

# Chapter 16

## Thermodynamics

p. 647 – 677

### Spontaneity

**Spontaneous process:**

Ex.

**Nonspontaneous process:**

Ex.

**What have we learned about spontaneity during this course?**

1) Q vs. K?

2) So.....

**Spontaneous process** occurs when a system moves \_\_\_\_\_ equilibrium.

**Nonspontaneous process** occurs when a system moves \_\_\_\_\_ equilibrium.

Is a spontaneous always fast?

One thermodynamic quantity that gives information on spontaneity is \_\_\_\_\_.

## Enthalpy Review

For a chemical reaction:

$$\Delta H_{\text{rxn}} =$$

All reactions result either in the net release or net absorption of heat.

**Exothermic Reaction** ( $PE_{\text{products}} < PE_{\text{reactants}}$ )

- 1.
- 2.
- 3.

**Endothermic Reaction** ( $PE_{\text{products}} > PE_{\text{reactants}}$ )

- 1.
- 2.
- 3.

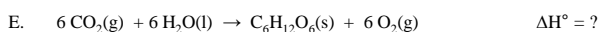
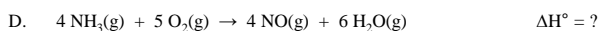
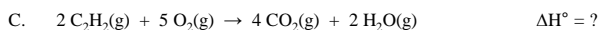
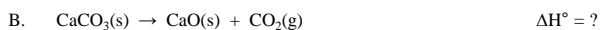
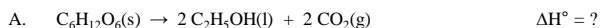
**NOTE: Not all exothermic reactions are spontaneous, and similarly, not all endothermic reactions are nonspontaneous.**

### Standard Heat/Enthalpy of Reaction, $\Delta H_{\text{rxn}}^{\circ}$

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_f^{\circ} (\text{products}) - \sum \Delta H_f^{\circ} (\text{reactants})$$

$\Delta H_f^{\circ} = 0$  for elements in their standard state under standard conditions.

1. Calculate the standard enthalpy for the reactions below, given the  $\Delta H_f^{\circ}$  values in the table to the right.



Substance	$\Delta H_f^{\circ}$ (kJ/mol)
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.7
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1260
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{l})$	-285.8
$\text{C}_2\text{H}_2(\text{g})$	+226.7
$\text{NH}_3(\text{g})$	-46.1
$\text{NO}(\text{g})$	+90.2
$\text{H}_2\text{O}(\text{g})$	-241.8
$\text{CaCO}_3(\text{s})$	-1206.9
$\text{CaO}(\text{s})$	-635.1

## Entropy, S

*A measure of the amount \_\_\_\_\_.*

State with a large S:

State with a small S:

A spontaneous change is favored by \_\_\_\_\_ in entropy.

$$\text{Change in Entropy} = \Delta S = S_{\text{final}} - S_{\text{initial}} = S_{\text{products}} - S_{\text{reactants}}$$

### Positive $\Delta S$

\*  
\*  
\*

### Negative $\Delta S$

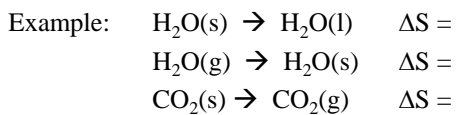
\*  
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## Predicting the Sign of the Entropy Change

1. For a chemical reaction we can predict sign of  $\Delta S$  using:

$$S_{\text{(solid)}} < S_{\text{(liquid)}} \ll S_{\text{(gas)}}$$

most ordered state                      most disordered state

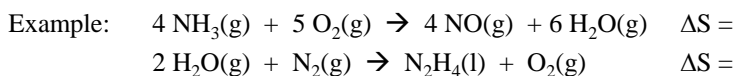


2. Entropy change is positive ( $\Delta S > 0$ ) if the number of moles of gas increases on going from reactants to products.

$$\Delta n_{\text{gas}} = n_{\text{gas, products}} - n_{\text{gas, reactants}}$$

If  $\Delta n_{\text{gas}} > 0$ , then  $\Delta S > 0$

If  $\Delta n_{\text{gas}} < 0$ , then  $\Delta S < 0$



- When a salt is dissolved in an aqueous solution  $\Delta S = \pm$  dependent on substance  
 Ex.  $I_2(s) \rightarrow I_2(aq)$   $\Delta S =$   
 $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$   $\Delta S =$   
 $FeSO_4(s) \rightarrow Fe^{2+}(aq) + SO_4^{2-}(aq)$   $\Delta S =$
- Effect of Temperature on entropy: as Kelvin Temp. increases, entropy increases  
 Ex.  $O_2(g)$  at  $100^\circ C$  vs.  $O_2(g)$  at  $200^\circ C$
- More complicated molecules have higher entropy.  
 Ex.  $CH_4(g)$  vs.  $C_4H_{10}(g)$

