

GIBBS FREE ENERGY AND EQUILIBRIUM

**CONSTANT
BY**

**PRAKRITI DIWAN
B.PHARMA 2nd SEMESTER**

➤ Gibbs Free Energy (G)

The energy associated with a chemical reaction that can be used to do work.

➤ G is a function of
Enthalpy (H)

a measure of the energy (heat content) of the system at constant pressure.

Entropy (S)

a measure of the randomness (disorder) of the system.

- Chemical systems contain energy which depends on their structure - This is H (enthalpy or heat content).

When a chemical structure changes there is a change in H (ΔH)

heat can be released to the surroundings ($-\Delta H$)

heat can be taken up form surroundings ($+\Delta H$)

- Is ΔH the only factor that dictates if a reaction can occur?

NO

- change in entropy (disorder) that accompanies the reaction (ΔS) also has a role.

➤ So.....

The free energy of a system is the sum of its enthalpy (H) plus the product of the temperature (Kelvin) and the entropy (S) of the system.

$$G = H - TS$$

The free energy of a substance = stored heat energy - inherent disorder at a reference temperature

- e.g. Block of ice in hot water - the ice melts (a favourable reaction)



- The ice takes heat from the surrounding water (therefore ΔH is +ve)
Ordered water molecules in ice become randomised after melting (therefore entropy has increased ΔS is +ve).



puddle of water
(no structure)

maximum entropy
minimum order

- Increasing entropy or randomness provides a driving force for this reaction.
- ΔH or ΔS do not predict if a reaction is favourable. But the Gibbs free energy change (ΔG) does:

- The change in Gibbs free energy (ΔG) for a reaction quantitatively measure the energy available to do useful work. It is related to the change in enthalpy and the change in entropy:

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

- If the reaction is run at constant temperature, this equation can be written as follows.

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

- The change in the free energy of a system that occurs during a reaction can be measured under any set of conditions.
- If the data are collected under standard-state conditions, the result is the:

standard-state free energy of reaction (G°).

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

- **NOTE:** The units of H is **kJ** and the units of S is **J/K**. Since G is generally reported in **kJ**, we can divide S by 1000 to convert it to units of **kJ/K**
- **NOTE:** The temperature in the free energy equation must be in Kelvin, so we must convert the given temperature in Celsius to Kelvin by adding **273.15**.

Standard-state conditions

- But what is the standard conditions?
- The partial pressures of any gases involved in the reaction is 0.1 MPa.
- The concentrations of all aqueous solutions are 1 M.
- Measurements are also generally taken at a temperature of 25°C (298 K)
- The biological standard free energy ΔG° are:
pH = 7 & Temp = 37 C°
1 M concentrations of reactants and products.

- ΔG° is negative for any reaction for which ΔH° is negative and ΔS° is positive. We can therefore conclude that any reaction for which ΔG° is negative should be

Favorable, or spontaneous: $\Delta G^\circ < 0$

- Conversely, ΔG° is positive for any reaction for which ΔH° is positive and ΔS° is negative. Any reaction for which ΔG° is positive is therefore:

Unfavorable or non-spontaneous reactions: $\Delta G^\circ > 0$

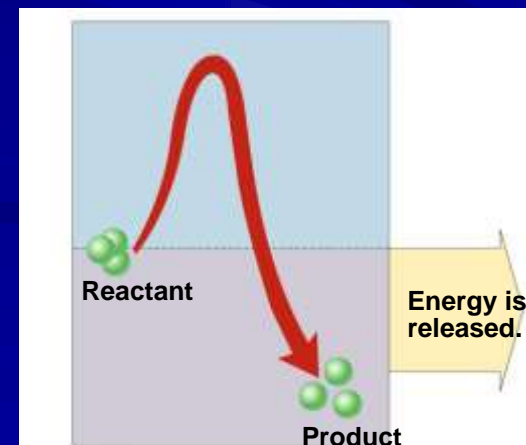
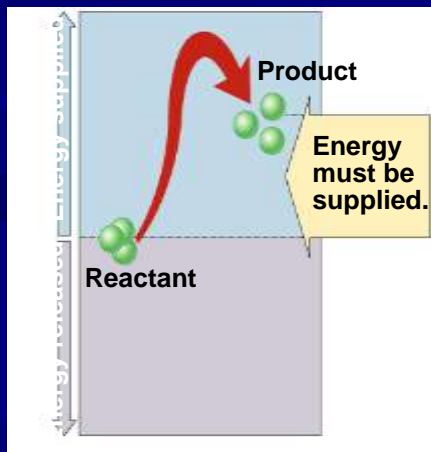
Summary

Lecture no.4

<i>Favorable Conditions</i>	<i>Unfavorable Conditions</i>
$\Delta H^{\circ} < 0$	$\Delta H^{\circ} > 0$
$\Delta S^{\circ} > 0$	$\Delta S^{\circ} < 0$
$\rightarrow \Delta G^{\circ} < 0$ SPONTANEOUS	$\rightarrow \Delta G^{\circ} > 0$ NON-SPONTANEOUS

