

Paper : Physical Chemistry (IA)

Topic : Chemical Equilibrium

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Application of Law of Mass Action to Homogeneous Liquid Phase Equilibria : →

The chemical equilibrium in which all the reactants and products are in the liquid phase, are referred to as the liquid equilibria. In this type of equilibria, all the reactants and products are miscible liquids. Equilibria of such reactions is expressed only in terms of K_c . K_p is determined only in gaseous phase equilibria.

An important example of this type of equilibrium is the esterification of acetic acid by ethyl alcohol. Reaction between Acetic acid and Ethyl alcohol to form Ethyl acetate : - The reaction takes place as follows:



At $t=0$	a	b	0	0
At equilibrium	(a-x)	(b-x)	x	x

Let- a moles of acetic acid and b moles of ethyl alcohol are heated together in a sealed tube at 100°C so that the equilibrium is reached. Let x moles of ethyl acetate is formed at equilibrium. If V is the volume of the system then the various concentration terms at equilibrium are given by

$$[\text{CH}_3\text{COOH}] = \frac{a-x}{V} ; [\text{C}_2\text{H}_5\text{OH}] = \frac{b-x}{V} ;$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5] = \frac{x}{V} ; [\text{H}_2\text{O}] = \frac{x}{V}$$

The equilibrium constant expression may be written as

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$\text{or, } K_c = \frac{\frac{x}{V} \cdot \frac{x}{V}}{\left(\frac{a-x}{V}\right) \left(\frac{b-x}{V}\right)}$$

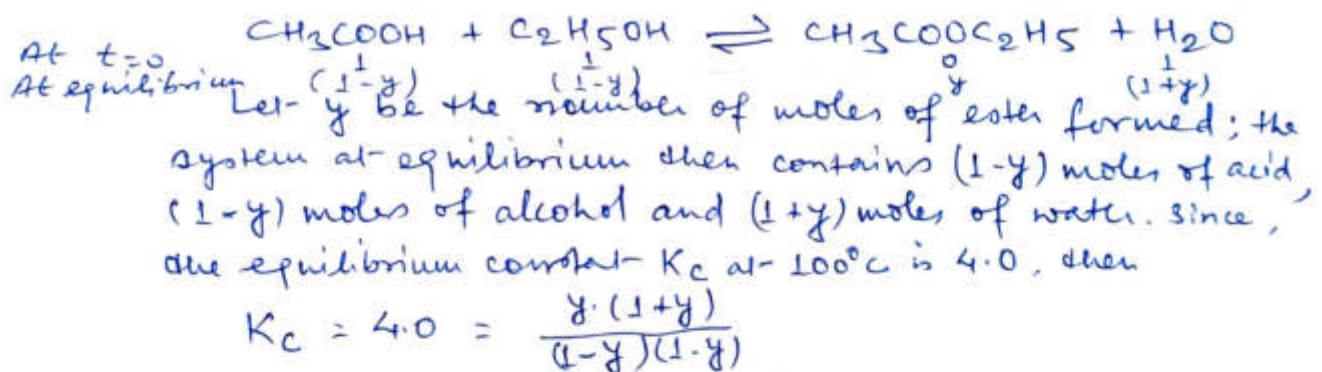
$$\text{or, } K_c = \frac{x^2}{(a-x)(b-x)} \quad \text{--- (13)}$$

From the above expression we see that K_c does not contain any volume terms. Hence, K_c is not affected by the change in volume.

In determining K_c it is assumed that various components are present in dilute solution. If the solutions are concentrated, better results are obtained by using (i) mole fractions and (ii) activities in place of molar concentrations.

