Analogies to illustrate dynamic equilibrium

A bucket having a hole at the bottom and the bucket is filled with the same rate as the rate with which water is coming out. Hence, the level of water remains same.

Characteristics of chemical equilibrium

At a given temperature, the measurable properties like pressure, concentration, density or colour remain constant in chemical equilibrium.
Chemical equilibrium can be attained from either side (forward and backward reactions).
It can be attained in less time in the presence of a catalyst. A catalyst cannot affect chemical equilibrium as it only affects the rate of both the reactions, forward and backward, to the same extent.
It is dynamic in nature.

Active mass

Active mass is defined as the molar concentration i.e. number of gram-moles per litre. Active mass of pure solid/liquid is always 1. Molar concentration is directly proportional to density.

Equilibrium constant

The equilibrium constant of a chemical reaction is the value of the reaction quotient when the reaction has reached equilibrium. An equilibrium constant value is independent of the analytical concentrations of the reactant and product species in a mixture, but depends on temperature and on ionic strength.
The product of the molar concentration of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentrations of the reactants raised to the power of its stoichiometric coefficient at constant temperature is known as equilibrium constant.

Characteristics of equilibrium constant

1. The equilibrium constant has a definite value for every reaction at a particular temperature.
2. The value of equilibrium constant is independent of the original concentration of reactants.
3. The value of equilibrium constant tells the extent to which a reaction proceeds in the forward or reverse direction. If the value of K is larger, then the equilibrium concentration of the components on the right hand side of the reaction will be greater than the components on the left hand side of the reaction. Hence, the reaction proceeds to a greater extent and vice versa.
4. The equilibrium constant is independent of the presence of catalyst. This is because the catalyst affects the rate of forward reaction and backward reactions equally.

Use of equilibrium constant for predicting the extent of reaction, direction

Large value of the equilibrium constant shows that forward reaction is favoured. Intermediate value of K shows that the concentration of the reactants and products are comparable. Low value of K shows that the backward reaction is favoured.
If Q=K then the reaction is in equilibrium.
If Q>K, the reaction will proceed in the backward direction.
If Q<K, the reaction will proceed in the forward direction.
Q is the concentration quotient or reaction quotient.

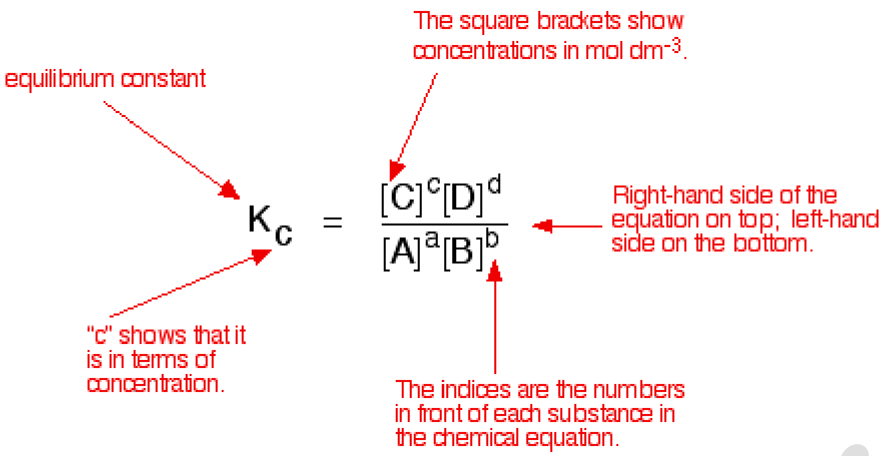
Calculation of degree of dissociation at equilibrium

$$K_a = \frac{\alpha^2 C}{(1-\alpha)}; \; pK_a = -\log K_a$$

Factors affecting degree of dissociation

(i) At normal dilution, value of it is nearly 1 for strong electrolytes, while it is very less than 1 for weak electrolytes.
(ii) Higher the dielectric constant of a solvent more is its ionising power. Water is the most powerful ionising solvent as its dielectric constant is highest.
(iii) Dilution of solution Amount of solvent
(iv) Degree of ionisation of an electrolyte in solution increases with rise in temperature.
(v) Presence of common ion: The degree of ionisation of an electrolyte decreases in the presence of a strong electrolyte having a common ion.

Concentration of reactants and products at equilibrium



Factors affecting equilibrium

The factors that can influence equilibrium are change in concentration, change in pressure (or volume), and change in temperature. First, the reaction must be at equilibrium.

Le Chatelier's principle

LE CHATELIER'S PRINCIPLE		
STRESS	**SHIFT**	**WHY?**
increase concentration of a substance	*away* from substance	extra concentration needs to be used up
decrease concentration of a substance	*towards* substance	need to produce more of substance to make up for what was removed
increase pressure of system	towards *fewer* moles of gas	for gas: pressure increase = volume decrease
decrease pressure of system	towards *more* moles of gas	for gas: pressure decrease = volume increase
increase temperature of system	*away* from heat/ energy *exothermic* reaction is favored	extra heat/ energy must be used up
decrease temperature of system	*towards* heat/ energy *exothermic* reaction is favored	more heat/ energy needs to be produced to make up for the loss
add a catalyst	NO SHIFT	The rates of both the forward and reverse reactions are increased by the same amount.