**Third Law of Thermodynamics:**

The entropy of a perfectly ordered crystalline substance is zero at absolute zero (0 K)

**Sample Questions**

Predict the sign of  $\Delta S$  in the system for each of the following processes:

- $CaSO_4(s) \rightarrow CaO(s) + SO_3(g)$
- $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$
- $I_2(s) \rightarrow I_2(aq)$ ; dissolution of iodine in water
- $I_2(g) \rightarrow 2 I(g)$
- $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$
- $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
- $CO_2(g)$  at  $100^\circ C \rightarrow CO_2(g)$  at  $82^\circ C$

**Standard Entropy of Reaction,  $\Delta S_{rxn}^\circ$**   
 $\Delta S_{rxn}^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$

**Standard Molar Entropy,  $S^\circ$**

The entropy of one mole of a pure substance at 1 atm pressure and  $25^\circ C$ . (J/K.mol)

Predict the sign of and then calculate the standard entropy change for the following reactions:

- $N_2O_4(g) \rightarrow 2 NO_2(g)$   $\Delta S_{rxn}^\circ = ?$
- $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$   $\Delta S_{rxn}^\circ = ?$
- $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$   $\Delta S_{rxn}^\circ = ?$
- $2 H_2O_2(l) \rightarrow 2 H_2O(l) + O_2(g)$   $\Delta S_{rxn}^\circ = ?$
- $2 Na(s) + Cl_2(g) \rightarrow 2 NaCl(s)$   $\Delta S_{rxn}^\circ = ?$

Substance	$S^\circ$ (J/K.mol)
$NO_2(g)$	240.0
$N_2O_4(g)$	304.2
$N_2(g)$	191.5
$H_2(g)$	130.6
$NH_3(g)$	192.3
$CaCO_3(s)$	92.9
$CaO(s)$	39.7
$O_2(g)$	205.0
$Na(s)$	51.2
$Cl_2(g)$	223.0
$NaCl(s)$	72.1
$CO_2(g)$	213.6
$H_2O_2(l)$	110
$H_2O(l)$	69.9

### Entropy and the Second Law of Thermodynamics

Spontaneous processes are favored by \_\_\_\_\_. But for a given reaction  $\Delta H = \pm$  and  $\Delta S = \pm$ . **To determine whether or not a reaction is spontaneous, must look at the interplay between these two factors,  $\Delta H$  and  $\Delta S$ , with T (temperature).**

How, then, can we decide whether a reaction will occur spontaneously?

Define new thermodynamic quantity called Gibbs free-energy change,  $\Delta G$ , where:

$$\Delta G = \Delta H - T\Delta S \quad (\text{under nonstandard conditions})$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\text{under standard conditions})$$

#### First Law of Thermodynamics

In any process, spontaneous or nonspontaneous, the total internal energy of a system and its surroundings is constant.

#### Second Law of Thermodynamics

In any spontaneous process, the total entropy of a system and its surroundings always increases.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Specifically,

If  $\Delta S_{\text{total}} > 0$ , the reaction is **spontaneous**

If  $\Delta S_{\text{total}} < 0$ , the reaction is **nonspontaneous**

If  $\Delta S_{\text{total}} = 0$ , the reaction mixture is at **equilibrium**

### Spontaneity and Gibbs free energy

Where did this equation,  $\Delta G = \Delta H - T\Delta S$ , come from and what does it tell us about spontaneity?

To relate Gibbs free energy change and spontaneity we consider the relationship that comes from the Second Law of Thermodynamics:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$\text{but ... } \Delta S_{\text{system}} = \text{_____} \text{ and } \Delta S_{\text{surr}} = \text{_____}$$

substituting these expressions into the 2<sup>nd</sup> Law and rearranging gives ...

Specifically,

If  $\Delta G < 0$ , the reaction is \_\_\_\_\_.

If  $\Delta G > 0$ , the reaction is \_\_\_\_\_.

If  $\Delta G = 0$ , the reaction mixture is \_\_\_\_\_.

