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## Chemical Equilibrium -2

## Lechtlier"S Principle \&Problems on $\mathbf{K}_{\mathbf{C}}$ \& $\mathbf{K}_{\mathbf{P}}$

## 1. Calculating Equilibrium Concentrations

In case of a problem in which we know initial concentrations but do not know any of the equilibrium concentrations, the following steps shall be followed:

Step 1: Write the balanced equation for the reaction.
Step 2: Under the balanced equation, make a table that lists for each substance involved in the reaction
(a) The initial concentration.
(b) The change in concentration on going to equilibrium, and
(c) The equilibrium concentration.

In constructing the table, define x as the concentration ( $\mathrm{mol} / \mathrm{L}$ ) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x .

Step 3: Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x . If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4: Calculate the equilibrium concentrations from the calculated value of $x$.
Step 5: Check your results by substituting them into the equilibrium equation.

## Factors Affecting the Equilibrium and Le chatelier's Principle

Le chatelier's principle is applicable for both physical as well as chemical equilibria.

The equilibrium depends on concentration, temperature and pressure.

## Le chatelier's principle

"If a chemical reaction at equilibrium is subjected to a change in temperature, pressure (or) concentration at the reactants or products that govern the chemical equilibrium position shifts in the direction in which this change is reduced (or) nullified".

## Effect of Concentration

Increase in concentration of reactants favours the shift of equilibrium towards products side (forward reaction is favoured).
Increase in the concentration of the products favours the shift of equilibrium towards the reactant side. (Backward reaction is favoured).
Let us take the reaction.

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftarrows 2 \mathrm{HI}(\mathrm{~g})
$$

If $\mathrm{H}_{2}$ is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction where in $\mathrm{H}_{2}$ is consumed, i.e., more of $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ react to form HI and finally the equilibrium shifts in right (forward) direction.

Decrease the concentration of the reactants in the reaction mixture favours the backward reaction. Removal of products from the system at the equilibrium will cause a shift in the equilibrium position of the reaction in the direction of formation of products (favours the forward direction)

## Effect of Pressure

Pressure has no effect on equilibrium when $\Delta n=0$ (i.e. $n_{p}=n_{r}$ ).
E.g. $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftarrows 2 \mathrm{HI}(\mathrm{g})$
i. Pressure has effect on equilibrium with different mole number ( $n_{p} \neq n_{r}$ ). When pressure increases, equilibrium shifts in a direction of decrease of volume or towards less number of moles or molecules.
E.g. $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftarrows 2 \mathrm{NH}_{3}(\mathrm{~g})$

For this increase of pressure favours the forward reaction as number of moles decreases.
ii. Decrease of external presure on the reaction at equilibrium favours the reaction in the direction in which the volume (or) number of moles or molecules increases.

$$
\mathrm{PCl}_{5(\mathrm{~g})} \rightleftarrows \mathrm{PCl}_{3(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})}
$$

For this decrease of pressure favours the forward reaction as number of moles increases.
iii. Pressure does not show any marked effect on equilibrium reactions taking place in the solution phase or in the solid phase.

## Effect of Temperature

Increase of temperature of the equilibrium system favours endothermic reactions.
Decrease of temperature of the equilibrium system favours exothermic reactions.
Ex: (1) Synthesis of ammonia by Haber's process: $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftarrows 2 \mathrm{NH}_{3}(\mathrm{~g})$ $\Delta \mathrm{H}=-92.0 \mathrm{~K} . \mathrm{J}$.
High pressure and low temperature are favourable conditions. 200 atms pressure, 773 K temperature, Fe is catalyst mixed with molybdenum promoter are favourable conditions for the formation of $\mathrm{NH}_{3}$.
$\mathbf{E g}(2)$ : Manufacture of $\mathrm{SO}_{3}$ by contact process

$$
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftarrows 2 \mathrm{SO}_{3}(\mathrm{~g}) \quad \Delta H=-189 \mathrm{KJ}
$$

i. High pressures favour the forward reaction since there is decrease in volume. But in the contact process high pressures are not used since towers used in the manufacture are corroded by the acid at high pressure. Thus a pressure of 1.5 to 2 atm . is used.
ii. Low temperature favours the forward reaction but at low temperature the reaction is too slow. Therefore an optimum temperature of 673 K is used .
iii. A catalyst vanadium pentoxide or platinised asbestos is used to speed up the reaction.

## Effect of Addition of Inert Gas

a) Addition of inert gas at constant volume: The total pressure of the system is increased. But the partial pressure of each reactant and product remains the same. Hence no effect on the state of equilibrium.
b) Addition of inert gas at constant pressure. The total volume is increased, the number of moles per unit volume of each reactant and product is decreased. Hence equilibrium will shift to the side where number of moles is increased E.g. $P C_{5}(g) \rightleftarrows \mathrm{PCl}_{3}(g)+\mathrm{Cl}_{2}(\mathrm{~g})$

Effect of Catalyst: Catalyst has no influence on the equilibrium. This is because, catalyst favours the rate of forward and backward reactions equally. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

