1ST LAW OF THERMODYNAMICS

- Thermodynamics is concerned with the energy changes that accompany chemical and physical processes.
- The 1st Law of Thermodynamics is the "Law of Conservation of Energy". Energy can neither be created nor destroyed. In other words, energy of the universe is constant.
- For example, when a book is dropped, some of the potential energy of the book is changed to kinetic energy, which is then transferred to the atoms of air and floor as random motion. As a result, some of the energy of the book is converted to the same quantity of thermal energy.
- Applying this concept to a chemical reaction (shown below), the reaction of carbon and oxygen produces a quantity of energy, which is released as heat. This energy flow results from the lowering of the PE stored in the bonds of reactant as they react to form products.



- Potential energy has been converted to thermal energy, but the energy content of the universe remains constant, according to the first law of thermodynamics.
- Although the first law of thermodynamics provides the means for accounting of energy, it gives no hint as to why a particular process occurs in a given direction. This is the main question to be considered in this chapter.

low PE

SPONTANEOUS & NONSPONTANEOUS PROCESSES

• A spontaneous process is one that occurs without outside intervention. A spontaneous process may be fast or slow.

high PE

Spontaneous Physical Change: (ball rolling from the top of a hill)

Spontaneous Chemical Change: (reaction of solid potassium with liquid water)

 $2 \text{ K}(s) + \text{H}_2O(l) \xrightarrow{spontaneous} 2 \text{ KOH}(aq) + \text{H}_2(g)$

- Earlier we studied the factors that affect the rate of reaction. These include activation energy, temperature, concentration and catalyst. Study of kinetics of a reaction focuses on the pathway between the reactants and products.
- Thermodynamics, on the other hand, tells us whether a reaction is spontaneous based only on the properties of the reactants and products. The predictions of thermodynamics do not require knowledge of the pathway between reactants and products.
- Thermodynamics principles will provide an explanation of why, under a given set of conditions a process will occur in one direction, but never in the opposite direction.









ENTROPY & SPONTANEITY

- What common characteristic causes processes to be spontaneous in one direction only?
- The first candidate in our search might be enthalpy (ΔH), which is equivalent to heat of reaction at constant pressure (q_p). However, although most spontaneous processes are exothermic, some spontaneous processes are endothermic.
- Another quantity that can be considered is *entropy* (*S*). Entropy is the thermodynamic quantity that is a measure of the randomness or *disorder* in a system.
- Entropy is a state function—the quantity of entropy in a substance depends only on variables that determine the state of the substance (temperature and pressure). Entropy is measured in units of J/K.
- Entropy increases when the disorder in a sample of the substance increases. For example, consider the melting of ice at 0°C and 1 atm.



- The driving force for a spontaneous process is an increase in the entropy of the universe.
- The *second law of thermodynamics* states that for any spontaneous process, the *entropy of the universe increases* ($\Delta S_{univ} > 0$).
- Therefore, the *criterion for spontaneity is the entropy of the universe*. Processes that increase the entropy of the universe–those that result in greater dispersal or randomization of energy–occur spontaneously.
- Entropy can be formally defined as the thermodynamic quantity that describes the number of arrangements (positions and/or energy levels) that are available to a system in a given state.
- To better understand entropy and its relationship to spontaneity, let consider the following example: the expansion of a gas into a vacuum (a spontaneous process with no change in enthalpy).



ENTROPY & SPONTANEITY

- When the valve between the flasks opens, the gas in the left flask spontaneously expands into a vacuum. Since the pressure against the expansion is zero, no work is done by the gas.
- However, even though the total energy of the gas does not change, the entropy does change. This can easily be seen by the various ways the gas can distribute itself in the flasks (3 of which are shown on the right).
- Probability analysis indicates that it would be more probable to find the atoms in state C (6 states) compared to either states A or B. And it can also be seen that state C has greater entropy than either state A or B.





• Therefore, the change of entropy in transitioning from state A to state C is positive because state C has greater entropy than state A.

 $\Delta S = S_{\text{final}} - S_{\text{initial}}$ $\Delta S > 0$

ENTROPY CHANGE FOR A PHASE TRANSITION

• The entropy of a sample of matter increases as it changes state from a solid to a liquid or from a liquid to a gas. This is due to the increase in disorder of molecules in liquid compared to solid and gas compared to liquid.



