



## Chapter 18

# Entropy, Free Energy, and Equilibrium

## Part II

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## Spontaneity of a Process Considering Only the System

- Starting from the 2<sup>nd</sup> law of thermodynamics for a *spontaneous* process:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (1)$$

Also, we have:  $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}} / T \quad (2)$

Substituting (2) into (1) gives:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$

$$T \Delta S_{\text{univ}} = T \Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

In terms of only the system:

$$\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} < 0 \quad (3)$$

At constant  $T$  and  $P$ , the **process is spontaneous** only when the change of entropy and enthalpy of the system is such that  $\Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  is **less than zero**.

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## Gibbs Free Energy

- **Gibbs free energy** (or simply free energy) is another thermodynamic quantity and is defined as:

$$G = H - TS$$

The change in Gibbs free energy for a *system* at constant temperature is:

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

Getting back to equation ③, we have for a *spontaneous* process:

$$\Delta G = \Delta H - T \Delta S < 0$$

- $\Delta G < 0$  ; the forward reaction is spontaneous.
- $\Delta G > 0$  ; the forward reaction is nonspontaneous.
- $\Delta G = 0$  ; the reaction is at equilibrium.



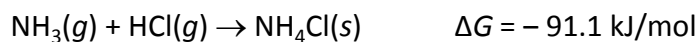
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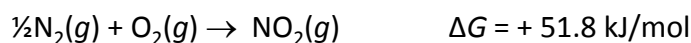
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## Gibbs Free Energy

- Free energy can be defined as *the energy available to do work*. Thus, if a particular process is accompanied by a release of usable energy ( $\Delta G$  is *negative*), this fact *guarantees* that it is *spontaneous*, and no need to consider what happens to the rest of the universe.
- Here are few examples at 25°C:



*spontaneous*



*nonspontaneous*

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## Predicting the Sign of $\Delta G$

- The sign of  $\Delta G$  can be predicted from knowing the sign of  $\Delta H$  and  $\Delta S$  for a reaction.

$$\Delta G = \Delta H - T\Delta S < 0$$

When $\Delta H$ Is	And $\Delta S$ Is	$\Delta G$ Will Be	And the Process Is
Negative	Positive	Negative	Always spontaneous
Positive	Negative	Positive	Always nonspontaneous
Negative	Negative	Negative when $T\Delta S < \Delta H$ Positive when $T\Delta S > \Delta H$	Spontaneous at low $T$ Nonspontaneous at high $T$
Positive	Positive	Negative when $T\Delta S > \Delta H$ Positive when $T\Delta S < \Delta H$	Spontaneous at high $T$ Nonspontaneous at low $T$

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## Standard Free-Energy Change

- The **standard free energy** ( $\Delta G^\circ_{\text{rxn}}$ ) of a system is the change in free energy when **reactants** in their **standard states** are converted to **products** in their **standard states**.
- Standard states are:
  - Gases            1 atm            [  $\text{O}_2(g)$ ,  $\text{CO}_2(g)$ ,  $\text{CH}_4(g)$  ]
  - Liquids           Pure liquid    [  $\text{H}_2\text{O}(l)$ ,  $\text{C}_2\text{H}_5\text{OH}(l)$  ]
  - Solids            Pure solid     [  $\text{Na}(s)$ ,  $\text{Mg}(s)$ ,  $\text{AlCl}_3(s)$  ]
  - Elements        The most stable form at 1 atm and  $25^\circ\text{C}$
  - Solutions        1 M concentration

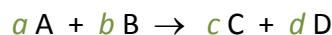
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## Standard Free-Energy Change

- Consider the following equation:



The change in standard free-energy ( $\Delta G^\circ_{\text{rxn}}$ ) is:

$$\Delta G^\circ_{\text{rxn}} = [c \Delta G^\circ_f(\text{C}) + d \Delta G^\circ_f(\text{D})] - [a \Delta G^\circ_f(\text{A}) + b \Delta G^\circ_f(\text{B})]$$

In general, the change of entropy of a chemical reaction (a system) is given by:

$$\Delta G^\circ_{\text{rxn}} = \sum n \Delta G^\circ_f(\text{products}) - \sum m \Delta G^\circ_f(\text{reactants})$$

where  $n$  and  $m$  are the stoichiometric coefficients of the reactants and products in a given equation.

