

# BIOL 157: BIOLOGICAL CHEMISTRY

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## Lecture 7 CHEMICAL EQUILIBRIUM

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# Lecture objectives

- Examples of chemical systems in equilibrium
- Law of mass action
- Equilibrium constant, reaction quotient
- Heterogeneous and homogenous equilibria
- Properties of a system in equilibrium
- Le Chatelier's principle and factors affecting equilibrium
- Some examples of industrial processes in chemical equilibrium

# Reversible reactions and chemical equilibrium

- Hydrochloric acid is a strong acid.
- In aqueous solution, it completely dissociates as follows:  
$$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-.$$
- There is almost complete dissociation of HCl in water, so the dissociation is essentially irreversible.
- The neutralization reaction between equimolar amounts of NaOH and HCl is another example of an irreversible reaction:  
$$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}.$$
- At the end of the reaction, only the products, H<sub>2</sub>O and NaCl would be present.

- There will be no reactants present. in the same way, upon the dissociation of HCl in water, there will be no undissociated HCl molecule present.
- The situation in reversible reactions is quite different.
- Ethanoic acid, a weak organic acid dissociates in water to a slight extent.
- The dissociation is shown as
$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+.$$
- The reaction between ethanoic acid and ethanol is an esterification reaction.
- This is another reversible reaction which is represented by the following equation:
$$\text{Ethanol} + \text{Ethanoic acid} \rightarrow \text{ester} + \text{water}$$

- At the initial stages, only ethanol and ethanoic acid are present: there will be no products but with time, an ester and water begin to form in the reaction mixture.
- As the products continue to form in the forward direction, some of the products can also combine in the backward direction to give back the reactants.
- At some point, the rate of backward reaction becomes equal to the rate of forward reaction.
- At this stage, an equilibrium is said to have been attained.
- When equilibrium is reached, there will be no observable change in the concentrations of the reactants and products.

- Knowing the concentrations of reactants and products at equilibrium, we can calculate an equilibrium constant ( $K_c$ ) as follows for the ethanol- ethanoic acid system:

$$k_c = \frac{[Ester][Water]}{[Ethanol][Acid]}$$

- Generally, for a chemical reaction in an equilibrium like  $aA + bB \rightleftharpoons cC + dD$ , the equilibrium constant at a fixed temperature is

$$k_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- where a, b, are the coefficients of the reactants in the balanced equation, while c and d are the coefficients of the products.
- The equation is the mathematical form of the law of mass action first proposed by Cato Goldberg and Peter Waage.
- This law relates the equilibrium constant to the concentration of reactants and products at equilibrium.

# *Reaction quotient (Q)*

- The reaction quotient refers to any ratio of concentration of products to reactants as a reversible reaction progresses.
- So several reaction quotients can be calculated.
- It is only when equilibrium is attained that the reaction quotient becomes equivalent to the equilibrium constant.
  - When  $Q < k$ , net forward reaction will take place: reaction will go to the right
  - $Q = k$ , no net change takes place as the system is in equilibrium
  - $Q > k$ , net backward or reverse reaction will take place: reaction goes to the left

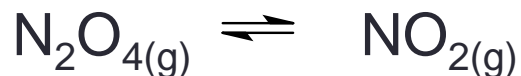
## ***Magnitude of equilibrium constant and its implications***

- The equilibrium constant gives an idea about the extent of the reaction or the position equilibrium.
- When  $k > 1$ , it means that the equilibrium mixture contains more of the products than reactants;
  - so the equilibrium position is shifted towards the right.
- On the other hand, when  $k < 1$ , the equilibrium mixture will contain more of the reactants than products;
  - i.e. the equilibrium position is shifted towards the left.
- Also, when  $k = 1$  then concentration of reactants and products at equilibrium are comparable.



## *Different ways of expressing equilibrium constants*

- Homogenous equilibrium occurs if all the reactants and products in the equilibrium occur in the same phase.
- An example of homogenous equilibrium is the dissociation of  $\text{N}_2\text{O}_{4(\text{g})}$  to  $\text{NO}_{2(\text{g})}$  ; the two occur in the gaseous state.



- $k_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
- $k_c$  means that in this form of expressing the equilibrium constant, the concentrations of the reactant and products are given in units of moles per litre.
- Where gases are involved, the equilibrium constant can be expressed in terms of partial pressure.