- We can therefore predict the sign of ΔS for processes involving changes of state (or phase change).
- In general, entropy increases ($\Delta S > 0$) for each of the following:
 - the phase transition from a solid to a liquid (melting or fusion)
 - ➤ the phase transition from a solid to a gas (sublimation)
 - ➤ the phase transition from a liquid to a gas (vaporization)
 - > an increase in the number of moles of a gas during a chemical reaction

Examples:

- 1. Predict the sign of ΔS for each of the following processes:
 - a) the boiling of water $\Delta S =$
 - b) $I_2(g) \rightarrow I_2(s)$ $\Delta S =$
 - c) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta S =$

HEAT TRANSFER & CHANGES IN ENTROPY OF SURROUNDINGS

- The criterion for spontaneity is an increase in the entropy of the universe. However, there are several spontaneous processes that include a decrease in entropy. For example, when water freezes below 0°C, the entropy of the water decreases, yet the process is spontaneous.
- The 2^{nd} Law of Thermodynamics states that for a spontaneous process, the entropy of universe increases ($\Delta S_{univ} > 0$). In the example above, even though the entropy of water decreases, the entropy of the universe must increase in order for the process to be spontaneous.
- Similar to the distinction of a system and surroundings in thermodynamics, we can distinguish between the entropy of the system and the surroundings. In the example of the freezing water, ΔS_{sys} is the entropy change of water, and the ΔS_{surr} is the entropy change of the surroundings.
- The entropy change of the universe is then the sum of the entropy changes of the system and the surrounding.

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

• If a spontaneous process includes a decrease in ΔS_{sys} , then it would follow that there must be a greater increase in ΔS_{surr} in order for the ΔS_{univ} to increase.



- Since freezing of water is an exothermic process, it would follow that the heat given off by the process increases the entropy of the surroundings by a greater amount than the decrease of entropy of the system, making it a spontaneous process.
- To summarize:
 - An exothermic process increases the entropy of the surroundings.
 - > An endothermic process decreases the entropy of the surroundings.

TEMPERATURE DEPENDENCE OF ΔS_{surr}

- Because of the large increase in ΔS_{surr} , the freezing of water is spontaneous at low temperatures. However, freezing of water is NOT spontaneous at high temperatures. Why?
- Units of entropy are J/K. Therefore, entropy is a measure of energy dispersal (joules) per unit temperature (K). The higher the temperature, the lower the amount of entropy change for a given amount of energy dispersed.
- Water does not freeze spontaneously at high temperatures, because the increase in ΔS_{surr} is small compared to decrease in ΔS_{sys} , making ΔS_{univ} negative.



$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$
 (for water freezing)

QUANTIFYING ENTROPY CHANGE OF SURROUNDINGS & SYSTEM

- We know that when a system exchanges heat with surroundings, it changes the entropy of the surroundings. At constant pressure, q_{sys} can be used to quantify the entropy change of the surroundings.
- In general,
 - > A process that emits heat into the surroundings ($q_{sys} = negative$) *increases* the entropy of the surroundings (positive ΔS_{surr})
 - A process that absorbs heat from the surroundings ($q_{sys} = positive$) *decreases* the entropy of the surroundings (negative ΔS_{surr})
- The magnitude of the change in entropy of the surroundings is proportional to the magnitude of the q_{sys} .

$$\Delta S_{surr} \quad \alpha \quad -q_{sys}$$

• It can also be shown that for a given amount of heat exchanged with the surroundings, the magnitude of ΔS_{surr} is inversely proportional to the temperature.

$$\Delta S_{surr} \alpha 1/T$$

- Combining the above relationships: $\Delta S_{surr} = \frac{-q_{sys}}{T}$
- At constant pressure, $q_{sys} = \Delta H_{sys}$. Therefore,

$$\Delta \mathbf{S}_{surr} = \frac{-\Delta \mathbf{H}_{sys}}{\mathbf{T}} \quad (\text{constant P, T})$$

Examples:

1. Calculate ΔS_{surr} for the melting of ice (Heat absorbed = Heat of Fusion = ΔH_{fus} = 6.0 kJ/mol)

$$\Delta S_{surr} = \frac{-\Delta H_{fus}}{T} = \frac{-6.0 \times 10^3 \text{ J}}{273 \text{ K}} = -22 \text{ J/K}$$

2. Liquid ethanol, C₂H₆O (l), at 25 °C has an entropy of 161 J/(mol x K). If the heat of vaporization (ΔH_{vap}) at 25 °C is 42.3 kJ/mol, what is the entropy of the vapor in equilibrium with the liquid at 25 °C?