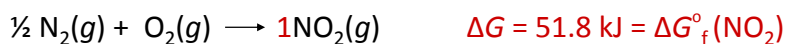
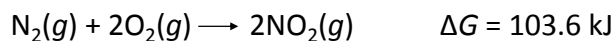
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## Standard Free Energy of Formation

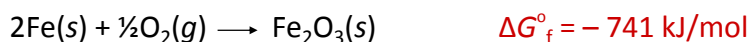
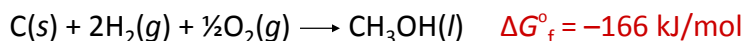
- The standard free energy of formation ( $\Delta G^\circ_f$ )** of a compound is the change in free energy that occurs when 1 mole of that compound is formed from elements in their standard states.
  - It is very similar to the concept of the standard enthalpy of formation ( $\Delta H^\circ_f$ ) that you learned in CHEM 101.



Elements @ standard states

$$\Delta G^\circ_f = 0$$

$$\Delta G^\circ_f = 51.8 \text{ kJ/mol}$$



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## Standard Free-Energy Change

### Exercise:

Calculate the standard free-energy change for the following reaction at 25°C.



$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \sum n \Delta G^\circ_f(\text{products}) - \sum m \Delta G^\circ_f(\text{reactants}) \\ &= 2[\Delta G^\circ_f(\text{KCl}(s))] + 3[\Delta G^\circ_f(\text{O}_2(g))] - 2[\Delta G^\circ_f(\text{KClO}_3(s))] \\ &= 2[-408.3 \text{ kJ/mol}] + 3[0] - 2[-289.9 \text{ kJ/mol}] \\ &= -816.6 - (-579.8) = -236.8 \text{ kJ/mol}\end{aligned}$$

- The reaction is spontaneous.
- A negative  $\Delta G^\circ$  corresponds to a larger equilibrium constant ( $K$ ), while a positive  $\Delta G^\circ$  corresponds to a smaller equilibrium constant ( $K$ ).

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## Standard Free-Energy Change

### Exercise:

The reaction  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$  has  $\Delta H^\circ = 177.8$  kJ/mol and  $\Delta S^\circ = 160.5$  J/K · mol. Predict the spontaneity of the reaction at room temperature and at 1000°C.

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

What is the temperature above which the reaction would favor the formation of  $\text{CaO}(s)$  and  $\text{CO}_2(g)$  ?

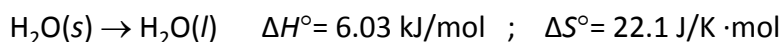
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## Standard Free-Energy Change

- The temperature affects the sign of  $\Delta G^\circ$  of chemical reactions.
- Consider the melting of ice:



$T$ (°C)	$T$ (K)	$\Delta H^\circ$ (J/mol)	$\Delta S^\circ$ (J/K · mol)	$\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T}$ (J/K · mol)	$\Delta S_{\text{univ}} = \Delta S^\circ + \Delta S_{\text{surr}}$ (J/K · mol)	$T\Delta S^\circ$ (J/mol)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J/mol)
-10	263	$6.03 \times 10^3$	22.1	-22.9	-0.8	$5.81 \times 10^3$	$+2.2 \times 10^2$
0	273	$6.03 \times 10^3$	22.1	-22.1	0	$6.03 \times 10^3$	0
10	283	$6.03 \times 10^3$	22.1	-21.3	+0.8	$6.25 \times 10^3$	$-2.2 \times 10^2$

\*Note that at 10°C,  $\Delta S^\circ$  ( $\Delta S_{\text{sys}}$ ) controls, and the process occurs even though it is endothermic. At -10°C, the magnitude of  $\Delta S_{\text{surr}}$  is larger than that of  $\Delta S^\circ$ , so the process is spontaneous in the opposite (exothermic) direction.

