

First Law of Thermodynamics

- _____
- Therefore, the total energy of the universe is a constant.
- Energy can, however, _____ from one form to another or _____ from a system to the surroundings or vice versa

Spontaneous Processes

- Spontaneous processes _____
- Characteristics of spontaneity:
 1. _____
 - A nail will spontaneously rust but not spontaneously unrust
 2. _____
 - Above 0°C it is spontaneous for ice to melt.
 - Below 0°C the reverse process (freezing) is spontaneous.
 - At 0°C both processes are in equilibrium and neither reaction is favored

Example: Determine whether the following processes are spontaneous:

- a) when a piece of metal heated to 150°C is added to water at 40°C , the water gets hotter
- b) water at room temperature decomposes into $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$
- c) Benzene vapor, $\text{C}_6\text{H}_6(\text{g})$, at a pressure of 1atm, condenses to a liquid at the normal boiling point of benzene, 80.1°C

What is the driving force for reactions?

- Thought used to be just enthalpy – _____
 - **negative ΔH is “good” – more favorable**
 - leads to lower potential energy, which is more stable
BUT.....
- We do have reactions that are **endothermic** that occur **spontaneously**
- So another driving force could be **ENTROPY (S)!**
Units = $\text{J/mol} \times \text{K}$
** NOTE THE UNITS! The standard for this is in J, while ΔH is in kJ/mol

Entropy

- _____ in a system
- Described as the # of possible arrangements that are available to the system
- Reactions will “ _____ ”
 - Entropy tends to increase with increases in
 - _____
 - _____
 - _____
 - State change
 - Entropy increases with the freedom of motion of molecules.
 - **Therefore,** _____
 - Solubility
 - **Generally, when a** _____,

Example:

1. Choose the sample of matter that has a greater entropy in each pair:
 - a) 1mol NaCl(s) or 1mol HCl(g)
 - b) 2mol HCl(g) or 1mol HCl(g)
 - c) 1mol of HCl(g) or 1mol Ar(g)
2. Predict whether ΔS is positive or negative for each of the following processes:
 - a) $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$
 - b) $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$
 - c) $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$
 - d) $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$

Second Law of Thermodynamics

- _____
and the entropy of the universe does not change for reversible processes.

Standard Changes in Entropy

- Standard entropy changes for a reaction can be estimated in a manner analogous to that by which ΔH is estimated: $\Delta S^\circ = \Sigma \Delta S^\circ(\text{products}) - \Sigma \Delta S^\circ(\text{reactants})$

Example:

1. Calculate the entropy of the following reaction: $2\text{NiS}(s) + 3\text{O}_2(g) \rightarrow 2\text{SO}_2(g) + 2\text{NiO}(s)$.

The standard molar entropies for each substance is given below.

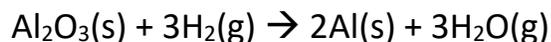
$\text{SO}_2 = 248 \text{ J/mol K}$

$\text{O}_2 = 205 \text{ J/mol K}$

$\text{NiO} = 38 \text{ J/mol K}$

$\text{NiS} = 53 \text{ J/mol K}$

2. Calculate the standard entropy change for the reaction below at 298K:



S° values:

$\text{Al}_2\text{O}_3 = 51 \text{ J/mol K}$

$\text{H}_2 = 130.58 \text{ J/mol K}$

$\text{Al} = 28.32 \text{ J/mol K}$

$\text{H}_2\text{O} = 188.83 \text{ J/mol K}$

Third Law of Thermodynamics

- _____
 - ONLY AT ABSOLUTE ZERO!
 - H_f of an element = 0, but the S of one is usually NOT – be careful!

Gibbs Free Energy

- Can be thought of as the _____
- Mathematically combines enthalpy and entropy to predict whether a reaction at constant temperature and pressure will be spontaneous
- **$\Delta G = \Delta H - T \Delta S$**
 1. If _____, the forward reaction is spontaneous.
 2. If _____, the system is at equilibrium.
 3. If _____, the reaction is spontaneous in the reverse direction.

