Chemical Equilibrium

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Irreversible reactions

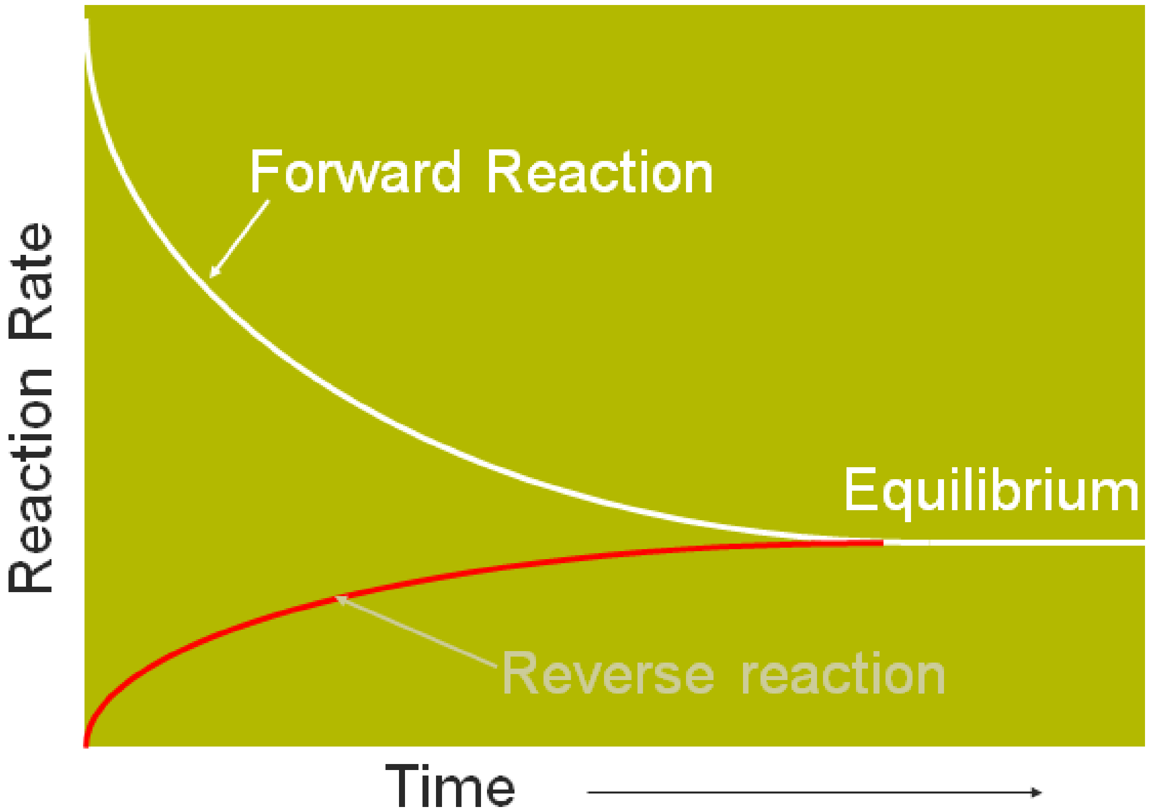
- A chemical process in which all the reactants change into a product. By mixing the products the reactants cannot be obtained.
- All irreversible reactions go to almost100 % completion.

Reversible Reactions

- A reaction in which not only the reactants react to form the products under certain conditions but the products also react to form reactants under the same conditions. Or
- A reaction which takes place in the forward reaction and the backward reaction at the same time.
- Reversible reactions are represented like this

$$\rightleftharpoons$$

Graphical representation



Equilibrium

- Represents a state of a process in which the properties like temperature, pressure, concentration, of the system do not show any change with the passage of time.

Physical Equilibrium

- Physical equilibrium: If the opposing processes involved only change of state it is called a physical equilibrium

Chemical Equilibrium

- If the opposing processes involve chemical changes or chemical reactions the equilibrium is said to be a chemical equilibrium

Conditions to attain equilibrium

- Only closed systems attain equilibrium (mostly for reactions involving gases)
- For every equilibrium there is some observable property that attains constancy e.g the color of the reaction mixture would remain constant, the pressure remains constant, concentration of reactants would remain constant etc.

Contd…

- Equilibrium is dynamic in nature – even though there is constancy in the measurable property there is change happening all the time.
- At equilibrium there exists an expression involving the concentration if the substances which remains constant for the given temperature.
- The magnitude of the equilibrium constant (obtained from the equilibrium expression) represents the extent of the reaction

Law of mass action

- The rate of a reaction is proportional to the products of the concentrations of the reactants, each raised to the power equal to its coefficient as represented by a balanced chemical equation

Equilibrium constant K_c

- The product of the molar concentrations of the products, each raised to the power equal to its coefficient divided by the product of the molar concentrations of the reactants, each raised to the power equal to its coefficient is constant at constant temperature and is called Equilibrium constant