The process is :

- $\Delta G^\circ$  is -ve ○ spontaneous at 10°C. (Ice melts at this temperature)
- $\Delta G^\circ$  is +ve ○ nonspontaneous at -10°C. (Ice does not melt at this temperature)
- $\Delta G^\circ$  is 0 ○ at equilibrium at 0°C. (Ice and water are at equilibrium at this temperature)

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## Relationship between $\Delta G$ and $\Delta G^\circ$

- Most of the reactions take place in states other than their standard states. Thus, in order to determine spontaneity of a reaction, we need to know how to calculate  $\Delta G$  when the reaction is not occurring at standard states.

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

where:

- $\Delta G$  is the non-standard free energy.
- $\Delta G^\circ$  is the standard free energy (from appendix 2).
- $R = 8.314 \text{ J/K} \cdot \text{mol}$
- $T$  is in Kelvin.
- $Q$  is the reaction quotient.

Examples of *nonstandard states*:

- Solutions with concentrations other than 1 M.
- Gases having pressures other than 1 atm.

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## Relationship between $\Delta G$ and $\Delta G^\circ$

▪ Exercise:



How does the value of  $\Delta G$  change when the pressures of the  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  gases are changed to 0.25 atm, 0.45 atm and 0.30 atm, respectively at 25°C?

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

First of all calculate  $\Delta G^\circ$  using appendix 2.

$$\Delta G^\circ = [2(-95.27 \text{ kJ/mol})] - [0 + 0] = -190.54 \text{ kJ/mol}$$

Secondly, calculate  $Q$ .

$$Q_p = \frac{(P_{\text{HCl}})^2}{(P_{\text{H}_2})(P_{\text{Cl}_2})} = \frac{(0.30)^2}{(0.25)(0.45)} = 0.80$$

Cont.  $\rightarrow$

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## Relationship between $\Delta G$ and $\Delta G^\circ$

Thirdly, find the non-standard free energy.

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

$$\Delta G = -190540 \text{ J/mol} + (8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(0.80)$$

$$\Delta G = -191.09 \text{ kJ/mol}$$

The reaction becomes *more spontaneous* since the free energy is more negative. Thus, more  $\text{HCl}$  will be formed with the given pressures.

The reaction will continue producing more  $\text{HCl}$  and consuming more  $\text{H}_2$  and  $\text{Cl}_2$  until  $Q_p = K_p$ .

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## Relationship between $\Delta G^\circ$ and $K$

At equilibrium:

$$Q = K \text{ and } \Delta G = 0$$

Thus, at equilibrium:

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

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

The larger the value of  $K$ , the more negative  $\Delta G^\circ$  becomes, and the reaction proceeds more towards the product side.

**TABLE 18.4** Relationship Between  $K$  and  $\Delta G^\circ$  as Predicted by Equation 18.15

$K$	$\ln K$	$\Delta G^\circ$	Result at Equilibrium
$> 1$	Positive	Negative	Products are favored.
$= 1$	0	0	Neither products nor reactants are favored.
$< 1$	Negative	Positive	Reactants are favored.

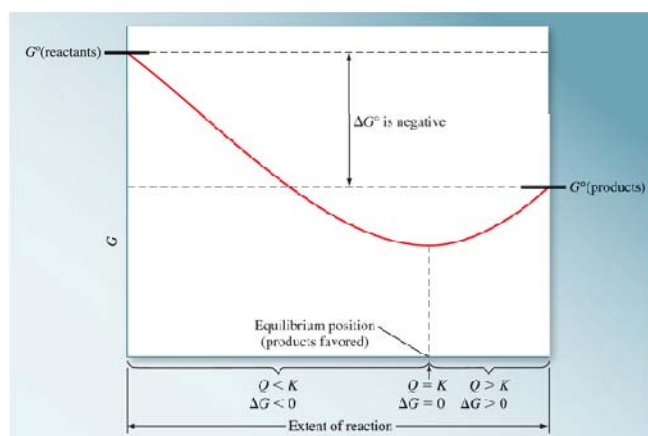
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## Relationship between $\Delta G^\circ$ and $K$