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

Problem with units:

$$\Delta H = \text{kJ/mole}$$

$$\Delta S = \text{J / mole} \times \text{K}$$

$$T = \text{K}$$

*****Convert J to kJ*****

Example:

1. Calculate the standard free energy change for the formation of NO(g) from N₂(g) and O₂(g) at 298K given that $\Delta H^\circ = 180.7 \text{ kJ}$ and $\Delta S^\circ = 24.7 \text{ J/K}$. Is the reaction spontaneous under these conditions?

2. A particular reaction has a $\Delta H^\circ = 24.6 \text{ kJ}$ and $\Delta S^\circ = 132 \text{ J/K}$ at 298K. Calculate ΔG° . Is the reaction spontaneous under these conditions?

Standard Free Energy Changes

- Analogous to standard enthalpies of formation are standard free energies of formation,

$$\Delta G^\circ: \Delta G^\circ = \sum \Delta G^\circ(\text{products}) - \sum \Delta G^\circ(\text{reactants})$$

Example:

1. Calculate the free-energy change for the following reaction at 298K:
 $\text{P}_4(\text{g}) + 6\text{Cl}_2(\text{g}) \rightarrow 4\text{PCl}_3(\text{g})$. What is ΔG° for the reverse reaction?

G° values:

$$\text{P}_4 = 24.4 \text{ kJ/mol}$$

$$\text{Cl}_2 = 0 \text{ kJ/mol}$$

$$\text{PCl}_3 = -269.6 \text{ kJ/mol}$$

2. The ΔH° for the combustion of propane is -2220 kJ : $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
 - a) Predict whether ΔG° for this reaction is more or less negative than ΔH°

 - b) Calculate ΔG° . Was your prediction correct?

G° values:

$$\text{C}_3\text{H}_8 = -23.47 \text{ kJ/mol}$$

$$\text{O}_2 = 0 \text{ kJ/mol}$$

$$\text{CO}_2 = -394.4 \text{ kJ/mol}$$

$$\text{H}_2\text{O} = -237.13 \text{ kJ/mol}$$

Spontaneity: Free Energy and Temperature

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

ΔH	ΔS	ΔG	Reaction Characteristics
-	+	-	
+	-	+	
-	-	+ or -	
+	+	+ or -	

Example:

1. The Haber process is used for the production of ammonia: $\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \rightarrow 2 \text{NH}_3 (\text{g})$

Assume ΔH° and ΔS° for this reaction do not change with temperature.

a) Predict the direction in which ΔG° for this reaction changes with increasing temperature

b) Calculate the ΔG° values for the reaction at 25°C and 500°C.

	H°	S°
H_2	0 kJ/mol	130.58 J/mol K
N_2	0 kJ/mol	191.50 J/mol K
NH_3	-46.19 kJ/mol	192.5 J/mol K

Spontaneity HW

Entropy-Spontaneity

- Which of the following processes are spontaneous (circle all that apply)?
 - Salt dissolves in H₂O
 - A clear solution becomes a uniform color after a few drops of dye are added
 - Iron rusts
 - You clean your bedroom
- When the environment is contaminated by a toxic or potentially toxic substance (for example, from a chemical spill or the use of insecticides), the substance tends to disperse. How is this consistent with the second law of thermodynamics?

