

# General Chemistry II

## Chapter 18 Lecture Notes

### Entropy, Free Energy and Equilibrium

#### The Three Laws of Thermodynamics

1. Energy can never be created or destroyed, only altered in form
2. The entropy (disorder) of the *universe* is always increasing. The entropy of a *system* increases in a spontaneous process
3. The entropy of a substance can be zero only for a perfect crystalline substance and only at 0 K.

#### Spontaneous Processes and Entropy

Chemical and physical changes may be spontaneous or nonspontaneous. The spontaneity of a process is driven both by enthalpy change (a negative  $\Delta H$  favoring the forward reaction) but also by the increase in *entropy*, or disorder of the system. A more disordered product is more likely to form than a more ordered one. Most exothermic processes such as fuel burning are spontaneous, but a few *endothermic* processes such as solution of sodium nitrite in water (ice pack) can also be spontaneous. An important factor in the spontaneity of a process is the increase in entropy (disorder) of the system. A system at equilibrium does not undergo an entropy change, because *net* change is not occurring.

Ex: The combustion of glucose is highly spontaneous both because it is exothermic and because there is a large increase in entropy. Try to imagine the reverse reaction occurring spontaneously by the assembly of glucose from carbon dioxide gas and water vapor.

A simple way to understand the entropy of a *physical* spontaneous process is the distribution of gas molecules between two connected flasks, starting with just one gas molecule.

Entropy Facts:

- Entropy units are joules/K · mol. For a specified amount of substance, units are joules/K. Entropy values are generally small, in the joule rather than kJ range.
- The entropy of a liquid is greater than that of a solid. The entropy of a gas is always *much* greater than that of the corresponding liquid.
- The entropy of any substance increases with increasing temperature because greater molecular motion increases disorder.
- If a change such as photosynthesis involves an entropy *decrease*, there is a greater entropy *increase* elsewhere in the universe.
- It is possible to assign an *absolute entropy* value to any substance, given the fact that a *perfect crystal* at *absolute zero* has zero entropy. (Remember, there is no way to determine absolute enthalpy.) The entropy of any substance at a finite temperature will be greater than zero. Any sample less ordered than a perfect crystal will have a positive entropy.
- **Standard Entropy** is defined as the absolute entropy of a substance at 25 °C.

## The Second Law of Thermodynamics

The entropy of the *universe* increases in a spontaneous process and stays the same in an equilibrium process.

For a nonequilibrium process:  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

For an Equilibrium Process:  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$

There is no possible process where the entropy of the universe *decreases*.

It's possible for the entropy of a system to decrease, but that results in a *greater* corresponding entropy increase in the rest of the universe.

## Entropy Changes In the System

For a chemical reaction  $aA + bB \rightarrow cC + dD$

Change in entropy is the difference between the sum of the standard entropies of the products and the sum of the standard entropies of the reactants.

Molar coefficients must be applied since tabulated  $S^\circ$  values are in J/mol.

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

If the sum of reactant entropies is less than sum of product entropies,  $\Delta S^\circ$  is positive.

Some rules for predicting  $\Delta S$  signs (and magnitudes):

- If all reactants and products are solid, then  $\Delta S \sim 0$ .
- If moles of gaseous reactants equals moles of gaseous products, then  $\Delta S \sim 0$ .
- If moles of gaseous products less than moles of gaseous reactants, then  $\Delta S$  strongly negative.
- If moles of gaseous products more than moles of gaseous reactants, then  $\Delta S$  strongly positive.

Ex: Predict, then calculate  $\Delta S$  for the process  $O_2(s) \rightarrow O_2(g)$

Predict large positive  $\Delta S$

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

$$\Delta S^\circ = 1 \text{ mol } O_2(g) \times 205.0 \text{ J/K} \cdot \text{mol} - 1 \text{ mol } O_2(s) \times 101 \text{ J/K} \cdot \text{mol}$$

$$\Delta S^\circ = 104 \text{ J/K} \cdot \text{mol}$$

Ex: Predict, then calculate  $\Delta S$  for the process  $O_2(g) \rightarrow 2 O(g)$

(Predict a large positive  $\Delta S$ )

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

$$\Delta S^\circ = 2 \text{ mol } O(g) \times 160.95 \text{ J/K} \cdot \text{mol} - 1 \text{ mol } O_2(g) \times 205.0 \text{ J/K} \cdot \text{mol}$$

$$\Delta S^\circ = 321.90 \text{ J/K} \cdot \text{mol} - 205.0 \text{ J/K} \cdot \text{mol} = 116.9 \text{ J/K} \cdot \text{mol}$$