$$\Delta G^\circ = -RT \ln K$$

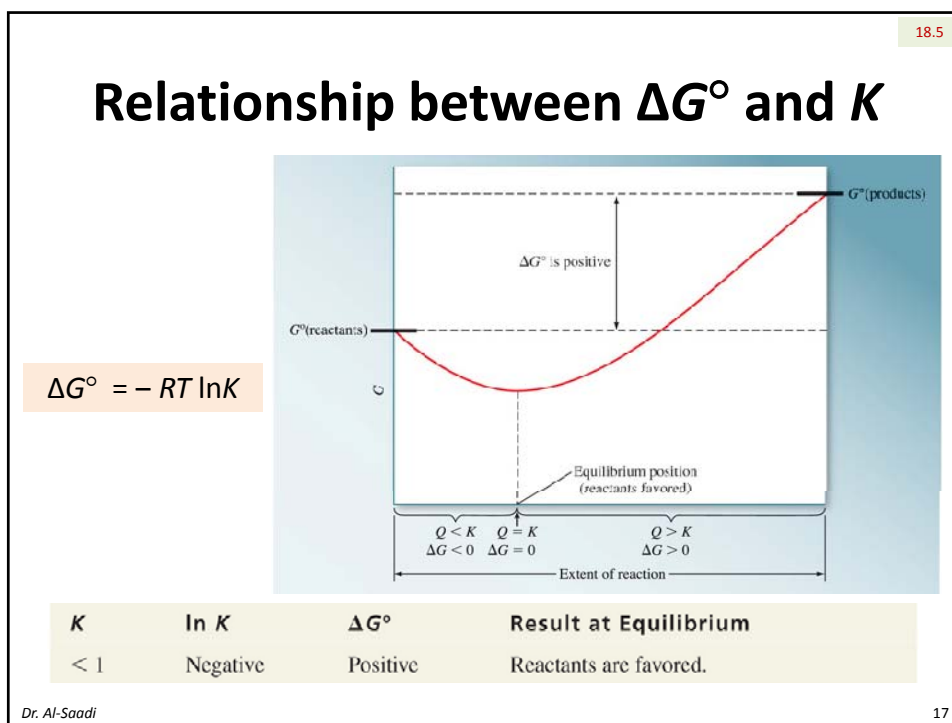


$K$	$\ln K$	$\Delta G^\circ$	Result at Equilibrium
$> 1$	Positive	Negative	Products are favored.

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## Relationship between $\Delta G^\circ$ and $K$

- Example:  
Using the table of standard free energies, calculate the equilibrium constant,  $K_p$ , for the following reaction at 25°C.

$$2\text{HCl}(g) \rightleftharpoons \text{H}_2(g) + \text{Cl}_2(g)$$

$$\Delta G^\circ = [0 + 0] - [2(-95.27 \text{ kJ/mol})]$$

$$= 190.54 \text{ kJ/mol (nonspontaneous)}$$

Substitute into:

$$\Delta G^\circ = -RT \ln K$$

$$190.54 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln K_p$$

$$K_p = 3.98 \times 10^{-34}$$

$K < 1$  (reactants are favored)

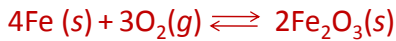
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## Relationship between $\Delta G^\circ$ and $K$

- Example:

The overall reaction for corrosion is:



The  $\Delta H_f^\circ$  for  $\text{Fe}_2\text{O}_3(s)$  is  $-826 \text{ kJ/mol}$ , and  $S^\circ$  ( $\text{J/K}\cdot\text{mol}$ ) for  $\text{Fe}_2\text{O}_3(s)$ ,  $\text{Fe}(s)$  and  $\text{O}_2(g)$  are 90, 27 and 205, respectively. Calculate  $K$  for this reaction at  $25^\circ\text{C}$ .

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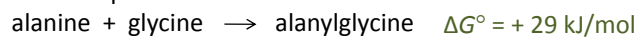
## Thermodynamics of Living Systems

- Thermodynamics have a great effect in biological sciences, such as processes taking place inside our bodies.
- Many chemical reactions carried out inside the body (such as DNA and protein formation) are **not** spontaneous, but they can proceed through **coupled reactions**.