Equilibrium constant

- For the reaction jA + kB $\rightleftharpoons$ lC + mD

  - For any reaction
  - $jA + kB \rightleftharpoons lC + mD$
  - $K = \dfrac{[C]^l[D]^m}{[A]^j[B]^k}$ $\dfrac{\text{PRODUCTS}^{\text{power}}}{\text{REACTANTS}^{\text{power}}}$
  - K is called the equilibrium constant.
  - $\rightleftharpoons$ is how we indicate a reversible reaction

Units of k

- Are determined by the various powers and units of concentrations.
- They depend on the reaction.
- The unit does not matter only the magnitude matters

Kc is CONSTANT

- For a given temperature. (Changes with temperature)
- Temperature affects rate.
- The equilibrium concentrations don't have to be the same only K.
- Equilibrium position is a set of concentrations at equilibrium.
- There are an unlimited number.

Q_c Concentration Quotient

- Can be used to predict the direction of a reversible reaction.
- If the system has not attained equilibrium and we use the equilibrium concentration expression to calculate the ratio of concentrations then we call the value obtained as Qc or Concentration quotient

Qc and extend of reaction

- If Qc = Kc the system is in equilibrium
- If Qc > Kc Reaction will proceed in the backward direction to make Qc small Less reactants
- If Qc < Kc Reaction will proceed in the forward reaction so as to increase the value of Qc by increasing the numerator (products) Less products
- If Kc is very large reaction goes to almost to completion
- If Kc<1 We have more reactants than products
- If Kc > 1 We have more products than reactants

What does ‘Kc’ tell you

- The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium is attained.

Kc contd….

- If the reaction is reversed the value of the equilibrium constant is inversed (write eqn)
- If equilibrium constant for the forward reaction is Kc = 40
- The equilibrium for the backward reaction is
- $K'_c = 1/40 = 2.5$

Kc contd.......

- If the equation (having equilibrium constant K) is divided by 2, the equilibrium constant for the new equation is the square root of K
- $N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad = Kc$
- $\frac{1}{2} N_2 + 3/2 H_2 \rightleftharpoons NH_3 \quad = \sqrt{Kc}$

Kc contd……..

- If the equation having equilibrium constant Kc is multiplies by 2, the equilibrium constant for he new equation is the square of K (K^2)

Kc contin.......

- If the equation having the equilibrium constant Kc is written in two steps having equilibrium constant K_1 and K_2 then the equilibrium constant for the reaction will be $Kc = K_1 \times K_2$
- Kc is not affected by a catalyst in a chemical reaction

Kc contin……. Value of Kc

- If the value of Kc = 1
- Half the reactants have changed into products
- 50 % of the reaction is complete

Kc contin……. Value of Kc

- $Kc = 1 \times 10^{-10}$
- Since the value of K is very small the reaction is essentially incomplete.

Kc contin……. Value of Kc

- Kc = 1 x 10^{10}
- Since the value of K is very large the reaction has gone almost to completion

Factors affecting equilibrium

- Change in concentration of reactants or products
- Change of temperature of the system
- Change of pressure of the system
- Addition of catalyst
- Addition of some inert gas

Le Chatelier's Principle

- If a stress is applied to a system at equilibrium, the position of the equilibrium will shift to reduce the stress.
- 3 Types of stress

Change amounts of reactants and/or products

- Adding product makes Q>K ←
- Removing reactant makes Q>K ←
- Adding reactant makes Q<K →
- Removing product makes Q<K →
- Determine the effect on Q, will tell you the direction of shift

Change Pressure

- By changing volume
- System will move in the direction that has the least moles of gas.
- Because partial pressures (and concentrations) change a new equilibrium must be reached.
- System tries to minimize the moles of gas.

Change in Pressure

- By adding an inert gas
- Partial pressures of reactants and product are not changed
- No effect on equilibrium position

Change in Temperature

- Affects the rates of both the forward and reverse reactions.
- Doesn't just change the equilibrium position, changes the equilibrium constant.
- The direction of the shift depends on whether it is exo- or endothermic

Exothermic

- $\Delta H < 0$
- Releases heat
- Think of heat as a product
- Raising temperature push toward reactants.
- Shifts to left.

Endothermic

- $\Delta H > 0$
- Absorbs heat
- Think of heat as a reactant
- Raising temperature push toward products.
- Shifts to right.

Addition of inert gases

- If the reaction takes place at constant volume (closed vessel) this will not change the molar concentration of the reactants and products ($C = n/V$) hence the state of equilibrium will remain unaffected

Addition of inert gases

- If the reaction takes place at constant pressure (there will be change in volume) thus there will be change in concentration this will alter the state of equilibrium and there will be change in concentration of reactants or products to attain a new equilibrium

$$N_2 + 3H_2 \rightleftharpoons 2NH_3, \Delta H = -92.5 \text{ kJ}$$

- Effect of temperature
- Effect of pressure
- Effect of concentration

$N_2 + O_2 \rightleftharpoons 2NO$, $\Delta H = +180.7$ kJ

- Effect of temperature
- Effect of pressure
- Effect of concentration