### Signs of Enthalpy, Entropy, and Gibbs Free-Energy Changes

$\Delta H$	$\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Spontaneity
			Spontaneous at all temperatures
			Spontaneous at low temperatures where $\Delta H$ outweighs $T\Delta S$ Nonspontaneous at high temperatures where $T\Delta S$ outweighs $\Delta H$
			Nonspontaneous at all temperatures
			Spontaneous at high temperatures where $T\Delta S$ outweighs $\Delta H$ Nonspontaneous at low temperatures where $\Delta H$ outweighs $T\Delta S$

#### Crossover Temperature

**Definition:**

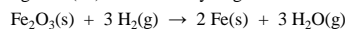
**Equation:**

#### Sample Questions

1. Consider the oxidation of iron metal:  $4 \text{Fe(s)} + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{Fe}_2\text{O}_3(\text{s})$   
Is this reaction spontaneous at 25 °C?

	$\text{Fe}_2\text{O}_3(\text{s})$	$\text{O}_2(\text{g})$	$\text{Fe(s)}$
$\Delta H_f^\circ$ (kJ/mol)	-824.2	0	0
$\Delta S^\circ$ (J/K.mol)	87.4	205.0	27.3

2. Iron metal can be produced by reducing iron (III) oxide with hydrogen:



- Is this reaction spontaneous under standard-state conditions 25 °C?
  - At what temperature will the reaction become spontaneous?
3. Consider the decomposition of gaseous  $\text{N}_2\text{O}_4$ :
- $$\text{N}_2\text{O}_4(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) \quad \Delta H^\circ = +57.1 \text{ kJ}; \Delta S^\circ = +175.8 \text{ J/K}$$
- Is this reaction spontaneous under standard conditions at 37°C?
  - Estimate the Celsius temperature at which the reaction becomes spontaneous.

## Standard Gibbs Free Energy Change ( $\Delta G^\circ$ ) For Reactions

### Standard State Conditions

- \* Solids, liquids, and gases in pure form and gases at 1 atm pressure
- \* Solutes at 1 M concentration
- \* Specified temperature (does not have to be 25°C since value of  $\Delta G^\circ$  so dependent on temp)

Standard Gibbs Free-Energy Change ( $\Delta G^\circ$ ) can be calculated:

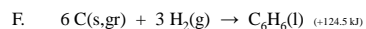
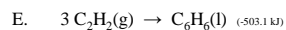
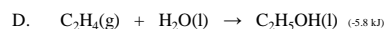
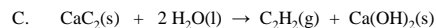
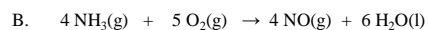
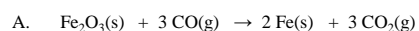
- 1.
- 2.

### Standard Gibbs free-energy of formation $\Delta G_f^\circ$

- \*
- \*

### Sample Questions

1. Calculate the standard Gibbs free-energy change for the following reactions under standard state conditions



Substance	$\Delta G_f^\circ$ (kJ/mol)
$\text{Fe}_2\text{O}_3(\text{s})$	-742.2
$\text{CO}(\text{g})$	-137.2
$\text{CO}_2(\text{g})$	-394.4
$\text{NH}_3(\text{g})$	-16.5
$\text{NO}(\text{g})$	86.6
$\text{H}_2\text{O}(\text{l})$	-237.2
$\text{CaC}_2(\text{s})$	-64.8
$\text{C}_2\text{H}_2(\text{g})$	209.2
$\text{Ca}(\text{OH})_2(\text{s})$	-898.6
$\text{C}_2\text{H}_4(\text{g})$	68.1
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-174.9
$\text{CH}_3\text{OH}(\text{g})$	-161.9
$\text{C}_6\text{H}_6(\text{l})$	124.5

**Gibbs Free-Energy Change Under Non-Standard Conditions  
( $\Delta G$ ): Composition of Reaction Mixture**

We can calculate the free energy change,  $\Delta G$ , for a reaction when reactants and products are present at non-standard pressures and concentrations using ...

$$\Delta G = \Delta G^\circ + RT \ln Q$$

If  $\Delta G < 0$ , the reaction is \_\_\_\_\_ and  $Q$  \_\_\_\_\_  $K$ .

If  $\Delta G > 0$ , the reaction is \_\_\_\_\_ and  $Q$  \_\_\_\_\_  $K$ .

If  $\Delta G = 0$ , the reaction is \_\_\_\_\_ and  $Q$  \_\_\_\_\_  $K$ .

**Relationship Between Gibbs Free Energy Change and the  
Equilibrium Constant ( $K$ )**

We can therefore derive a relationship between the Gibbs free-energy and the equilibrium constant.

At equilibrium....

$$\Delta G = 0 \text{ and } Q = K \text{ and } \Delta G = \Delta G^\circ + RT \ln Q$$

more specifically ...

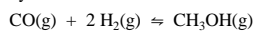
If  $K$  \_\_\_ 1,  $\Delta G^\circ$  \_\_\_ 0, and the reaction is \_\_\_\_\_.