 $C_2H_6O(l) \rightarrow C_2H_6O(g)$ $\Delta H_{vap} = +42.3 \text{ kJ/mol}$ $\Delta S_{sys} = (S_{gas} - S_{liq}) > 0$

$$\Delta S_{sys} = \frac{q_{sys}}{T} = \frac{\Delta H_{vap}}{T} = \frac{+42.3 \text{ kJ/mol}}{298 \text{ K}} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} = 142 \text{ J/K mol}$$

$$S_{gas} = S_{liq} + \Delta S_{sys} = 161 \ J/K + 142 \ J/K = 303 \ J/K$$

3. Consider the combustion of propane gas:

$$C_{3}H_{8}(g) + 5 O_{2}(g) \rightarrow 3 CO_{2}(g) + 4 H_{2}O(g)$$
 $\Delta H_{sys} = -2044 \text{ kJ}$

a) Calculate the ΔS_{surr} associated with this reaction occurring at 25°C.

- b) Determine the sign of ΔS_{sys}
- c) Determine the sign of ΔS_{univ} . Will this reaction be spontaneous?

GIBBS FREE ENERGY

• The relationships between enthalpy change in a system and the entropy change in the surroundings is shown below:

$$\Delta \mathbf{S}_{\mathbf{surr}} = \frac{-\Delta \mathbf{H}_{\mathbf{sys}}}{\mathbf{T}}$$

• Also, for any process, the entropy change of the universe is the sum of the entropy change of the system and the entropy change of the surroundings.

$$\Delta \mathbf{S}_{univ} = \Delta \mathbf{S}_{sys} + \Delta \mathbf{S}_{surr}$$

• Combining the two relationships above leads to the following relationship:

$$\Delta \mathbf{S}_{univ} = \Delta \mathbf{S}_{sys} - \frac{\Delta \mathbf{H}_{sys}}{\mathbf{T}}$$

• Multiplying equation above with –T, we arrive at the expression:

$$-\mathbf{T} \Delta \mathbf{S}_{\mathbf{univ}} = \Delta \mathbf{H}_{\mathbf{sys}} - \mathbf{T} \Delta \mathbf{S}_{\mathbf{sys}}$$

• Willard Gibbs (American physicist) combined together the concepts of enthalpy (H) and entropy (S) into a single thermodynamic function called Gibbs Free Energy (G), defined as shown below:

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

• The change in free energy (ΔG) is expressed as:

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

- Since ΔS_{univ} is a criterion for spontaneity, ΔG is also a criterion for spontaneity (but opposite in sign), and is commonly called chemical potential because it is analogous to mechanical potential energy.
- Just as mechanical systems tend toward lower potential energy, chemical systems tend toward lower Gibbs free energy.



Chapter 18

GIBBS FREE ENERGY

Summarizing Gibbs Free Energy (at constant T & P):

- ΔG is proportional to the negative of ΔS_{univ} .
- A *decrease in Gibbs free energy* ($\Delta G < 0$) corresponds to a *spontaneous* process.
- An *increase in Gibbs free energy* ($\Delta G > 0$) corresponds to a *nonspontaneous* process.



Conclusion:

• ΔG gives a composite of the two factors that contribute to spontaneity (ΔH and ΔS)

SPONTANEITY & FREE ENERGY

• Consider the following situations:

Case 1:



 $H_2O(l) \rightarrow H_2O(g) \qquad \Delta H^\circ = +40.7 \text{ kJ} \text{ (at } 100^\circ \text{C})$

SPONTANEITY & FREE ENERGY

| TABLE 17.1 The Effect of ΔH , ΔS , and T on Spontaneity | | | | | | |
|---|----|--|-----------------------------------|--|--|--|
| ΔΗ | Δs | Low Temperature | High Temperature | Example | | |
| - | + | Spontaneous ($\Delta G < 0$) | Spontaneous ($\Delta G < 0$) | $2 \text{ N}_2 \text{O}(g) \longrightarrow 2 \text{ N}_2(g) + \text{O}_2(g)$ | | |
| + | | Nonspontaneous ($\Delta G > 0$) | Nonspontaneous ($\Delta G > 0$) | $3 0_2(g) \longrightarrow 2 0_3(g)$ | | |
| - | - | Spontaneous ($\Delta G < 0$) | Nonspontaneous ($\Delta G > 0$) | $H_2O(l) \longrightarrow H_2O(s)$ | | |
| + | + | Nonspontaneous ($\Delta { m G} > 0$) | Spontaneous ($\Delta G~<$ 0) | $H_2O(l) \longrightarrow H_2O(g)$ | | |

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Examples:

- 1. Predict the conditions (high temperature, low temperature, all temperatures or no temperatures) under which each reaction below is spontaneous:
 - a) $H_2O(g) \rightarrow H_2O(l)$
 - b) $CO_2(s) \rightarrow CO_2(g)$
 - c) $2 \operatorname{NO}_2(g) \rightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)$ (endothermic)
- 2. For the reaction shown below, calculate ΔG at 25°C and determine whether the reaction is spontaneous. If the reaction is not spontaneous at 25°C, determine at what temperature (if any) the reaction becomes spontaneous.