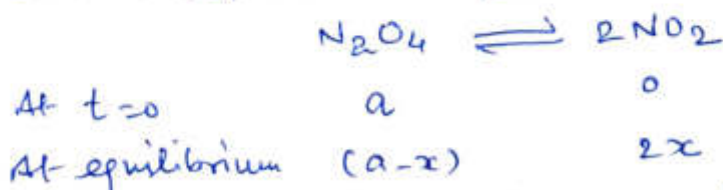
Problem: Calculate the percent of acid that is esterified when a mixture consisting initially of 1 mole of acetic acid, 1 mole of ethanol and 1 mole of water attains equilibrium at 100°C . (K_c at 100°C is 4.0).

Solution: The equilibrium is represented as



On solving it we get $y = 0.54$. Therefore 54 percent of the acid is esterified.

Dissociation of Nitrogen tetraoxide into Nitrogen dioxide in Chloroform Solutions: — This is another example of homogeneous equilibria in liquid phase. The equilibria at 82°C is represented as follows:



Let a moles of N_2O_4 is heated in a sealed vessel at 82°C so that the equilibrium is reached. Let x moles of NO_2 is formed at equilibrium. If V is the volume

of the vessel then the various concentration terms at equilibrium are given by

$$[\text{N}_2\text{O}_4] = \frac{(a-x)}{V} ; [\text{NO}_2] = \frac{2x}{V}$$

Now the equilibrium constant follows as :

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x/V)^2}{(a-x)/V} = \frac{4x^2}{(a-x)V}$$

$$\text{or, } K_c = \frac{4x^2}{(a-x)V} \quad \text{--- (14)}$$

Here in this expression, K_c contains volume terms. Hence, K_c is affected by change of volume.

Problem: A solution is made up of 0.5 mole of N_2O_4 in 450 ml of chloroform. Calculate the concentration of NO_2 in the solution at equilibrium at 82°C . (given $K_c = 1.08 \times 10^{-5}$)

Solution: Let y be the number of moles that have dissociated leaving $(0.5-y)$ mole of N_2O_4 and forming $2y$ moles of NO_2 in 450 ml (= 0.45 litre) of solution mixture at equilibrium.

$$\text{Hence } K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2y/0.45)^2}{(0.5-y)/0.45} = \frac{4y^2}{(0.5-y) \cdot 0.45}$$

$$\text{or, } 1.08 \times 10^{-5} = \frac{4y^2}{(0.5-y) \cdot 0.45}$$

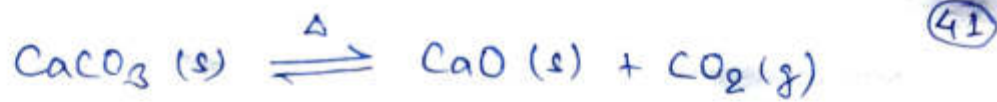
$$\text{or, } y = 7.8 \times 10^{-4} \text{ mole}$$

$$\begin{aligned} \text{The concentration of } \text{NO}_2 &= \frac{2y}{0.45} \\ &= \frac{2 \times 7.8 \times 10^{-4}}{0.45} \\ &= 3.5 \times 10^{-3} \text{ moles per litre.} \end{aligned}$$

Application of Law of Mass Action to Heterogeneous Equilibria :- (i.e. Equilibria in Heterogeneous Systems)

Heterogeneous reactions involve two or more phases, one of which is a solid or liquid. The application of law of mass action to heterogeneous equilibria is based on the fact that the activity of a pure solid or liquid is always taken as unity at all temperatures up to fairly high pressures.

Consider the decomposition of calcium carbonate upon heating to form calcium oxide and carbon dioxide is an example of solid gas (i.e. heterogeneous) equilibrium. If the reaction is carried out in a closed vessel, the following equilibrium is established:



The thermodynamic equilibrium constant K_a for this reaction is given by

$$K_a = \frac{a_{\text{CaO}} \cdot a_{\text{CO}_2}}{a_{\text{CaCO}_3}} \quad (15)$$

where $a(s)$ represent the activities. But so long as the pressure are not too high, the activities of two solids CaCO_3 and CaO are unity, i.e. $a_{\text{CaCO}_3} = a_{\text{CaO}} = 1$, so that the equation (15) becomes

$$K_p = a_{\text{CO}_2} \quad (16)$$

Again, if it is assumed that the gas involved behaves ideally, the activity is proportional to its partial pressure in the equilibrium state, i.e. P_{CO_2} and equation (16) becomes

$$K_p = P_{\text{CO}_2} \quad (17)$$

It follows, therefore, that when dealing with heterogeneous equilibria, only the activities or pressures of the gaseous constituents are involved in writing the expression for the equilibrium constant and the presence of pure solid or liquid phases, irrespective of their amount, can be completely ignored. K_p 's of heterogeneous reactions are generally called as "condensed equilibrium constants".

Other Examples of Heterogeneous Equilibria : \rightarrow

Dissociation of solid Ammonium hydrosulphide : -

Ammonium hydrosulphide dissociates on heating into ammonia and hydrogen sulphide as shown below:



Applying the law of mass action and remembering that the activity of solid is unity in heterogeneous equilibria, we get the expression for the condensed equilibrium constant, K_p as

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} \quad (18)$$

where P_{NH_3} and $P_{\text{H}_2\text{S}}$ are the partial pressures of ammonia and hydrogen sulphide respectively. This equation can be tested by adding one or other of

the gases to the systems in equilibrium at constant volume and determining K_p . This was always found to be constant.

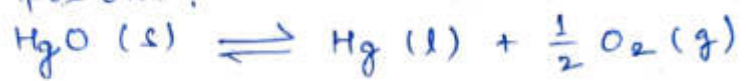
Decomposition of liquid Water :- The equilibrium reaction takes place as follows



The condensed equilibrium constant for this reaction is given by

$$K_p = P_{\text{H}_2}^2 \cdot P_{\text{O}_2} \quad \text{--- (19)}$$

Dissociation of Mercuric oxide :- The reaction takes place as follows :



We see the equilibrium involves one solid, one liquid and one gaseous phase. The condensed equilibrium constant for this equilibrium is given by

$$K_p = P_{\text{O}_2}^{1/2} \quad \text{--- (20)}$$

The Le Chatelier's Principle :->

In 1884, the French Chemist Henry Le Chatelier proposed a general principle which applies to all systems in equilibrium. This principle qualitatively describes the effect of changing the reaction conditions of an equilibrium. It can be stated as follows:

"If a system at equilibrium is disturbed by a change in temperature, pressure or concentrations of the components, the system will shift its equilibrium position so as to counteract the effect of that disturbance." or,

"When a stress is applied on a system in equilibrium, the system tends to adjust itself so as to reduce the stress." or,

"All the equilibria have tendency to retain their original state if disturbed by changing reaction conditions such as concentration, pressure, temperature etc."

It makes qualitative predictions about the response

of a system at equilibrium when various changes in external conditions are made.

1. Effect of change in concentration of reactant or product on equilibrium :- For the special case of concentration change the Le Chatelier's principle can be restated as: "When concentration of any of the reactants or products is changed, the equilibrium shifts in a direction so as to reduce the change in concentration that was made."

If a chemical system is at equilibrium and we add a substance (either a reactant or a product), the reaction will shift so as to reestablish equilibrium by consuming part of the added substance. Conversely, removal of a substance will result in the reaction moving in the direction that forms more of that substance.

Thus,

- (i) addition of reactant/s or removal of product/s in equilibrium mixture will favour forward reaction.
- (ii) addition of product/s or removal of reactant/s in equilibrium mixture will favour backward reaction.

Consider, for example, the ammonia synthesis reaction:



When N_2 is added (or NH_3 is removed) from an equilibrium mixture, the reaction shifts from left to right, forming more NH_3 and decreasing $[\text{N}_2]$ and $[\text{H}_2]$ to restore a new equilibrium.

If the products of a reaction can be removed continuously, the reacting system can be continuously shifted from left to right to form more products. The yield of NH_3 in Haber's process can be increased dramatically by liquifying NH_3 , the liquid NH_3 is removed and the N_2 and H_2 are recycled to produce more NH_3 .