Proteins are polymers made from connecting different amino acids together. However, formation of proteins from amino acids is a **nonspontaneous** process.

For example:



Amino acids

Protein molecule

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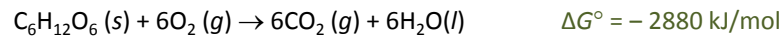
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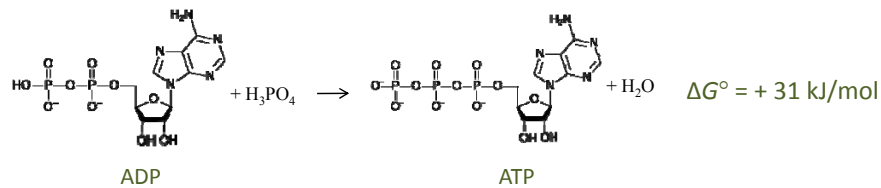
## Thermodynamics of Living Systems

### Tracking chemistry inside our bodies:

- Metabolism process:



- The free energy released from metabolism is used to synthesize energy-storage molecules called adenosine triphosphate (ATP):



- Based on the body needs, ATP are hydrolyzed back to ADP and releases 31 kJ/mol of free energy, that can be utilized to drive unfavorable (*nonspontaneous*) important chemical reactions, such as protein synthesis.

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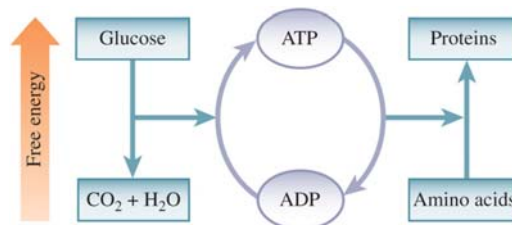
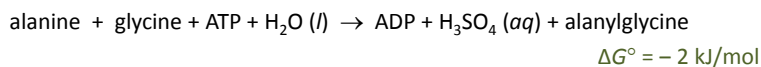
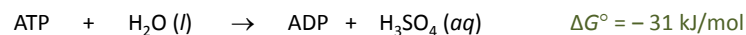
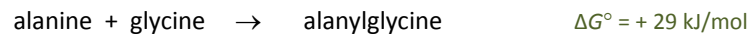
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## Thermodynamics of Living Systems

### Tracking chemistry inside our bodies:

- With the help of enzymes, the *nonspontaneous* protein synthesis reaction inside the body is *coupled* to the *spontaneous* ATP hydrolysis to favor the formation of proteins as follows:



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## Exercises

- For which process is  $\Delta S$  negative?
  - 1) Evaporation of 1 mol of  $\text{CCl}_4(l)$ .
  - 2) Mixing 5 mL ethanol with 25 mL water.
  - ✓ 3) Compressing 1 mol Ne at constant temperature from 1.5 atm to 0.5 atm.
  - 4) Raising the temperature of 100 g Cu from 275 K to 295 K.
  - 5) Grinding a large crystal of KCl to powder.

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## Exercises

- Which of the following shows a decrease in entropy?
  - ✓ 1) Precipitation
  - 2) Gaseous reactants forming a liquid
  - 3) A burning piece of wood
  - 4) Melting ice
  - 5) Two of these

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## Exercises

- At 1 atm, liquid water is heated above 100°C.  $\Delta S_{\text{surr}}$  for this process is:
  - 1) greater than zero.
  - ✓ 2) less than zero.
  - 3) equal to zero.
  - 4) more information is needed to answer this question.

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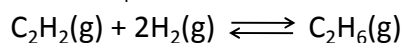
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## Exercises

- Given the following free energies of formation:

	$\Delta G^\circ_f$
$\text{C}_2\text{H}_2(\text{g})$	209.2 kJ/mol
$\text{C}_2\text{H}_6(\text{g})$	-32.9 kJ/mol

Calculate  $K_p$  at 298 K for:



- 1)  $9.07 \times 10^{-1}$
- 2) 97.2
- 3)  $1.24 \times 10^{31}$
- ✓ 4)  $2.72 \times 10^{42}$
- 5)  $7.55 \times 10^{51}$

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