$$CCl_4(g) \rightarrow C(s, graphite) + 2 Cl_2(g)$$
 $\Delta H = +95.7 \text{ kJ}$ $\Delta S = 142.2 \text{ J/K}$

ENTROPY CHANGES IN CHEMICAL REACTIONS

- Similar to the ΔH° for a reaction, we can define the *standard entropy change for a reaction (\Delta S^{\circ})* as the entropy for a process in which all reactants and products are in their standard states.
- The standard states are defined as:

Gas: pure gas at pressure exactly 1 atm.

Liquid or Solid: pure substance at most stable form and pressure of 1 atm and temperature of 25°C.

Solution: concentration of 1 M.

• Since entropy is a state function, the standard change in entropy of a reaction is:

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

• The standard molar entropy (S°) of a substance is needed to calculate the Δ S° for a reaction. The standard molar entropy of a substance is measured against the absolute value of zero as defined by the 3rd law of thermodynamics.

Third Law of Thermodynamics:

• The third law of thermodynamics states that:

The entropy of a perfect crystal at absolute zero (0 K) is zero

- A perfect crystal at 0 K has only one possible way to arrange its components.
- Standard molar entropy values for substances are tabulated in textbooks and available in Appendix II.



STANDARD MOLAR ENTROPY

• The standard entropy of any substance is affected by the state of the substance, molar mass, molecular complexity and the extent of dissolution.

| ٠ | As the molar mass | nolar mass of a substance increases, the value of standard | | | S°(J/mol⋅K) | | |
|---|----------------------|--|----------------------------------|-------|--------------------------------|-------|--|
| | of noble gases incre | gases increases progressively from He to Xe. | | | | 126.2 | |
| ٠ | Similarly, the stand | Ne(g) | 146.1 | | | | |
| | | ne enumple de | <i>S</i> ^o (.1/mol⋅K) | | Ar(g) | 154.8 | |
| | | $H_2O(l)$ $H_2O(g)$ | 70.0 188.8 | | Kr(g) | 163.8 | |
| • | In general, | 1917an baas a | | | Xe(g) | 169.4 | |
| | | S° _{gas} | $> S^{\circ}_{liq} > S^{\circ}$ | solid | © 2011 Pearson Education, Inc. | | |

• For a given state of matter, standard molar entropy also increases with molecular complexity. For example, consider the following:

| | Molar Mass (g/mol) | \mathcal{S}° (J/mol·K) | | Molar Mass (g/mol) | \mathcal{S}° (J/mol·K) |
|------------------------|--------------------|---------------------------------|------------------|--------------------|---------------------------------|
| $\operatorname{Ar}(g)$ | 39.948 | 154.8 | $\mathrm{CO}(g)$ | 28.01 | 197.7 |
| NO(g) | 30.006 | 210.8 | $C_2H_4(g)$ | 28.05 | 219.3 |

Examples:

- 1. Rank each set of substances below in order of increasing standard molar entropy (S°) :
 - a) $I_2(g), F_2(g), Br_2(g), Cl_2(g)$

b) NH_3 (g), Ne (g), SO₂ (g), CH₃CH₂OH (g), He (g)

CALCULATING ΔS° FOR A REACTION

- Recall that the entropy usually increases in the following situations:
 - (a) <u>A reaction in which a molecule is broken into two or more smaller molecules.</u>

Example: fermentation of glucose (grape sugar) to alcohol:

$$C_6H_{12}O_6(s) \longrightarrow 2 C_2H_5OH(l) + 2 CO_2(g)$$

1 large molecule 4 smaller molecules

(b) <u>A reaction in which there is an increase in moles of gas.</u>This may result from a molecules breaking up, in which case Rule (a) and Rule (b) are related.

Example: the burning of acetylene in oxygen:

$$2 C_2 H_2(g) + 3 O_2(g) \longrightarrow 4 CO_2(g) + 2 H_2 O(g)$$
5 moles of gas
$$\Delta n \text{ gas} = 6 - 5 = +1$$

• The standard entropy change (ΔS°) for a reaction can also be calculated from the standard entropies of reactants and products as shown below:

$$\Delta S^{\circ} = \Sigma nS^{\circ} (\text{products}) - \Sigma nS^{\circ} (\text{reactants})$$

Examples:

1. For each pair of substances, choose the one with the higher expected value of standard molar entropy. Explain the reasons for your choices.

| a) CO (g) C | $CO_2(g)$ |
|-------------|-----------|
|-------------|-----------|

