## Spontaneity and Gibbs Free Energy

Read from Lesson 3: Spontaneity and Gibbs Free Energy in the Chemistry Tutorial Section, Chapter 17 of The Physics Classroom.

Part a: <u>Predicting Spontaneity with Gibbs Free Energy</u>

Part b: Gibbs Free Energy and Equilibrium

# $\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$

## 1. Gibbs Free Energy

- **Definition:** Gibbs free energy (G) is a thermodynamic function combining enthalpy (H), entropy (S), and temperature (T): **G** = **H T**•**S**
- Change in Gibbs Free Energy:  $\Delta G = \Delta H T\Delta S$
- Driving Forces:
  - o  $\Delta$ **H (enthalpy change):** Reflects energy spread; negative  $\Delta$ H favors spontaneity.
  - o  $T\Delta S$  (entropy term): Reflects matter spread; positive  $\Delta S$  favors spontaneity.
- Spontaneity Criteria:
  - o  $\Delta G < 0 \rightarrow$  spontaneous process
  - o  $\Delta G > 0 \rightarrow$  non-spontaneous (reverse is spontaneous)
  - $\Delta G = 0 \rightarrow equilibrium$
- **Gibbs free energy predicts spontaneity** and connects thermodynamics with equilibrium.  $\Delta G$  tells us **not only** if a reaction **occurs** but also how far it **proceeds**.

## 2. Temperature Dependence

- When  $\Delta H$  and  $\Delta S$  are in opposition, **temperature determines spontaneity**:
  - o  $\Delta H < 0$ ,  $\Delta S < 0 \rightarrow$  spontaneous at low T
  - $\Delta$ H > 0,  $\Delta$ S > 0  $\rightarrow$  spontaneous at high T
  - $\circ$   $\Delta H < 0$ ,  $\Delta S > 0 \rightarrow$  spontaneous at all T
  - $\Delta$ H > 0,  $\Delta$ S < 0  $\rightarrow$  non-spontaneous at all T
- Threshold Temperature:  $T_{threshold} = \Delta H/\Delta S$
- At this temperature,  $\Delta G = 0$  (equilibrium point).

#### 3. Magnitude of $\Delta G$

- Large negative  $\Delta G \rightarrow$  reaction strongly favors products (nearly complete).
- Small negative  $\Delta G \rightarrow$  reaction favors products but reaches equilibrium before completion.
- **Positive**  $\Delta G \rightarrow$  reaction favors reactants.

#### 4. Gibbs Free Energy and Equilibrium Constant

- At equilibrium:  $\Delta G = 0$  and Q = K.
- Relationship between  $\Delta G^{\circ}$  and K:  $\Delta G^{\circ}$  =  $R \bullet T \bullet lnK$  and  $K = e^{-\Delta G^{\circ}/RT}$
- Interpretation:
  - $\Delta G^{\circ} < 0 \rightarrow K > 1 \rightarrow \text{products favored.}$
  - $\Delta G^{\circ} > 0 \rightarrow K < 1 \rightarrow \text{reactants favored.}$
  - $\Delta G^{\circ} = 0 \rightarrow K \approx 1 \rightarrow balanced$  equilibrium.

#### 5. Non-Standard Conditions

- General equation:  $\Delta \mathbf{G} = \Delta \mathbf{G}^{\circ} + \mathbf{R} \cdot \mathbf{T} \cdot \mathbf{ln} \mathbf{Q}$
- Q (reaction quotient) reflects current concentrations/pressures.
- As reaction proceeds, Q changes, and  $\Delta G$  shifts until equilibrium ( $\Delta G = 0$ , Q = K).



## **Chemical Thermodynamics**

## **Ouestions**

- 1. How does the magnitude of  $\Delta G$  relate to the "extent" of a reaction?
- 2. For each of the following hypothetical reactions, analyze the signs of  $\Delta H$  (enthalpy change) and  $\Delta S$  (entropy change). State whether the reaction is spontaneous at "low temperatures," "high temperatures," "all temperatures," or "no temperatures":

a) 
$$\Delta H = +150 \text{ kJ}$$
,  $\Delta S = +250 \text{ J/K}$ 

b) 
$$\Delta H = -75$$
 kJ,  $\Delta S = -120$  J/K

c) 
$$\Delta H = -200 \text{ kJ}$$
,  $\Delta S = +50 \text{ J/K}$ 

d) 
$$\Delta H = +10 \text{ kJ}$$
,  $\Delta S = -5 \text{ J/K}$ 

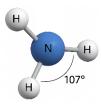
- 3. Consider the formation of magnesium oxide from its elements:  $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$ Given that  $\Delta H = -601.6 \text{ kJ}$  and that  $\Delta S = 26.9 \text{ J/K}$ :
  - a. Is this reaction exothermic or endothermic?
  - b. Does it increase or decrease the disorder of the system?
  - c. Calculate the  $\Delta G^{^{\circ}}$  for the reaction at  $25~^{\circ}C.$  Is the reaction spontaneous at this temperature?
  - d. Calculate the  $\Delta G^{\circ}$  for the reaction at 596 K. Is the reaction spontaneous at this temperature?
- 4. Octane ( $C_8H_{18}$ ) is a straight-chain alkane and a component of gasoline.
  - a. Write the balanced equation for the combustion of octane with oxygen to produce carbon dioxide gas and liquid water.



b. Without using thermodynamic data, predict whether  $\Delta G^{\circ}$  for this reaction is more negative or less negative than  $\Delta H^{\circ}$ . Explain your reasoning

## **Chemical Thermodynamics**

- 5. Reaction A has a large negative  $\Delta H$  and a small negative  $\Delta S$ . Reaction B has a small negative  $\Delta H$  and a large positive  $\Delta S$ .
  - a. Under what temperature conditions could **Reaction B** be spontaneous while **Reaction A** is not?
  - b. Explain your reasoning in terms of  $\Delta G$ .
- 6. Consider the phase change: NH<sub>3</sub>(I)  $\rightarrow$  NH<sub>3</sub>(g). The  $\Delta$ H = +23.3 kJ/mol and  $\Delta$ S = +97.4 J/mol·K.
  - a. How much heat is released or absorbed when 53.47 g of  $NH_3(l)$  evaporates?



- b. Calculate the  $\Delta G^{\circ}$  for the reaction at 250 K. Is the reaction spontaneous at this temperature?
- c. Calculate the  $\Delta G^{\circ}$  for the reaction at 550 K. Is the reaction spontaneous at this temperature?
- d. At which temperature is the process at equilibrium?
- e. What is the normal boiling point (in °C) of ammonia?
- 7. Suppose a reaction is at nonstandard conditions, and  $\mathbf{Q}$  (the reaction quotient) >  $\mathbf{K}$ . Answer these questions about this reaction and explain your reasoning.
  - a. What sign will  $\Delta G$  have?
  - b. Will the reaction proceed in the forward or reverse direction to reach equilibrium?