text{reactants}}$$

$$\Delta H^\circ = [(2 \text{ mol})(-46 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (3 \text{ mol})(0 \text{ kJ/mol})] = -92 \text{ kJ}$$

$$\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(2 \text{ mol})(193 \text{ J/(K} \cdot \text{mol)})] - [(1 \text{ mol})(192 \text{ J/(K} \cdot \text{mol)}) + (3 \text{ mol})(131 \text{ J/(K} \cdot \text{mol)})]$$

$$\Delta S^\circ = [386 \text{ J/K}] - [585 \text{ J/K}] = -199 \text{ J/K}$$

$$\Delta H = -92 \text{ kJ}$$

$$\Delta S = -199 \text{ J/K} = -0.199 \text{ kJ/K}$$

$$T = 25.0^\circ\text{C} = 298.15 \text{ K}$$

$$\Delta G = ? \quad T_{\text{eq}} = ?$$



$$\Delta G = \Delta H^\circ - T\Delta S^\circ = (-92 \text{ kJ}) - (298.15 \text{ K})(-0.199 \text{ kJ/K})$$

$$\Delta G = -33 \text{ kJ at } 25.0^\circ\text{C}$$

Since  $\Delta G < 0$ , the reaction is Spontaneous

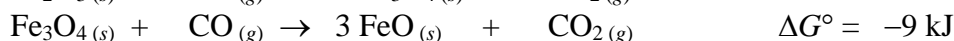
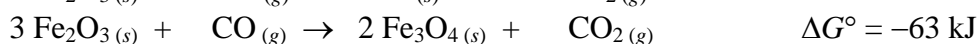
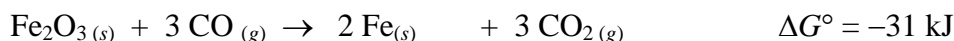
$$\Delta G = \Delta H^\circ - T\Delta S^\circ \quad 0 = \Delta H^\circ - T\Delta S^\circ \text{ at equilibrium}$$

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

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-92 \text{ kJ}}{-0.199 \text{ kJ/K}} = 462.312 \text{ K} \quad (T_{\text{eq}} = 169^\circ\text{C})$$

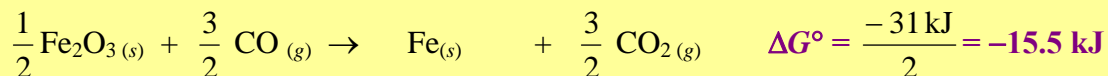
For the reaction to go forward,  $T$  must be kept below  $169^\circ\text{C}$ .

**Example 5:** Given the following data,

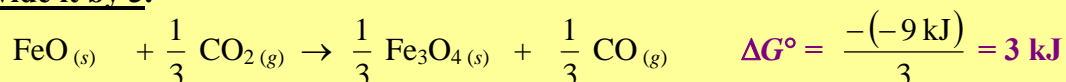


calculate the  $\Delta G^\circ$  for the reaction  $\text{FeO}(\text{s}) + \text{CO}(\text{g}) \rightarrow \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$

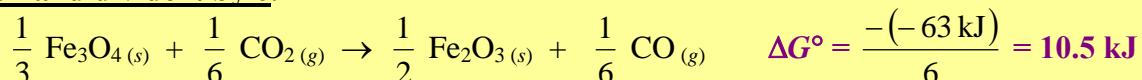
Since 1 mole of  $\text{Fe}(\text{s})$  is found on the product side of the final equation, we must divide the 1<sup>st</sup> equation by 2.



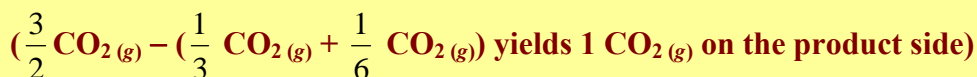
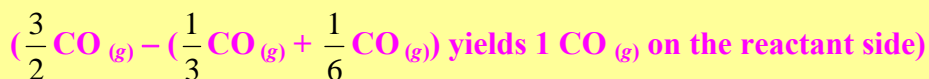
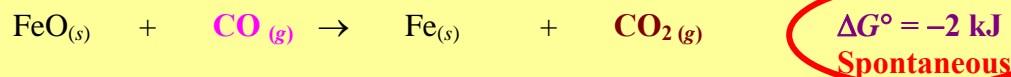
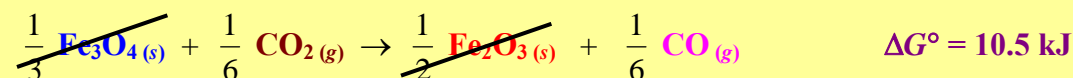
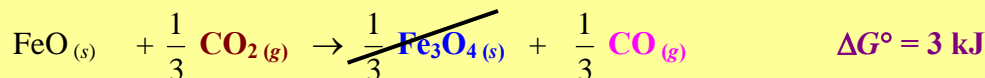
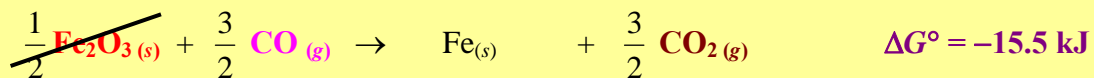
Because 1 mole of  $\text{FeO}(\text{s})$  is located at the reactant side of the final equation, we must flip the 3<sup>rd</sup> equation and divide it by 3.



Now we have to cancel out  $\frac{1}{2}$  mole of  $\text{Fe}_2\text{O}_3(\text{s})$  from the modified 1<sup>st</sup> equation. Hence, we must flip the 2<sup>nd</sup> equation and divide it by 6.



Now we add the equation and cancel equal moles of same chemicals found on both sides.



### Assignment

18.5 pg. 811–813 #17 to 20, 42, 44, 51, 52, 54, 56 to 61