- b) CH₃OH (l) CH₃OH (g)
- c) Ar (g) CO_2 (g)
- d) NO₂ (g) $CH_3CH_2CH_3$ (g)

- 2. Predict the sign of ΔS° for each reaction shown below. If you cannot predict the sign for any reaction, state why.
 - a) $C_2H_2(g) + 2 H_2(g) \rightarrow C_2H_6(g)$ $\Delta S^\circ =$
 - b) $N_2(g) + O_2(g) \rightarrow 2 \text{ NO}(g) \qquad \Delta S^\circ =$
 - c) $2 C (s) + O_2 (g) \rightarrow 2 CO (g)$ $\Delta S^{\circ} =$
- 3. Using tabulated S° values in your text, calculate Δ S° for the reactions shown below:

 $4 \text{ NH}_3\left(g\right) \ + \ 5 \text{ O}_2\left(g\right) \ \ \rightarrow \ \ 4 \text{ NO}\left(g\right) \ + \ 6 \text{ H}_2 \text{O}\left(g\right)$

CALCULATING STANDARD FREE ENERGY CHANGES

• The standard free energy change (ΔG°) for a reaction is the criterion for its spontaneity, and can be calculated by 3 different methods.

Method 1:

- Earlier in this chapter we learned how to use tabulated values of $\Delta H^{\circ}{}_{f}$ and S° to calculate ΔH° and ΔS° for a reaction.
- We can now use the ΔH° and ΔS° values to calculate the ΔG° value for a reaction, using the equation:

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

• Since ΔH°_{f} and S° values are tabulated at 25°C, the equation above should only be valid at 25°C. However, since ΔH°_{f} and S° values are affected very little by temperature, we can estimate the ΔG° values for temperatures other than 25°C.

Examples:

1. Given ΔH°_{f} and S° values shown below, calculate ΔG° for the reaction shown below, and determine if the reaction is spontaneous.

| | Reactant or product | $\Delta H_{ m f}^{ m o}$ (kJ/mol) | \mathcal{S}° (J/mol·K) |
|--|---------------------|-----------------------------------|---------------------------------|
| $SO_2(\sigma) + \frac{1}{2}O_2(\sigma) \rightarrow SO_2(\sigma)$ | $SO_2(g)$ | -296.8 | 248.2 |
| | $O_2(g)$ | 0 | 205.2 |
| | $SO_3(g)$ | -395.7 | 256.8 |

2. Use the data in Appendix IIA of your text to calculate ΔH° , ΔS° and ΔG° at 25°C for the reaction shown below. Is the reaction spontaneous? If not, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25°C?

$$NH_4Cl(s) \rightarrow HCl(g) + NH_3(g)$$

CALCULATING STANDARD FREE ENERGY CHANGES

Method 2:

• Because free energy is a state function, change in free energy or reactions (ΔG°) can also be calculated from the free energy of the reactants and products. In order to do this, we define the *free energy of formation* (ΔG°_{f}) for a substance as follows:

The free energy of formation (ΔG°_{f}) is the change in free energy when 1 mole of a compound in its standard state forms from its constituent elements in their standard states. The free energy of formation of pure elements in their standard states is zero.

• The free energy change of a reaction can then be calculated using the equation below:

$$\Delta G^{\circ} = \sum n \Delta G^{\circ}_{f} (products) - \sum m \Delta G^{\circ}_{f} (reactants)$$

Examples:

1. Calculate the standard free energy change (ΔG°) for the following reaction at 25 °C, using standard free energies of formation given below:

| $Na_2CO_3(s)$ + | $\mathrm{H}^{+}(\mathrm{aq})$ | \longrightarrow | $2 \text{ Na}^+(\text{aq}) +$ | $HCO_3^{-}(aq)$ |
|-----------------|-------------------------------|-------------------|-------------------------------|-----------------|
| - 1048.1 | 0 | | - 261.9 | - 587.1 |

 ΔG°_{f} (kJ/mol) :

$$\Delta G^{\circ} = [(2) \ x \ (-261.9) + (-587.1)] - [(-1048.1) + 0] \ kJ = -62.8 \ kJ$$

2. Calculate the standard free-energy change (ΔG°) for the reaction shown below, and determine whether it is spontaneous or not. (Use ΔG°_{f} values in your textbook).