If  $K$  \_\_\_ 1,  $\Delta G^\circ$  \_\_\_ 0, and the reaction is \_\_\_\_\_.

If  $K$  \_\_\_ 1,  $\Delta G^\circ$  \_\_\_ 0, and the reaction is \_\_\_\_\_.

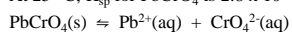
**Sample Questions**

1. Methanol,  $\text{CH}_3\text{OH}$ , an important alcohol is used in the manufacture of adhesives, fibers, and plastics, is synthesized by the reaction:

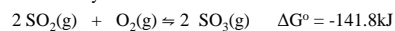


Use the thermodynamic data in slide 14 to calculate the equilibrium constant for this reaction at 25 °C.

2. At 25 °C,  $K_{\text{sp}}$  for  $\text{PbCrO}_4$  is  $2.8 \times 10^{-13}$ . Calculate the standard free-energy change at 25 °C for the reaction:



3. Sulfuric acid is produced in larger amounts by weight than any other chemical. It is used in manufacturing fertilizers, oil refining, and hundreds of other processes. An intermediate step in the industrial process for the synthesis of  $\text{H}_2\text{SO}_4$  is the catalytic oxidation of sulfur oxide:



Calculate  $\Delta G$  at 25 °C given the following sets of partial pressures:

100. atm  $\text{SO}_2$ , 100. atm  $\text{O}_2$ , and 1.0 atm  $\text{SO}_3$
- 2.0 atm  $\text{SO}_2$ , 1.0 atm  $\text{O}_2$ , and 10. atm  $\text{SO}_3$
- Each reactant and product at a partial pressure of 1.0 atm
- Calculate the equilibrium constant  $K_p$  at 25 °C

4. Using the thermodynamic data in slide 14 calculate the equilibrium constant for the following reaction at 25 °C.  
 $2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$  ( $7 \times 10^{34}$ ) Hint: Calculate  $\Delta G^\circ$  first.
5. Calculate the equilibrium constant for the following reaction at 25 °C and at 200. °C for the following reaction:  
 $\text{PCl}_5(\text{g}) \rightleftharpoons \text{Cl}_2(\text{g}) + \text{PCl}_3(\text{g})$   $\Delta G^\circ = +37.2 \text{ kJ}$ ;  $\Delta H^\circ = 87.9 \text{ kJ}$ ;  $\Delta S^\circ = 170.2 \text{ J/K}$  ( $25^\circ\text{C} = 3.01 \times 10^3$ ;  $200^\circ\text{C} = 0.15$ )
6. For the reaction  
 $\text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$ ;  $\Delta H^\circ = -1323 \text{ kJ}$ ;  $\Delta S^\circ = -30.0 \text{ J/K}$
- Is the reaction spontaneous in the forward direction under the following conditions:  $P_{\text{C}_2\text{H}_4} = 20. \text{ atm}$ ;  $P_{\text{O}_2} = 0.020 \text{ atm}$ ;  $P_{\text{CO}_2} = 0.010 \text{ atm}$ , and  $P_{\text{H}_2\text{O}} = 0.010 \text{ atm}$  at 25 °C? (yes)
  - Under the same conditions is the reaction spontaneous in the forward direction at 750. °C? (yes)

7. The equilibrium constant,  $K_p$ , is 4.40 at 2000. K for the reaction  
 $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$
- Calculate  $\Delta G^\circ$  at 2000. K for the reaction. ( $-24.6 \text{ kJ/mol}$ )
  - Calculate  $\Delta G$  for the reaction when the partial pressures are  $P_{\text{H}_2} = 0.25 \text{ atm}$ ,  $P_{\text{CO}_2} = 0.78 \text{ atm}$ ,  $P_{\text{H}_2\text{O}} = 0.66 \text{ atm}$ , and  $P_{\text{CO}} = 1.20 \text{ atm}$ . ( $-1.3 \text{ kJ/mol}$ )
8. Consider the reaction for the formation of the cobalt ammonia complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$  below.  
 $\text{Co}^{3+}(\text{aq}) + 6 \text{NH}_3(\text{aq}) \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq})$   $K_f = 2.0 \times 10^7$  at 25 °C.
- Calculate the Gibbs free-energy under standard conditions for this reaction. ( $-42 \text{ kJ/mol}$ )
  - If  $[\text{Co}^{3+}] = 0.00500 \text{ M}$ ,  $[\text{NH}_3] = 0.10 \text{ M}$ , and  $[\text{Co}(\text{NH}_3)_6^{3+}] = 1.00 \text{ M}$  initially, is the reaction spontaneous in the forward direction? (no)