Entropy – Qualitative

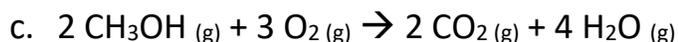
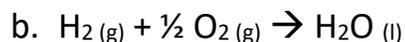
- Predict the sign of ΔS for each of the following:
 - the evaporation of alcohol
 - the freezing of water
 - compressing an ideal gas at constant temperature
- For each of the following pairs, circle the substance that has the larger standard entropy:
 - 1 mol of P₄ (g) at 300°C, 0.01 atm or 1 mol of As₄ (g) at 300°C, 0.01 atm
 - 1 mol of H₂O (g) at 100°C, 1 atm or 1 mol of H₂O (l) at 100°C, 1 atm
 - 1 mol of Ne (g) in 15.0 L or 1.0 mol of Ne (g) in 1.50 L
 - 0.5 mol of N₂ (g) at 298 K, 20.0 L or 0.5 mol of N₂ (g) at 498 K, 20.0 L
- Predict the sign of the entropy change of the system for each of the following reactions:
 - $\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \rightarrow 2 \text{NH}_3 (\text{g})$
 - $\text{CaCO}_3 (\text{s}) \rightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$
 - $3 \text{C}_2\text{H}_2 (\text{g}) \rightarrow \text{C}_6\text{H}_6 (\text{g})$
 - $2 \text{H}_2\text{S} (\text{g}) + \text{SO}_2 (\text{g}) \rightarrow 3 \text{S} (\text{s}) + 2 \text{H}_2\text{O} (\text{g})$
 - $2 \text{SO}_3 (\text{g}) \rightarrow 2 \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g})$

Entropy – Quantitative

6. Predict the sign of ΔS° expected for the following reactions. Then calculate the exact value of ΔS° for each reaction that follows.



Substance	S° Values (J/mol K)
$\text{C}_2\text{H}_6(\text{g})$	229.5
$\text{C}_6\text{H}_6(\text{l})$	172.8
$\text{H}_2(\text{g})$	130.58
$\text{O}_2(\text{g})$	205.0
$\text{H}_2\text{O}(\text{l})$	69.91
$\text{H}_2\text{O}(\text{g})$	188.83
$\text{CH}_3\text{OH}(\text{g})$	237.6
$\text{CO}_2(\text{g})$	213.6



GIBBS FREE ENERGY

Free Energy Concepts

1. Given the values of ΔH and ΔS , which of the following changes will be spontaneous at constant T and P?

a. $\Delta H = + 25 \text{ kJ}$, $\Delta S = + 5.0 \text{ J/K}$, $T = 300. \text{ K}$

b. $\Delta H = + 25 \text{ kJ}$, $\Delta S = + 100. \text{ J/K}$, $T = 300. \text{ K}$

c. $\Delta H = - 10.0 \text{ kJ}$, $\Delta S = + 5.0 \text{ J/K}$, $T = 298 \text{ K}$

d. $\Delta H = - 10.0 \text{ kJ}$, $\Delta S = -40. \text{ J/K}$, $T = 200. \text{ K}$

2. Classify the following reactions as spontaneous at all temperatures, nonspontaneous at all temperatures, spontaneous at low T, or spontaneous at high T:

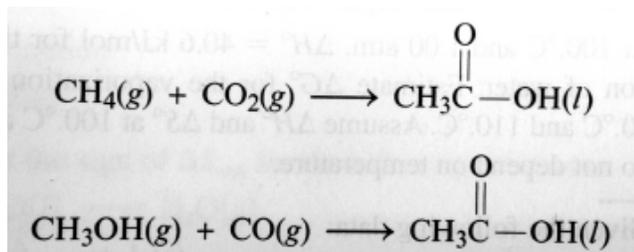


Free Energy Calculations

3. For the reaction at 298 K, $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$, the values of ΔH° and ΔS° are -58.03 kJ and -176.6 J/K, respectively.

- What is the value of ΔG° at 298 K?
- Assuming that ΔH° and ΔS° do not depend on temperature, at what temperature is $\Delta G^\circ = 0$?
- Is ΔG° negative or positive above this temperature?

4. Using thermodynamic data, calculate ΔH° , ΔS° , and ΔG° for the following reactions that produce acetic acid:



Which reaction would you choose as a commercial method for producing acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) under standard conditions? What temperature conditions would you choose for the reaction?

	H° (kJ/mol)	S° (J/mol K)
CH_4 (g)	-74.8	186.3
CO_2 (g)	-393.5	213.6
CH_3COOH (l)	-487.0	159.8
CH_3OH (g)	-201.2	237.6
CO (g)	-110.5	197.9