

# Biophysical chemistry

*Part A*

*Chapter: 2*

*Chemical Equilibrium*

*Lecture - 3*

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# Relationship between $\Delta G$ and $K_{eq}$ ,

Relationship between  $\Delta G$  and the reaction quotient  $Q$ :

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

where  $\Delta G^\circ$  indicates that all reactants and products are in their standard states. For a system at equilibrium ( $K=Q$ ),  $\Delta G = 0$  for a system at equilibrium. Therefore, we can describe the relationship between  $\Delta G^\circ$  and  $K$  as follows:

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

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

$$\Delta G^\circ = -2.303 RT \log K$$

The sign of  $\Delta G^\circ$  indicates whether the forward or reverse reaction is spontaneous.

we can have three possibilities depending on the sign of  $\Delta G^\circ$  for the reaction.

(1) If  $\Delta G^\circ$  is negative,  $\log K$  must be positive, products are favored over reactants at equilibrium..

(2) If  $\Delta G^\circ$  is positive,  $\log K$  must be negative and  $K$  is less than one and reactants are favored over products at equilibrium.

(3) If  $\Delta G^\circ = 0$ ,  $\log K = 0$  and  $K = 1$ . neither reactants nor products are favored at equilibrium.

# Relationship between $\Delta G$ and $K_{eq}$ ,

**SOLVED PROBLEM 1.** Calculate  $K$  for reaction which has  $\Delta G^\circ$  value  $-20$  kcal at  $25^\circ\text{C}$ .

We know that

$$\Delta G^\circ = -2.303 RT \log K$$

If  $\Delta G^\circ$  is given in calories

$$R = 1.99$$

$$T = 25 + 273 = 298 \text{ K}$$

The value of  $K$  from expression (a) may be calculated as

$$\begin{aligned} -\log K &= \frac{-\Delta G^\circ}{(2.303)(1.99)(298)} \\ &= \frac{(20,000)}{1365.75} = 14.7 \end{aligned}$$

Taking antilogs,

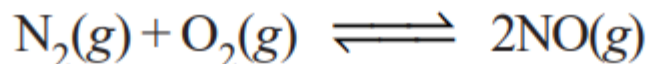
$$\log K = 0.7 + 14.0$$

Thus

$$K = 5 \times 10^{14}$$

# Relationship between $\Delta G$ and $K_{eq}$ ,

**SOLVED PROBLEM 2.** The standard free energy change for the reaction



is +173.1 kJ. Calculate  $K_p$  for the reaction at 25°C.

**SOLUTION**

## **SOLUTION**

Here, we will use the expression

$$\Delta G^\circ = -2.303 RT \log K_p$$

or

$$\log K_p = -\frac{\Delta G^\circ}{2.303 RT}$$

Substituting the values

$$\begin{aligned}\log K_p &= \frac{1.73 \times 10^5}{(2.303)(8.314)(298)} \\ &= -30.34\end{aligned}$$

Taking antilogs

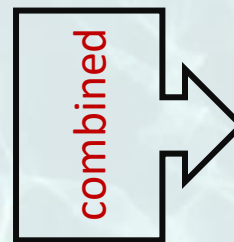
$$\begin{aligned}K_p &= 10^{0.66} \times 10^{-31} \\ &= \mathbf{4.6 \times 10^{-31}}\end{aligned}$$

## Relationship between $\Delta G$ and $K_{eq}$ ,

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

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

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



$$\Delta G = RT \ln \frac{Q}{K}$$

If a system is not at equilibrium,  $\Delta G$  and  $Q$  can be used to tell us in which direction the reaction must proceed to reach equilibrium

- If  $\Delta G < 0$ , then  $K > Q$ , and the reaction must proceed to the right to reach equilibrium.
- If  $\Delta G > 0$ , then  $K < Q$ , and the reaction must proceed to the left to reach equilibrium.
- If  $\Delta G = 0$ , then  $K = Q$ , and the reaction is at equilibrium.



# Applications of Chemical equilibrium in living systems

## Life at high altitudes and Hemoglobin production

In the human body, countless chemical equilibria must be maintained to ensure physiological well-being.

Flying from San Francisco, which is at sea level, to Mexico City, where the elevation is 2.3 km (1.4 mi), or scaling a 3-km mountain in two days can cause headache, nausea, extreme fatigue, and other discomforts. These conditions are all symptoms of hypoxia, a deficiency in the amount of oxygen reaching body tissues. In serious cases, the victim may slip into a coma and die if not treated quickly

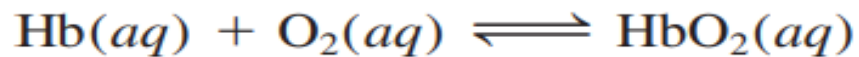


And yet a person living at a high altitude for weeks or months gradually recovers from altitude sickness and adjusts to the low oxygen content in the atmosphere, so that he or she can function normally.

# Applications of Chemical equilibrium in living systems

## Life at high altitudes and Hemoglobin production

The combination of oxygen with the hemoglobin (Hb) molecule, which carries oxygen through the blood, is a complex reaction, but for our purposes it can be represented by a simplified equation:



$$K_c = \frac{[\text{HbO}_2]}{[\text{Hb}][\text{O}_2]}$$

At an altitude of 3 km the partial pressure of oxygen is only about 0.14 atm, compared with 0.2 atm at sea level.

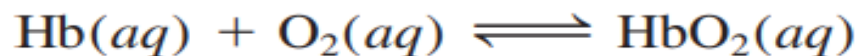
According to Le Châtelier's principle, a decrease in oxygen concentration will shift the equilibrium shown in the equation above from right to left.

This change depletes the supply of oxyhemoglobin, causing hypoxia

# Applications of Chemical equilibrium in living systems

## Life at high altitudes and Hemoglobin production

Given enough time, the body copes with this problem by producing more hemoglobin molecules.



The equilibrium will then gradually shift back toward the formation of oxyhemoglobin.

It takes two to three weeks for the increase in hemoglobin production to meet the body's basic needs adequately. A return to full capacity may require several years to occur.

Studies show that long-time residents of high-altitude areas have high hemoglobin levels in their blood—sometimes as much as 50 percent more than individuals living at sea level!