- For the  $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$  equilibrium, the equilibrium constant can also be expressed in terms of partial pressure ( $k_p$ ).
- $$k_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$
- where  $P_{\text{NO}_2}$  and  $P_{\text{N}_2\text{O}_4}$  are the equilibrium partial pressure of the two gases.
- The numerical values of the  $k_c$  and  $k_p$  will generally, be different, so we should make sure to indicate the one which is being used.
- Using the ideal gas equation there can be interconversions between  $k_p$  and  $k_c$ .

$$PV = nRT$$

$$P = \frac{n}{V}RT$$

- Since  $n/V$  refers to the moles per litre or concentration, which can be represented by  $M$ ;

$$P = MRT$$

- A general expression relating  $k_p$  to  $k_c$  can be shown as

$$k_p = k_c(RT)^{\Delta n}$$

- where  $\Delta n$  is the change in the number of moles of gas as the reactants form products.
- $\Delta n$  is the difference between the number of moles of products and number of moles of reactants (moles of product moles reactants).

# *Heterogenous equilibria*

- These are reversible reactions which involve reactants and products in different phases.
- An example is the decomposition of  $\text{CaCO}_3$  (limestone) at  $800^\circ\text{C}$  in a closed vessel,



- Being solids, the concentration of  $\text{CaCO}_3$  and  $\text{CaO}$  do not change as the reaction proceeds.
- The molar concentration of pure solid or liquid is constant at a given temperature.

- The equilibrium constant for the decomposition of  $\text{CaCO}_3$  can be written as

$$k_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

- But the concentrations of  $\text{CaCO}_3$  and  $\text{CaO}$  remain constant.

$$k_c = [\text{CO}_2]$$

- Since  $\text{CO}_2$  is a gas the last equation can be rewritten as

$$k_p = p\text{CO}_2$$

## Problem

The  $K_p$  for the reaction  $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$  is 1.1 at 150 °C. If the equilibrium partial pressure of  $\text{PCl}_5$  and  $\text{PCl}_3$  are 0.8 and 0.4 atmospheres respectively, what is the equilibrium partial pressure of chlorine?

## Problem

The equilibrium between CO and water vapour is shown as,

$$\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_{2(g)}$$

If 1 mole of CO and 0.8 mole of water are placed in a one litre flask and allowed to establish an equilibrium at a certain temperature, the concentration of  $\text{H}_2$  gas was found to be 0.4 mole per litre. Calculate the equilibrium constant for the reaction.

# *Properties of a system in equilibrium*

- Equilibrium is attained by reversible processes
- Equilibrium occurs in a closed system
- An equilibrium is a dynamic state in which the rate of forward reaction is equal to the rate of reverse reaction. Even though there is no observable change in the net reaction, at the molecular level there is the continuous interconversion between reactants and products.
- At equilibrium, the free energy change of the system is zero. This suggests that a system in equilibrium cannot do work.

- Arising from the fact that  $\Delta G = 0$  at equilibrium, then using the relation  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta H = T\Delta S$ . Thus, while entropy is maximized at equilibrium, enthalpy is lowered. At a specified temperature, there should be a balance between entropy and enthalpy.
- Equilibrium can be attained from either direction. Taking the  $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$  equilibrium as an example, we could start with either  $\text{N}_2\text{O}_4$  or  $\text{NO}_2$ , but the same equilibrium would be attained at a fixed temperature.
- From the law of mass action, an equilibrium constant can be calculated for all chemical systems in equilibrium.
  - The equilibrium constant does not depend on the initial concentration of reactants, but it varies with temperature.
  - Every reaction has got its characteristic constant at a fixed temperature.



# Factors affecting systems in equilibrium: the use of Le Chatelier's principle

- The following factors influence a chemical equilibrium:
  - Concentration
  - Temperature
  - Pressure (for gases)
  - Volume (gases)
  - Catalyst
- The Le Chatelier's principle enables us predict the direction the equilibrium will shift when there is a change in variables like concentration, pressure/volume and temperature.
- The principle states that if a stress is put on a system in equilibrium, the system is adjusted in such a way as to get rid of the imposed stress.
- A stress in this context refers to changes in the stated variables.