2. Effect of change in pressure or volume on equilibrium :- To predict the effect of a change of pressure, Le Chatelier's principle may be stated as: "When pressure is increased on a gaseous equilibrium reaction, the equilibrium will shift

in a direction which tends to decrease the pressure."

The pressure of a gaseous reaction at equilibrium is determined by the total number of molecules it contains. If the forward reaction proceeds by the reduction of molecules, it will be accompanied by a decrease of pressure of the system and vice versa.

Again, decreasing the pressure by increasing the volume causes a shift in the direction that produces more gas molecules.

For the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, there are two mole of gas on the right side and 4 mole of gas on the left side of the chemical equation. Consequently an increase in pressure (i.e. decrease in volume) leads to the formation of NH_3 and the reaction shifts towards the side with fewer gas molecules.

For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, there are two mole of gas on the right side and one mole of gas on the left side. The total pressure of equilibrium is increased by decreasing volume. According to the Le Chatelier's principle, the equilibrium shifts to the side that reduces the total moles of gas i.e. in the backward direction. Therefore a decrease in pressure (increase in volume) will lead to the formation of NO_2 .

In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the number of moles of gaseous product equals the number of moles of gaseous reactants and thus change of pressure has no effect on such equilibrium.

It is also possible to change the total pressure of the system without changing its volume. The pressure can be increased by adding any one of the gaseous reacting components to the system. The total pressure of the system may also be increased by adding inert gases as they are not involved in the chemical reaction.

3. Effect of change in temperature on equilibrium:

To predict the effect of a change of temperature,

(15)

Le Chatelier's principle may be stated as: "When temperature of a reaction is increased, the equilibrium shifts in a direction in which heat is absorbed."

It may be noted that changes in concentrations or total pressure causes shifts in equilibrium without changing the value of equilibrium constant, K . In contrast almost every equilibrium constant changes its value as the temperature changes.

A simple way to deduce the temperature dependence of the equilibrium is to assume heat as a chemical reagent. In an endothermic reaction, we can treat heat as a reactant, whereas in an exothermic reaction, we can treat heat as a product:

Endothermic : Reactants + Heat \rightleftharpoons Products

Exothermic : Reactants \rightleftharpoons Products + Heat

In an endothermic reaction, heat is absorbed as reactants are converted to products; thus, the equilibrium shifts to the right, in the direction of products and K increases.

In an exothermic reaction, the opposite occurs. Heat is absorbed as products are converted to reactants, so the equilibrium shifts to the left and K decreases.

Thus,

Exothermic : Increasing T results in a decrease in K .

Endothermic : Increasing T results in an increase in K .

In general we can say that the increase of temp. favours the reverse change in an exothermic reaction and the forward change in an endothermic reaction.

Formation of NH_3 from N_2 and H_2 : - The synthesis of NH_3 is an exothermic reaction.



When the temperature of the system is raised, the equilibrium will shift to the left which (backward reaction) absorbs heat. This results in the lower yield of ammonia. On the other hand, by lowering the temp. of the system, the equilibrium will shift to the right which evolves heat (i.e. due to exothermic in nature). This would increase the yield of ammonia. But with decreasing temperature, the rate of reaction is slowed down

considerably and the equilibrium is reached slowly. Thus, in the commercial production of ammonia, it is not feasible to use temperature lower than 500°C .

4. Effect of catalyst on equilibrium :-

The catalyst does not alter the value of equilibrium constant for any reversible reaction. It simply helps in approaching the equilibrium at an earlier stage by catalyzing equally both in forward and backward reactions.

Recommended Books

1. Essentials of Physical Chemistry
By Arun Bahl, B.S. Bahl and G.D. Tuli
 2. A Text Book of Physical Chemistry
By K.K. Sharma and L.K. Sharma
 3. Principles of Physical Chemistry
By Puri, Sharma and Pathania
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