Effect of a catalyst on a system in equilibrium

A catalyst speeds up the forward and back reaction to the same extent. Because adding a catalyst doesn't affect the relative rates of the two reactions, it can't affect the position of equilibrium.

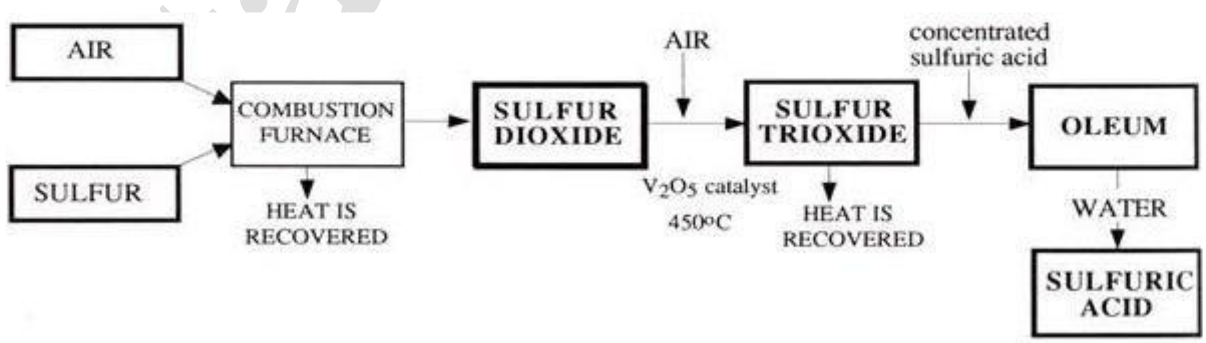
Applications of Le Chatelier's principle

Effect of temperature on solubility: Some solids absorb heat while some evolve heat on dissolution. Hence, according to this principle solubility of the former class of solids increases with rise of temperature.
Effect of pressure on solubility: Since on dissolution of gas volume decreases, hence on increasing pressure, solubility of gas increases. On the other hand, if volume of the solution increases on dissolution of solid then solubility of the solid decreases with rise of pressure.
Effect of temperature and pressure on melting of ice: Since ice melts with absorption of heat and decreases in volume, hence both temperature and pressure effect the melting of ice. Since the change of ice into water is an endothermic process hence, with rise of temperature ice melts into water. Since volume of ice is more than that of water so increase of pressure favour melting.

Habers Process

The Haber Process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia. The reaction is reversible and the production of ammonia is exothermic. The catalyst is actually slightly more complicated than pure iron.

Contect process



Equilibrium

Equilibrium represents the state of a process in which the properties like pressure, temperature etc do not show any change with time.

Physical equilibrium

Dynamic equilibrium when rates of forward and backward reactions are equal.
Example: In a saturated solution, a solute is added to a solvent and the system reaches a point at which the rate of dissolution is equal to the rate at which the dissolved solute crystallizes.

Chemical equilibrium

Chemical equilibrium is the state, in which both reactants and products are present in concentrations which have no further tendency to change with time. Usually, this state results when the forward reaction proceeds at the same rate as the reverse reaction. Chemical equilibrium occurs when reaction changes chemically such as in decomposition.

Solid-liquid equilibrium

If some ice cubes and some water is placed in a thermos flask so that no heat can leave the system, the mass of ice and water is found to remain constant. However, two opposing processes occurring are melting of ice and freezing of water.

Liquid-vapour equilibrium

Vapor-liquid equilibrium (VLE) is a condition in which a liquid and its vapour are in equilibrium with each other, a condition or state where the rate of evaporation equals the rate of condensation on a molecular level such that there is no net vapor liquid interconversion. A substance at vapor-liquid equilibrium is generally referred to as a saturated fluid. For a pure chemical substance, this implies that it is at its boiling point.

Solid-vapour equilibrium

This type of equilibrium is attained for solids which undergo sublimation.
e.g., Sublimation of iodine in closed vessel. In the vessel, rate of evaporation of iodine solid is

equal to the rate of condensation of iodine vapour.

Solid-solution equilibrium

Suppose more sugar is added to a fixed volume of water, after a certain period no more sugar is dissolved and the sugar starts depositing at the bottom of the vessel. The solution is said to be saturated solution. Many sugar molecules dissolve from the surface of the undissolved sugar goes into the solution, the same number of molecules of sugar are deposited back on the surface. Both the rates are equal.

General characteristic of equilibria involving physical processes

At equilibrium, some observable property of the system becomes constant
It is dynamic in nature
At equilibrium, the concentration of the different substances become constant at constant temperature
The magnitude of the equilibrium constant represents the extent to which the reaction proceeds before attaining the equilibrium