# Changes in concentration

- Changes in concentration of either reactant or product do not change the value of the equilibrium constant, provided temperature is constant.
- However, changes in concentration can affect the composition of the equilibrium mixture.
- $\text{FeSCN}^{2+}_{(\text{aq})} \rightleftharpoons \text{Fe}^{3+}_{(\text{aq})} + \text{SCN}^{-}$   
Red                                      brown    colourless
- Iron (III) thiocyanate  $[\text{Fe}(\text{SCN})_3]$  dissolves in water, forming a red solution due to the presence of  $\text{FeSCN}^{2+}$  ion.
- The equilibrium established between  $\text{FeSCN}^{2+}$  and its dissociated ions in solution has been shown in the equation above.

- Take the case when sodium thiocyanate ( $\text{NaSCN}$ ) solution is added to the system.
- The stress will be the increased concentration of  $\text{SCN}^-$ .
- To offset or get rid of this stress,  $\text{Fe}^{3+}$  reacts with the added  $\text{SCN}^-$  in the reverse reaction to form  $\text{FeSCN}^{2+}$  leading to the deepening of the red colour.
- Thus in the face of the stress the equilibrium is shifted towards the left.
- If  $\text{Fe}_2(\text{SO}_4)_3$  solution is added, there will again be the deepening of the red colour.

- The stress introduced will be increased concentration of  $\text{Fe}^{3+}$  from the dissociation of Iron (III) sulphate (VI).
- To overcome the stress the added  $\text{Fe}^{3+}$  combines with  $\text{SCN}^-$  in the reverse reaction to form  $\text{FeSCN}^{2+}$ , so the equilibrium once again shifts towards the left.
- Despite these changes in concentration, once equilibrium is re-established, the equilibrium constant will be the same.
- If  $\text{Fe}^{3+}$  concentration is reduced, the equilibrium would be shifted towards the right, so the red colour will turn brownish.
- The addition of oxalate can serve to reduce the concentration of  $\text{Fe}^{3+}$  since this anion is able to bind  $\text{Fe}^{3+}$  strongly.

# *Pressure/volume changes*

- For gaseous systems, pressure and volume are inversely related:

$$pV = nRT \text{ or } p = n/v RT$$

- The greater the pressure, the smaller the volume.
- However, pressure changes do not affect solids and liquids. Pressure can be changed by the addition of a gaseous reactant or product to the equilibrium mixture or by the removal of a gaseous reactant or product.
- The pressure can also be changed by pressing a piston or pulling up a piston to change the volume.
- For gaseous reactions, pressure/volume changes affect reactions in which the moles of gaseous reactants and products of the equilibrium are not the same.

- Consider the following two equilibria;



- In the first equilibrium, there is increase in the number of moles as two moles of gas are formed from one mole of gas.
- But in the second example, there is reduction in the number of moles of gas as four moles of gaseous reactants are converted to two moles of products.
- Increasing pressure (by decreasing volume) shifts the equilibrium towards the side that has the smaller number of moles of gas.
- So in the  $\text{N}_2\text{O}_4 - \text{NO}_2$  equilibrium, increasing pressure favours the backward reaction.
- In the Haber process for the synthesis of  $\text{NH}_3$ , a high pressure of about 250 atmospheres is used.

- This is in line with the Le Chatelier's principle.
- With increased pressure, the reaction which is favoured is the direction with decreased number of moles which in this case is the forward reaction.
- A decrease in pressure (decrease in volume) will favour the reaction in which there is an increased number of gaseous molecules.
- Another point worth considering is that it is possible to change the pressure of a system without changing its volume.
- Assuming the  $\text{NO}_2$  -  $\text{N}_2\text{O}_4$  system is confined to a vessel of constant volume, it is possible to increase the total pressure in the vessel by introducing an inert gas like helium.

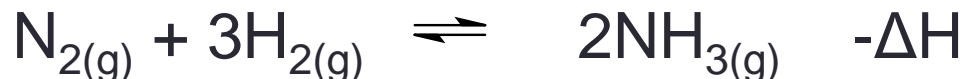
- This will increase the total gas pressure, but the mole fraction of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  will be decreased.
- However, the partial pressure of each gas (product of mole fraction and total pressure) does not change.
- Therefore, the presence of the inert gas does not affect the equilibrium.