EQUILIBRIUM: $G = 0$

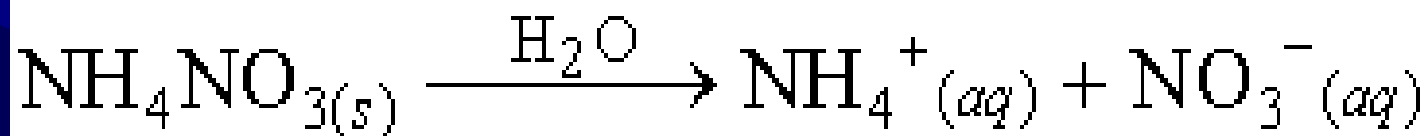
- Reactions are classified as either **exothermic** ($H < 0$) absorbs heat **or** **endothermic** ($H > 0$) releases heat on the basis of whether they give off or absorb heat.
- Reactions can also be classified as **exergenic** ($G < 0$) **or** **endergenic** ($G > 0$)



- If a reaction is favorable for both enthalpy ($H < 0$) and entropy ($S > 0$), then the reaction will be **SPONTANEOUS** ($G < 0$) at any temperature.
- If a reaction is unfavorable for both enthalpy ($H > 0$) and entropy ($S < 0$), then the reaction will be **NONSPONTANEOUS** ($G > 0$) at any temperature.
- If a reaction is favorable for only one of either entropy or enthalpy, the standard-state free energy equation must be used to determine whether the reaction is spontaneous or not:

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

Example of free energy calculation



Calculate H, S, and G for the above reaction to determine whether the reaction is spontaneous or not.

* See the tutorial sheet

Temperature and Free Energy

- If a reaction is favorable for enthalpy ($H < 0$), but unfavorable for entropy ($S < 0$), then the reaction becomes **LESS SPONTANEOUS** as temperature increases ($T \uparrow$).
 - **WHY?** - The standard-state free energy equation states that:
- If entropy is unfavorable, the S is negative. Subtracting a negative number is the same as adding the respective positive number. As the temperature increases, the TS factor (which is **ADDED** to the enthalpy if the entropy is unfavorable) increases as well. Eventually, the TS factor becomes larger than H and G becomes positive, i.e. the reaction is no longer spontaneous.

Free energy and Equilibrium Constants

- The following equation relates the standard-state free energy of reaction with the free energy of reaction at any moment in time during a reaction (not necessarily at standard-state conditions):

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

G = free energy at any moment

G = standard-state free energy

R = ideal gas constant = 8.314 J/mol-K

T = temperature (Kelvin)

lnQ = natural log of the **reaction quotient**

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

- **Note:** When $Q = K$, a reaction is at equilibrium.
- It was stated earlier that when $\Delta G = 0$, a reaction is at equilibrium. Let's consider the above reaction at equilibrium:

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

- If we move $RT \ln K$ to the opposite side by subtracting it from both sides, we get the following reaction which relates the free energy of a reaction to the equilibrium constant of a reaction:

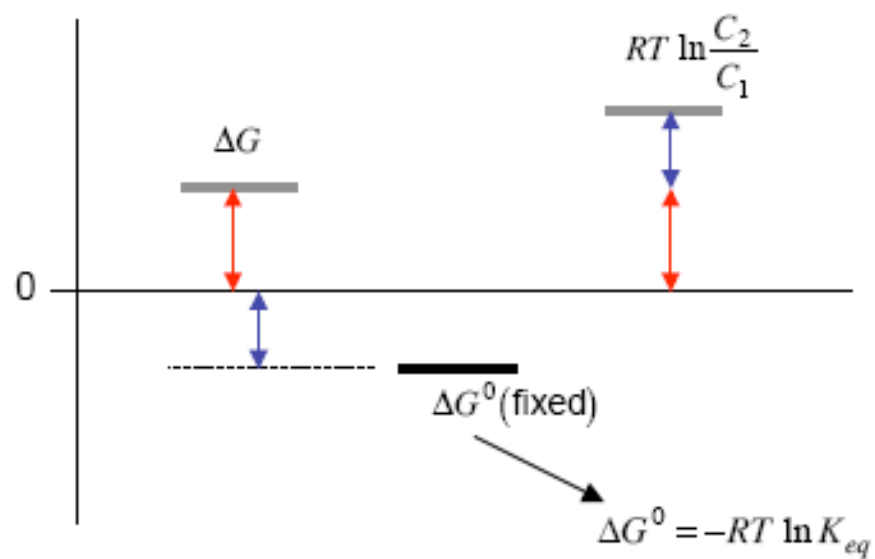
$$\Delta G^\circ = - RT \ln K$$

- Standard conditions are nothing like real biological conditions and ΔG° values (which are easy to determine) will not necessarily be the same as ΔG in the cell ..
- The actual cellular ΔG is related to ΔG° by:

$$\Delta G = \Delta G^{\circ} + RT \ln [\text{products}]/[\text{reactants}]$$

- The big problem is measuring the ever changing concentration of products and reactants in cells.

The general equation for ΔG at any point of the reaction



Free energy changes and the coupled reactions

- Example: the phosphorylation of glucose to glucose 6-phosphate:
Glucose + phosphate \longrightarrow G-6-phosphate
 $\Delta G^{\circ} = +3.3 \text{ kcal/mol}$ (unfavorable)

- Consider the hydrolysis of ATP:
ATP \longrightarrow ADP + Pi
 $\Delta G^{\circ} = -7.3 \text{ kcal/mol}$ (favorable)

Summing these reactions together:



$$\Delta G^{\circ} = +3.3 + (-7.3) = -4 \text{ kcal/mol (still favorable)}$$

(b) Chemical example