HETROGENEOUS EQUILIBRIA

If reactants and product are found in two or more phases, the equilibria describing them is called hetrogeneous equilibrium.

Example:
(i) $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$
(ii) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$
(iii) $Br_2(l) \rightleftharpoons Br_2(g)$

Equilibrium expression for them can be written as

(i) $K = [Pb^{2+}(aq)][Cl^-(aq)]^2$

(ii) $K_P = \dfrac{1}{P_{CO_2}}$; $K_C = \dfrac{1}{[CO_2(g)]}$

(iii) $K_P = P_{Br_2}(g)$; $K_C = [Br_2(g)]$

Note : We should calculate the value of K from the activities of the reactants and products rather than from their concentrations. However, the activity of a dilute solute is usefully approximated by its molar concentration, so we will use concentrations as approximated by its pressure (in atmospheres), so we use pressures for gases. However, we also can use molar concentrations of gases in our equilibrium calculations, because the molar concentration of a gas is directly proportional to its pressure. The activity of a pure solid or pure liquid is 1, and the activity of a solvent in a dilute solution is close to 1. It is because as pure solids and liquid took part in reaction, their concentration (or density) remain constant. Thus these species (solids, liquids, and solvents) are omitted from reactions quotients and equilibrium calculations.

UNIT OF EQUILIBRIUM CONSTANT

We have already noted that the value of an equilibrium constant has meaning only when we give the corresponding balanced chemical equation. Its value changes for the new equation obtained by multiplying or dividing the original equation by a number. The value for equilibrium constant, K_C is calculate substituting the concentration in mol/L and for K_P by substituting partial pressure in Pa, kPa, etc. in atm. Thus, units of equilibrium constant will turn out to be units based on molarity or pressure, unless the sum of the exponents in the numerator is equal to the sum of the exponents in the denominator. Thus for the reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_C and K_P do not have any unit
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$, K_C has unit $(mol/L)^{-2}$ and K_P has unit bar^{-2} or
$N_2O_4(g) \rightleftharpoons 2NO_2$, K_C has unit mol / L and K_P has unit bar

However, these days we express equilibrium constants in dimensionless quantities by specifying the standard state of the reactants and the products. The standard state for pure gas is 1 bar and now the partial pressure are measured with respect to this standard. Thus a pressure of 2 bar in term of this standard state is equal to 2 bar / 1 bar = 2, a dimensionless number. Similarly for a solute the standard state; C_0, is 1 molar solution and all concentrations are measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen.

APPLICATION OF EQUILIBRIUM CONSTANT

Before we consider the applications of equilibrium constants, let us consider its important features:

(i) The expression for equilibrium constant, K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.

(ii) The value of equilibrium constant is independent of initial concentration of the reactants and product. Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.