Ex: Predict, then calculate  $\Delta S^\circ$  for the reaction  $2Ni(s) + O_2(g) \rightarrow 2NiO(s)$

Predict large *negative*  $\Delta S^\circ$

$$\begin{aligned}
 \Delta S^\circ &= \Sigma S^\circ \text{ of products} - \Sigma S^\circ \text{ of reactants} \\
 &= 2 \text{ mol NiO} \times 38.58 \text{ J/K} \cdot \text{mol} - (2 \text{ mol Ni} \times 30.1 \text{ J/K} \cdot \text{mol} + 1 \text{ mol O}_2 \times 205.0 \text{ J/K} \cdot \text{mol}) \\
 &= 77.16 \text{ J/K} - 60.2 \text{ J/K} - 410.0 \text{ J/K} \\
 &= -393.0 \text{ J/K} \quad (\text{mostly due to disappearance of O}_2 \text{ gas having large entropy})
 \end{aligned}$$

### Entropy Changes In the Surroundings

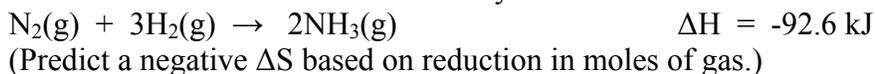
A change in system *entropy* will not directly affect the entropy of the surroundings, especially if the system is isolated (a closed system). However, for an exothermic process, heat is *released* to the surroundings, increasing the entropy of the surroundings.

The entropy increase in the surroundings is directly proportional to the enthalpy of the reaction, so  $\Delta S_{\text{system}} \propto -\Delta H_{\text{system}}/T$  Why the negative sign?

Without derivation,  $\Delta S_{\text{system}} = -\Delta H_{\text{system}}/T$

The *change* in the entropy of the surroundings is proportional to  $1/T$  (Significance?)

Ex: Calculation of  $\Delta S$  for the Haber synthesis of ammonia at 25°C.



First, calculate the  $\Delta S_{\text{reaction}}$  based on absolute entropies of reactants and products.

$$\begin{aligned}
 \Delta S_{\text{reaction}} &= S^\circ_{\text{products}} - S^\circ_{\text{reactants}} \\
 &= 2 \text{ mol NH}_3(\text{g}) \times 193.0 \text{ J/K} \cdot \text{mol} - 1 \text{ mol N}_2(\text{g}) \times 191.5 \text{ J/K} \cdot \text{mol} - 3 \text{ mol H}_2(\text{g}) \times 131.0 \text{ J/K} \cdot \text{mol} \\
 &= 386.0 \text{ J/K} - 584.5 \text{ J/K}
 \end{aligned}$$

$\Delta S = -198.5 \text{ J/K}$  (Prediction was correct. What about the entropy of the universe?)

Calculate  $\Delta S$  for the surroundings based on the reaction enthalpy, -92.6 kJ.

$$\Delta S_{\text{surroundings}} = -\Delta H/T = -92.6 \text{ kJ}/298 \text{ K} = + 311 \text{ J/K}$$

$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = -198.5 \text{ J/K} + 311 \text{ J/K} = +112 \text{ J/K}$  indicating the reaction will be spontaneous at 25°C. does this say anything about the *rate*? Why is it not observed to happen?

How is the Haber process carried out?

### The Third Law and Absolute Entropy

A system with the lowest possible randomness is a perfect crystal at absolute zero. There is no randomness in such a system because moving any of the particles to a different location in the crystal would not result in a different configuration. At absolute zero, there exists the minimum possible movement or freedom of movement. At any temperature above 0 K, the increase in entropy can be calculated. For that reason the absolute entropy of a system can be calculated, as opposed to *not* knowing the absolute enthalpy of a system. There is no way to determine the zero enthalpy of a system so the absolute enthalpy must remain unknown.

The entropy of a solid remains low even as temperature increases because the molecules are still held in position. When a solid melts, however, there is a large jump in entropy as the molecules suddenly acquire more freedom of position. As a liquid vaporizes, there is an even greater entropy jump because the molecules can move independently, without contact with one another. Heating a gas further increases its entropy because the particles move faster and acquire even more randomness.

### Gibbs Free Energy

A useful quantity for predicting the spontaneity of a reaction that takes into account the enthalpy change ( $\Delta H$ ), the entropy change ( $\Delta S$ ) and the absolute temperature of the system.

In any spontaneous process,  $\Delta S_{\text{universe}} > 0$ .