 $2 \text{ NOCl } (g) \longrightarrow 2 \text{ NO} (g) + Cl_2 (g)$

3. Calculate the standard free-energy change (ΔG°) for the reaction shown below, and compare with the value obtained by method 1 on the previous page. (Use ΔG°_{f} values in your textbook).

$$NH_4Cl(s) \rightarrow HCl(g) + NH_3(g)$$

CALCULATING STANDARD FREE ENERGY CHANGES

Method 3:

- Since free energy is a state function, the following relationships can be used to calculate ΔG for a reaction:
 - > If a chemical equation is multiplied by some factor, then ΔG for the reaction is also multiplied by the same factor.
 - \blacktriangleright If a chemical equation is reversed, then Δ G changes sign.
 - > If a chemical equation can be expressed as the sum of a series of steps, then ΔG for the overall equation is the sum of the free energies of reactions for each step.

Examples:

1. Find ΔG° for the reaction shown below:

 $3\ C\ (s)\ +\ 4\ H_2\ (g)\ \rightarrow\ C_3H_8\ (g)$ Use the following reactions with known ΔG° values:

| $C_{3}H_{8}(g) + 5 O_{2}(g) \rightarrow 3 CO_{2}(g) + 4 H_{2}O(g)$ | $\Delta G^{\circ} = -2074 \text{ kJ}$ |
|---|--|
| $C(s) + O_2(g) \rightarrow CO_2(g)$ | $\Delta G^{\circ} = -394.4 \text{ kJ}$ |
| $2 \operatorname{H}_2(g) + \operatorname{O}_2(g) \rightarrow 2 \operatorname{H}_2\operatorname{O}(g)$ | $\Delta G^{\circ} = -457.1 \text{ kJ}$ |

2. Determine ΔG° for the reaction shown below:

 $Fe_2O_3(s) + 3 CO(g) \rightarrow 2 Fe(s) + 3 CO_2(g)$ Use the following reactions with known ΔG° values:

$$\begin{array}{ll} 2 \ {\rm Fe} \ ({\rm s}) \ + \ 3/2 \ {\rm O}_2 \ ({\rm g}) \ \rightarrow \ {\rm Fe}_2 {\rm O}_3 \ ({\rm s}) & \Delta {\rm G}^\circ = -742.2 \ {\rm kJ} \\ {\rm CO} \ ({\rm g}) \ + \ \frac{1}{2} \ {\rm O}_2 \ ({\rm g}) \ \rightarrow \ {\rm CO}_2 \ ({\rm g}) & \Delta {\rm G}^\circ = -257.2 \ {\rm kJ} \end{array}$$

FREE ENERGY and USEFUL WORK

- In a spontaneous reaction:
 - ➤ the "free" energy is lowered as reactants change to products,
 - > the change in "free" energy is released as free-energy change(ΔG)
 - \blacktriangleright this " Δ G" can be harnessed to perform useful work



- In theory, all of the free-energy decrease liberated during a spontaneous chemical change can be used to do work (this would be w_{max})
- In practice, less work is obtained and the difference appears as an increase in entropy.
- For example, when a battery is used to run a motor, some of the energy of the battery is lost as heat due to the resistance in the wire. Therefore, less work is available for the motor.



FREE ENERGY CHANGES FOR NONSTANDARD STATES

- The standard free energy changes for a reaction (ΔG°) are only useful for a very narrow set of conditions where reactants and products are in their standard states.
- For example, consider the standard free energy change for evaporation of liquid water:

 $H_2O(l) \iff H_2O(g)$ $\Delta G^\circ = +8.59 \text{ kJ/mol}$

- Since ΔG° for this process is positive, it is nonspontaneous. Yet when water is spilled under ordinary conditions, it evaporates spontaneously. Why?
- This is because ordinary conditions are not standard states. For example, for water vapor, standard conditions are those were P_{H2O} would be 1 atm. Based on the ΔG° value given above, under these conditions, the water vapor would condense spontaneously.
- Free energy changes under nonstandard conditions (ΔG) can be calculated from ΔG° according to the equation below:





FREE ENERGY CHANGES FOR NONSTANDARD STATES

• The relationship of free energy change for evaporation of water and pressure of water can be seen from diagram below:



• Under *standard condition*, $Q = P_{H2O} = 1$ atm and $\Delta G = \Delta G^{\circ}$, as expected.

 $\Delta G = \Delta G^{\circ} + RT \ln (1) = +8.59 \text{ kJ/mol}$

• At *equilibrium*, where water vapor has a pressure of 0.0313 atm, $\Delta G = 0$ as shown below:

 $\Delta G = \Delta G^{\circ} + RT \ln (0.0313)$ = +8.59 + (8.314 J/molK)(298) ln (0.0313) = +8.59 kJ/mol -8.59 kJ/mol = 0

• Under *nonstandard condition*, $P_{H2O} = 0.005$ atm and ΔG can be calculated as shown below:

 $\Delta G = \Delta G^{\circ} + RT \ln (0.005)$ = +8.59 + (8.314 J/molK)(298) ln (0.005) = +8.59 kJ/mol -13.1 kJ/mol = -4.5 kJ/mol

• Under these conditions, since $\Delta G < 0$, evaporation would be spontaneous.

