Law Of Mass Action And Equilibrium Constant Expression

Learning Outcomes:

Students will be able to:

1. define Law Of Mass Action;
2. derive an expression for the Equilbrium Constant and its units;
3. state conditions for equilibrium and the ways of recognizing equilibrium;
4. write the equilibrium constant expression of a reaction.

Law of Mass Action:

We know that the reversibility and chemical equilibrium are related to each other. There is a rapid fall or increase in the concentrations of the reactants and products in the beginning and less rapid later on. This suggests that there must be some relationship between the concentration of active masses of the reacting species and the rate of the reaction. This led two Scandinavian scientists, Guldberg and Waage to put forward a law, known as Law of Mass Action.

Active Mass

concentration in terms of mole/dm^3

mole/dm^3 = [ ]

[A]

This law states that,

"The rate at which a substance reacts, is directly proportional to its active mass and the rate of a reaction is directly proportional to the product of the active masses of the reacting substances."

For example, consider a general reaction i.e.,

$$A + B \underset{kr}{\overset{kf}{\rightleftharpoons}} C + D$$

The active masses, in terms of molar concentration of A, B, C and D are represented by [A], [B], [C] and [D] respectively.

According to the Law of Mass Action:

The rate of forward reaction is proportional to [A] [B] and therefore the rate of forward reaction is equal to kf [A] [B], while the rate of reverse reaction = kr [C] [D] where kf and kr are the *rate of costants for* the forward and reverse reactions, respectively.

Rate of forward reaction $\propto$ [A][B]

Rate of Reverse reaction $\propto$ [C][D] animation

Equilibrium Constant (Kc):

In order to find out the effect of concentration on chemical equilibrium, it is necessary to derive the expression of its equilibrium constant which is denoted by Kc or Kp. Let us consider the following reaction and apply the law of mass action on it.

$$aA + bB \rightleftharpoons cC + dD$$ Eq. state

Rate of Forward reaction $\propto [A]^a [B]^b$

$= K_f [A]^a [B]^b$.....(i)

Rate of reverse reaction $\propto [C]^c [D]^d$

$= K_r [C]^c [D]^d$....(ii)

Since, at equilibrium state,

Rate of forward reaction = Rate of reverse reaction

$$\therefore \quad (i) = (ii)$$

$$\rightarrow K_f([A]^a [B]^b) = K_r [C]^c [D]^d$$

or

$$\left(\frac{K_f}{K_r}\right) = \frac{([C]^c [D]^d)}{([A]^a [B]^b)}$$

$$\frac{k_f}{k_r} = k_c$$

or

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

This is the expression of Kc, in which active masses of products are placed in the numerator while the active masses of reactants are placed in the denominator. In other words, equilibrium constant is the ratio of active masses of products and reactants at equilibrium.

Units for Equilibrium Constant:

As Kc is a ratio between the concentration of the product of the products to the concentration of the product of the reactants, therefore, it does not contain any unit.

animation

Ways of expressing Equilibrium Constant:

- There are different ways of expressing equilibrium constant, depending on the phases of reactants and products involved in the reaction.
- In reactions where all species are of same phases, we have what's called *Homogeneous Equilibrium*. The constant Kc means that the concentration are in molarity (mole/dm^3).

Consider the following example: $Kc = \dfrac{[NO_2]^2}{N_2O_4}$

What if the reaction was

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}?$$

In the previous example, the concentrations were in molarity.

Now that the species are gases, what do we do? According to the ideal gas law PV = nRT, at a constant temperature, the pressure is proportional to the concentration in molarity of gas.

Because of this, we can write the equilibrium constant as:

$$Kp = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

Where P_{NO_2} and $P_{N_2O_4}$ are equilibrium partial pressures of respective gases. Keep in mind, though, that Kc is not equal to Kp.

How to write Kc of Reactions

- Hydrolysis of Ester

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5][H_2O]}$$

oxidation of Ammonia

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$$

$$k_c = \frac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_2]^5}$$

Multiple Choice Questions

1. The rate of the reaction

$$A + B \rightarrow C + D$$

is directly proportional to

A. concentration of A only.
B. concentration of B only.
C. concentration of both C and D.
D. concentration of both A and B.

2. Which of the following is the correct equilibrium constant expression for the reaction given below?

$$aA + bB \rightarrow cC + dD$$

A. $Kc = \frac{[C]\ [D]}{[A]\ [B]}$

C. $Kc = \frac{[A]\ [B]}{[C]\ [D]}$

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

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

3. Equilibrium constant for the given reaction

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

is always independent of the initial concentration of

A. reactants only.
B. products only.
C. reactants and products both.
D. catalyst used.