Therefore, need to know the sign and magnitude of

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

The quantity always of most interest is  $\Delta S_{\text{system}}$

$\Delta S_{\text{surroundings}}$  usually not of interest and sometimes difficult to calculate.

In  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ , substitute  $-\Delta H_{\text{system}}/T$  for  $\Delta S_{\text{surroundings}}$ .

$$\text{Then } \Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T > 0$$

$$T\Delta S_{\text{universe}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}} > 0$$

$$-T\Delta S_{\text{universe}} = -T\Delta S_{\text{system}} + \Delta H_{\text{system}} < 0$$

(Note that for a spontaneous process,  $T\Delta S_{\text{universe}}$  will be greater than zero.

$-T\Delta S_{\text{universe}}$  and  $-T\Delta S_{\text{system}} + \Delta H_{\text{system}}$  will be less than zero.

The term  $-T\Delta S_{\text{system}} + \Delta H_{\text{system}}$  can be related to the Gibbs Free Energy,  $\Delta G$ .

$\Delta G$  can often be calculated easily and is a useful predictor of the spontaneity of a reaction.

$-T\Delta S_{\text{universe}}$  is related to the Gibbs Free Energy,  $\Delta G$ , the useful energy transferred to the surroundings.

(What are useful and nonuseful forms of energy?)

The original equation is  $G = H_{\text{system}} - TS_{\text{system}}$

$$\text{Then } \Delta G = \Delta H - T\Delta S - S\Delta T$$

To keep mathematics simple, many processes are calculated at constant temperature,  $\Delta T = 0$ , although the equation can be used for more complicated situations.

At constant T, the equation becomes,

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

This useful equation only involves only easily measured *system* parameters.

It predicts the direction of a reaction equilibrium and can also be used to calculate the temperature at which a reaction becomes spontaneous or nonspontaneous.

$\Delta G < 0$ : spontaneous reaction

$\Delta G = 0$ : a system at equilibrium

$\Delta G > 0$ : nonspontaneous reaction

### Standard Free-Energy Changes

$\Delta G^\circ_{\text{reaction}}$  applies to *standard conditions* of 1 atm, 25°C, and 1M concentrations.

( $\Delta G^\circ_{\text{formation}}$  values also available for allotropes and for nonstandard conditions.)

$\Delta G^\circ_{\text{formation}}$  for the most stable allotrope of any element = 0

$\Delta G^\circ_{\text{formation}}$  for any element or compound has units kJ/mol.

$\Delta G^\circ_{\text{reaction}}$  has units kJ only, and depends on the molar coefficients.

$$\Delta G^\circ_{\text{reaction}} = \sum n\Delta G^\circ_{\text{products}} - \sum n\Delta G^\circ_{\text{reactants}}$$

For the general chemical reaction  $aA + bB \rightarrow cC + dD$  (just as in entropy calculations)

$$\Delta G^\circ_{\text{reaction}} = c\Delta G^\circ_{\text{formationC}} + d\Delta G^\circ_{\text{formationD}} - a\Delta G^\circ_{\text{formationA}} - b\Delta G^\circ_{\text{formationB}}$$

Ex: Calculate the standard free-energy change for the reaction



$$\Delta G^\circ_{\text{reaction}} = c\Delta G^\circ_{\text{formationC}} + d\Delta G^\circ_{\text{formationD}} - a\Delta G^\circ_{\text{formationA}} - b\Delta G^\circ_{\text{formationB}}$$

$$\Delta G^\circ_{\text{reaction}} = 2 \text{ mol H}_2\text{O}(\text{l}) \times (-237.2 \text{ kJ/mol}) + 0 - 2 \text{ mol H}_2\text{O}_2(\text{l}) \times (-118.1 \text{ kJ/mol})$$

$$= -474.4 \text{ kJ/mol} + 236.2 \text{ kJ/mol} = -238.2 \text{ kJ/mol} \quad (\text{spontaneous})$$

(If the reverse reaction had been studied,  $\Delta G^\circ_{\text{reaction}} = +238.2 \text{ kJ/mol}$  (nonspontaneous))

### Applications of the Free-Energy Equation

It is very instructive to study the Gibbs Free-energy equation in detail.

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

How does  $\Delta G$  vary with  $\Delta H$ ,  $\Delta S$  and  $T$ ?

A large negative  $\Delta H$  makes a reaction more spontaneous.

A large positive  $\Delta S$  makes a reaction more spontaneous.

The effect of  $T$  depends on the sign of  $\Delta S$ .

- If  $\Delta S$  is positive, higher  $T$  makes a reaction more spontaneous

- If  $\Delta S$  is negative, higher T makes a reaction less spontaneous.