FREE ENERGY CHANGES FOR NONSTANDARD STATES

Examples:

1. For the reaction shown below:

 $2 \text{ NO}(g) + O_2(g) \rightarrow 2 \text{ NO}_2(g)$ $\Delta G^\circ = -71.2 \text{ kJ}$

Calculate ΔG under the following conditions:

 $P_{NO} = 0.100 \text{ atm}$ $P_{O2} = 0.100 \text{ atm}$ $P_{NO2} = 2.00 \text{ atm}$

2. Calculate ΔG for the reaction shown below if the reaction mixture consists of 1.0 atm N₂, 3.0 atm H₂ and 1.0 atm NH₃.

 $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$ $\Delta G^\circ = -33.32 \text{ kJ}$

FREE ENERGY AND EQUILIBRIUM

- ΔG° determines the spontaneity of a reaction when reactants and products are in their standard states.
- Previously we learned that equilibrium constant (K) determines how far a reaction proceeds, also a measure of spontaneity.
- Therefore, it would follow that free energy changes and equilibrium constant are related. This relationship is shown below:

 $\Delta G = \Delta G^{\circ} + RT \ln Q$ At equilibrium $0 = \Delta G^{\circ} + RT \ln K$ $\Delta G^{\circ} = -RT \ln K$

• It follows that:

| 1. For reactions involving only gases: | $\mathbf{K} = \mathbf{K}_{\mathbf{p}}$ |
|--|--|
| 2. For reactions involving only solutes in liquid solutions: | $\mathbf{K} = \mathbf{K}_{\mathbf{c}}$ |
| 3. For net ionic equations: | $\mathbf{K} = \mathbf{K}_{sp}$ |



RELATIONSHIP OF ΔG° , K, AND SPONTANEITY

$\Delta \mathbf{G}^{\circ} = -\mathbf{RT} \mathbf{ln} \mathbf{K}$

| When K > 1 | When $K \approx 1$ | When K <1 |
|--------------------------------|---------------------------------------|--|
| Reactants> Products | Reactants \iff Products | Reactants |
| log K > 0 | $\log \mathrm{K} pprox 0$ | log K < 0 |
| $\Delta G^{\circ} < 0$ | $\Delta { m G}^{ m o}pprox 0$ | $\Delta G^{\circ} > 0$ |
| Reaction is spontaneous | Reaction gives an equilibrium mixture | Forward reaction is non-spontaneous Reverse reaction is spontaneous |

Examples:

1. Use the standard free energies of formation given to determine the equilibrium constant (K) for the following reaction at 25 °C:

| | $N_{2}(g)$ | + $3 H_2(g)$ | \rightarrow | 2 NH ₃ (g) |
|--------------------------------------|------------|--------------|---------------|-----------------------|
| $\Delta {\rm G^{o}}_{ m f}$ (kJ/mol) | 0 | 0 | | -16.66 |

2. Use the standard free energies in your text to calculate ΔG° and K for the following reaction at 25 °C:

$$2 \operatorname{H}_{2}(g) + \operatorname{O}_{2}(g) \rightarrow 2 \operatorname{H}_{2}\operatorname{O}(g)$$

CHANGE OF FREE ENERGY WITH TEMPERATURE

- How can ΔG° be found for temperatures other than standard temperatures (25 °C)?
- An approximate method used to calculate ΔG°_{T} is based on the assumption that both ΔH° and ΔS° are constant with respect to temperature (only approximately true)
- Then: $\Delta G^{\circ}_{T} = \Delta H^{\circ} T\Delta S^{\circ}$ (a convenient approximation for ΔG°_{T}) <u>NOTE:</u> ΔG°_{T} is strongly temperature dependent $\Delta G^{\circ}_{T} = C$ hange in free Energy for a substance: \Rightarrow at 1 atm of pressure (standard pressure) and \Rightarrow at the specified temperature, T (nonstandard temperature) depends on the value of determined by

| | depends on the value of | | determined by | |
|-------------|-------------------------|--------------------|---------------|---------------|
| SPONTANEITY | | ΔG° _T - | | → TEMPERATURE |
| | | | | |

• It follows that **SPONTANEITY IS TEMPERATURE DEPENDENT**!

Meaning:

• Some chemical changes may be non-spontaneous at one temperature but spontaneous at another temperature.