# Changes in temperature

- A change in concentration, pressure or volume may alter the equilibrium position, but it does not change the value of the equilibrium constant.
- But a change in temperature can alter the equilibrium constant.  
Recall the reaction  $\text{N}_2\text{O}_{4(\text{g})} \rightleftharpoons 2\text{NO}_{2(\text{g})} + \Delta\text{H}$
- The positive enthalpy value for the reaction means that the forward reaction is endothermic.
- For such a reaction, when temperature is increased, the way the stress of increased temperature would be overcome is for the reaction which leads to the absorption of heat to be favoured.
- Therefore, increased temperature favours the dissociation of  $\text{N}_2\text{O}_4$  in the forward direction.

- The formation of ammonia from nitrogen and hydrogen gases is an exothermic process;



- If temperature is increased here too the direction of reaction in which heat is absorbed is favoured.
- Therefore, the increased temperature will shift the equilibrium towards the left, which is the decomposition of  $\text{NH}_3$ .
- Due to the shift more  $\text{N}_2$  and  $\text{H}_2$  will be formed, but less  $\text{NH}_3$ .
- So a new equilibrium would be established, with a new equilibrium constant at the higher temperature.

# *Presence of Catalyst*

- A catalyst increases the rate of attainment of the equilibrium, but the equilibrium position or the equilibrium constant remains unchanged.
- Adding a catalyst to a reaction mixture not equilibrium will speed up both the forward and reverse rates to achieve equilibrium mixture faster.
- Without the catalyst, the same equilibrium mixture will be obtained, but a longer time would be required.

# Steady state

- Living organisms are open systems in which there can be exchange of materials and energy with the surrounding.
- If there is the constancy of the concentration of some material in a living system, it does not mean the constancy in the levels of that material is due to the attainment of equilibrium.
- We have been made aware that equilibrium is characteristic of a close system.
- Since living organisms are open, they are said to be in a steady state in which the rate of transfer of matter and energy from the surrounding into the system is exactly balanced by the rate of transfer of matter and energy out of the system.

- A system in a steady state is capable of doing work because it is away from equilibrium, and the free energy change should be negative.
- In a system in a steady state, entropy production is minimum, but in a system in equilibrium, entropy is maximized.
- Systems in a steady state are also subject to regulation.

# Examples of systems in a steady state

- The level of glucose in the blood is in a steady state, either in the fed or fasting state..
- The level of  $^{14}\text{C}$  in the atmosphere in the form of  $^{14}\text{CO}_2$  is in a steady state
  - the rate at which  $^{14}\text{C}$  is formed (through neutron capture by  $^{14}\text{N}$ ) is equal to of disintegration of  $^{14}\text{C}$  (through  $\beta$ -emission).
- Oxygen concentration in the atmosphere is also almost constant because the rate of formation of oxygen by plants through photosynthesis is equal to the rate of utilization of oxygen by organisms.
- For a complex reaction made up of several steps, it could involve the formation of an intermediate in one step, followed by the use of that intermediate in the next step.



- This equation shows the reaction between an enzyme and its substrate to form an intermediate ES complex which can break down to form either product or substrate.

## Problem

Show that for the reaction,



# Reaction kinetics and equilibria in industrial processes

- Chemists are interested in converting reactants to products as quickly as possible, and as completely as possible.
- They are interested in how fast a product is made, and the yield.
- The first concern is that of kinetics, and the second is of equilibrium.
- The conditions for a reaction, such as temperature, concentration and pressure should be such that the optimum proportion of products will be in the equilibrium mixture.
- Then, the rate of attainment of the equilibrium should be fast.



- The choice of the conditions to achieve these ends should be based on the type of industrial process.

- In the contact process for the manufacture of  $\text{H}_2\text{SO}_4$ , the equilibrium for an important step is



- The reaction is exothermic and involves the formation of two moles of gaseous products from three moles of gaseous reactants.
- In accordance with the Le Chatelier's principle, the following two conditions will favour the reaction;
  - low temperature
  - increased pressure
- A very high yield of  $\text{SO}_3$  could be obtained at low temperature, but at such low temperatures, the reaction rate would be very slow.

- So there is a conflict between kinetic and equilibrium considerations in the choice of temperature.
- A compromise temperature of around 450 °C is used, together with the use of a suitable catalyst.
- Even though a high pressure can ensure a higher yield, there is a limit to the pressure that can be used.
- The higher the pressure to be used, the greater the capital cost of the industrial plant.
- The cost of maintenance of such a plant will also be high.