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

$\Delta H$	$\Delta S$	Sign of $\Delta G$
+	+	$\Delta G$ can be + or - Rxn is spontaneous at high T. At low T, the reverse rxn is spontaneous
+	-	$\Delta G$ is always positive. Only the reverse rxn is spontaneous
-	+	$\Delta G$ is always negative. The rxn is always spontaneous
-	-	Rxn is spontaneous at low T. At high T, the reverse rxn is spontaneous

### Effect of Temperature on Chemical Reactions:

The direction of equilibrium or the extent to which some reactions proceed is determined by temperature because of its effect on  $\Delta G$  through the magnitude of the  $-T \Delta S$  term

### Phase Transitions:

A system undergoing a phase transition (melting, evaporation, condensation, etc.) is at equilibrium so  $\Delta G$  is always zero. The equation  $\Delta G = \Delta H - T \Delta S$  then becomes  $\Delta H = T \Delta S$  or

$$\Delta S = \Delta H/T$$

This equation simply shows that entropy increases during an endothermic phase transition and decreases during an exothermic phase transition.

Ex: What is  $\Delta S$  for the vaporization of liquid argon if  $\Delta H_{\text{vap}} = 6.3 \text{ kJ/mol}$ . Argon's normal boiling point is  $-186 \text{ }^\circ\text{C}$ .

$$\Delta S = \Delta H/T = (6.3 \text{ kJ/mol})/87\text{K} \cdot 1000 \text{ J/kJ} = 72 \text{ J/mol} \cdot \text{K}$$

What is  $\Delta S$  for the condensation of argon vapor

### Free Energy and Chemical Equilibrium

The *most important result* of this chapter

$\Delta G$  changes with changing temperature and with reactant and product concentrations.

Without derivation to the equation  $\Delta G = -RT \ln K$

Important because K sometimes impossible to evaluate from the equilibrium expression.

Calculate K for the hypothetical reaction  $2\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CH}_3\text{OH}(\text{l})$ .

First, calculate  $\Delta G$  for the reaction.

$$\Delta G^\circ_{\text{reaction}} = \sum n \Delta G^\circ_{\text{products}} - \sum n \Delta G^\circ_{\text{reactants}}$$

$$\Delta G^\circ = 2 \text{ mol } 2\text{CH}_3\text{OH}(\text{l}) \times (-166.3 \text{ kJ/mol}) - 2 \text{ mol } \text{CH}_4(\text{g}) \times (-50.8 \text{ kJ/mol}) - 1 \text{ mol } \text{O}_2(\text{g}) \times 0 \text{ kJ/mol}$$

$$\Delta G^\circ = -332.6 \text{ kJ/mol} - 101.6 \text{ kJ/mol} = -434.2 \text{ kJ/mol}$$

Next solve  $\Delta G = -RT \ln K$  for  $K$

$$\begin{aligned} K &= \text{antiln}(-\Delta G/RT) = \text{antiln}(-434.2 \text{ kJ/mol}) (10^3 \text{ J/kJ}) / (8.314 \text{ J/mol} \cdot 298 \text{ K}) \\ &= \text{antiln}(-175) = 7.7 \times 10^{-77} \end{aligned}$$

Ex: Calculate  $\Delta G$  at 25 °C for the formation of the red-colored iron(III) thiocyanate complex.

At 25 °C  $K_{\text{eq}}$  equals 54 for the reaction  $\text{Fe}^{+3} + \text{SCN}^{-1} \leftrightarrow \text{FeSCN}^{+2}$

$$\begin{aligned} \Delta G &= -RT \ln K = -(8.314 \text{ J/mol} \cdot \text{K}) \cdot 298 \text{ K} \cdot \ln 54 = -(8.314 \text{ J/mol}) \cdot 298 \cdot 4.0 \\ &= -9.9 \text{ kJ/mol} \end{aligned}$$

### **Thermodynamics in Living Systems**

Most processes in living systems are nonspontaneous and involve a *decrease* in entropy, for instance, the synthesis of highly ordered protein. Many biological processes are driven by the burning of glucose to produce water and  $\text{CO}_2$  (which is expelled from the body causing a large entropy increase). The burning of glucose is coupled to the production of ATP from ADP and phosphate (entropy decrease). Then ATP is hydrolyzed back to ADP and phosphate and the energy released is used to drive the desired biochemical reaction usually resulting in a large entropy decrease for the organism.

Living organisms are highly ordered low-entropy complex systems that grow by causing a large increase in the entropy of their environment.