Examples:

1. Sodium Carbonate, Na₂CO₃, can be prepared by heating sodium hydrogen carbonate, NaHCO₃. Given the ΔH_f° and S° values below, estimate the temperature at which NaHCO₃ decomposes to products at 1 atm.

| | $2 \text{ NaHCO}_3(s)$ | \longrightarrow | Na ₂ CO ₃ | + | $H_2O(g)$ | + $CO_2(g)$ |
|---------------------------------------|------------------------|-------------------|---------------------------------|---|-----------|-------------|
| $\Delta H_{\rm f}^{\circ}$ (kJ/mol) : | -950.8 | | -1130.8 | | -241.8 | -393.5 |
| S° (J/K) : | 101.7 | | 138.8 | | 188.7 | 213.7 |

CHANGE OF FREE ENERGY WITH TEMPERATURE

Examples:

2. Given ΔH° and ΔS° values at 25°C, estimate ΔG° at 400 K for the reaction shown below:

$$2 \operatorname{SO}_2(g) + \operatorname{O}_2(g) \rightarrow 2 \operatorname{SO}_3(g)$$

 $\Delta H^{\circ} = -196.6 \text{ kJ} \qquad \Delta S^{\circ} = -189.6 \text{ J/K}$

3. Methanol can be prepared from reaction of CO and H_2 , as shown below:

 $CO (g) + 2 H_2 (g) \rightarrow CH_3OH (g)$ $\Delta H^\circ = -90.7 \text{ kJ} \qquad \Delta S^\circ = -221.5 \text{ J/K}$

a) Is this reaction spontaneous under standard conditions at 25°C?

b) Calculate ΔG° at 500 K. Is the reaction spontaneous under standard conditions at this temperature?

Answers to In-Chapter Problems:

| Page | Example No. | Answer |
|------|----------------|---|
| 5 | 1 | positive |
| | 2 | negative |
| | 3 | positive |
| 9 | 3a | $\Delta S_{surr} = +6.86 \times 10^3 \text{ J/K}$ |
| | 3b | $\Delta S_{sys} = +$ |
| | 3c | $\Delta S_{univ} = +$; reaction is spontaneous |
| 13 | 1a | spontaneous at low temperature; nonspontaneous at high temperature |
| | 1b | nonspontaneous at low temperature; spontaneous at high temperature |
| | 1c | nonspontaneous at low temperature; spontaneous at high temperature |
| | 2 | $\Delta G = +53.3$ kJ; reaction is not spontaneous The reaction becomes spontaneous at T = 673 K |
| 15 | 1a | |
| | 1b | |
| 16 | 1a | CO_2 (g) ; greater molar mass and complexity |
| | 1b | CH ₃ OH (g) ; gas phase |
| | 1c | CO_2 (g); greater molar mass and complexity |
| | 1d | CH ₃ CH ₂ CH ₃ ; greater complexity |
| 17 | 2a | $\Delta S = negative$ |
| | 2b | $\Delta S = inconclusive$ |
| | 2c | $\Delta S = \text{positive}$ |
| | 3 | $\Delta S^{\circ} = 178.8 \text{ J/K}$ |
| 18 | 1 | $\Delta G^{\circ} = -70.9 \text{ kJ}$; spontaneous |
| | 2 | $\Delta H^{\circ} = 176.2 \text{ kJ} \qquad \Delta S^{\circ} = 285.1 \text{ J/K} \qquad \Delta G^{\circ} = 91.2 \text{ kJ}$ nonspontaneous; becomes spontaneous at high temperature |
| 19 | 2 | $\Delta G^{\circ} = +41.0 \text{ kJ}$; nonspontaneous |
| | 3 | $\Delta G^{\circ} = 91.2 \text{ kJ}$; value is comparable to that calculated by method 1 |

| 20 | 1 | $\Delta G^{\circ} = -23 \text{ kJ}$ |
|----|----|---|
| | 2 | $\Delta G^{\circ} = -29.4 \text{ kJ}$ |
| 24 | 1 | $\Delta G = -50.7 \text{ kJ}$ |
| | 2 | $\Delta G = -41.5 \text{ kJ}$ |
| 26 | 1 | $K = 6.9 \times 10^5$ |
| | 2 | $K = 1.39 \times 10^{80}$ |
| 27 | 1 | T= 401.1 K |
| 28 | 2 | $\Delta G^{\circ}{}_{T} = -120.8 \text{ kJ}$ |
| | 3a | $\Delta G^{\circ} = -24.7 \text{ kJ}$; reaction is spontaneous at 25°C |
| | 3b | $\Delta G^{\circ}_{T} = +20.1 \text{ kJ}$; reaction is nonspontaneous at 500 K |