

SECTION 14

CHEMICAL EQUILIBRIUM

Many chemical reactions do not go to completion. That is to say when the reactants are mixed and the chemical reaction proceeds it only goes to a certain extent, and at the end there are measurable amounts of both reactants and products present in the system. A system is then said to be at equilibrium. A measure of how far a reaction goes is given by its "equilibrium constant" which can have very small or very large values. This section introduces the language used for these reactions, and some important classes.

Reversible reaction: A chemical reaction that can occur in both the forward and reverse direction and shown by two arrows, $\rightleftharpoons$. [e.g. $\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$ If solid lead chloride is added to water some dissolves; if aqueous solutions of soluble lead nitrate and soluble sodium chloride are mixed some solid lead chloride precipitates. The chemical reaction of the lead-acid battery, see *page 15-3*.] It is represented in the general case by:



Reaction Quotient: Symbol Q , a mathematical expression relating the concentrations of reactants and products at any stage of a reaction:

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

The expression for Q may be written down by inspection of the balanced chemical equation. It is the product of the instantaneous concentrations of the reaction products each raised to the power of its stoichiometric coefficient divided by the product of the instantaneous concentrations of the reactants each raised to the power of its stoichiometric coefficient. Here the square bracket notation, e.g. $[\text{A}]$, is used as the symbol for concentration rather than $c(\text{A})$. The form $c(\text{A})$, usually represents the overall concentration of a species disregarding any reactions which might have occurred. (See below, *equilibrium constant*.)

Chemical equilibrium: The state of a reversible chemical reaction when the rate of the reaction in the reverse direction equals that in the forward direction; there is no change in amounts or concentrations of reactants or products with time. As the reaction is occurring in both directions we called it **dynamic equilibrium**. It requires an input of energy to change the composition at equilibrium, i.e. to drive the reaction in the forward or reverse direction. A reaction at equilibrium is indicated by the use of two half arrows, $\rightleftharpoons$ as shown for the general case:



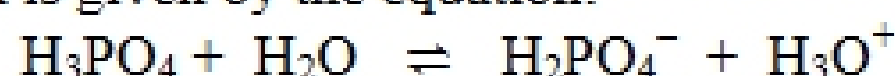
Equilibrium constant: Symbol K , a quantitative expression for the equilibrium composition of a chemical reaction. It is the value of the reaction quotient, Q , at equilibrium. Thus for the general reaction above

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

$$(K = [\text{C}]^c[\text{D}]^d / [\text{A}]^a[\text{B}]^b)$$

where $[\text{A}]$ etc. are the equilibrium concentrations of the reactant and product species present. Like Q the expression for K may be written down by inspection of the balanced chemical

equation. Again the square bracket notation is used for concentration. [e.g. For an aqueous 0.1 mol L^{-1} HCl solution, $c(\text{HCl}) = 0.1 \text{ mol L}^{-1}$, but the concentration of hydrogen chloride molecules actually present in the solution, $[\text{HCl}]$, is very low. For an aqueous 0.1 mol L^{-1} phosphoric acid solution, for which we would write $c(\text{H}_3\text{PO}_4) = 0.1 \text{ mol L}^{-1}$, the equilibrium actually existing in solution is given by the equation:



In this solution $[\text{H}_3\text{PO}_4] < 0.1 \text{ mol L}^{-1}$ because some of the phosphoric acid has been converted to dihydrogen phosphate. $c(\text{H}_3\text{PO}_4) = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-]$.]

Concentration equilibrium constant: Symbol K_c , an equilibrium constant in which the equilibrium composition is expressed in terms of concentration. [e.g. as above.]

Pressure equilibrium constant: Symbol K_p , an equilibrium constant in which the equilibrium composition is expressed in terms of partial pressures of reactants and products instead of concentrations, because the concentration of a gas is directly proportional to its pressure (partial pressure in a mixture of gases).

(From the ideal gas equation $pV = nRT$, $p = \frac{nRT}{V} = cRT$.)

Standard (reference) concentrations and pressures: Standard or reference concentrations and pressures are useful concepts. In solutions the common standard for solutes is 1 mol L^{-1} , and for a solvent (liquid) or solid the concentration of the pure solvent (liquid) or solid. For gaseous systems the standard state for partial pressure is 100 kPa.

Units of equilibrium constants, K : In principle, the magnitude and units of an equilibrium constant will depend on the stoichiometry of the reaction and on the chosen units of concentration. To avoid having different values for the same equilibrium constant chemists use the ratio of the concentration to a standard concentration, or ratio of the partial pressure to a standard pressure, and K is dimensionless, i.e. just a number without units. [e.g. In the above reaction of phosphoric acid with water the water is both a reactant and the solvent. As the concentration of water is almost independent of the concentration of the solute and of the position of equilibrium, its concentration is almost that of pure water, and thus the value of $[\text{H}_2\text{O}]$ to put into the expression for K is one ($[\text{H}_2\text{O}] = c(\text{H}_2\text{O})/c(\text{H}_2\text{O}) = 1$). Thus

$$K = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

where the values of the concentrations of the solute species are just the numerical values of their concentrations in units of mol L^{-1} . For gas phase equilibria using K_p the values put into the expression for K_p are the actual partial pressures of the gases each divided by 100 kPa.]

Position of equilibrium: A qualitative expression for the relative amounts of reactants and products present at equilibrium. The position of equilibrium may lie well to the left with only very small but measurable amounts of products present, or well to the right with only small but measurable amounts of reactants present, or anywhere in between. The magnitude of K is a quantitative measure of the position of the equilibrium. If K is large, then the numerator is much larger than the denominator, the concentration of the products is much greater than that of the reactants, and the equilibrium lies well to the right. If K is small the equilibrium lies well to the left, and only a small fraction of reactants are converted into products. The

magnitude of this expression remains constant whatever other species or reactions are involved, i.e. whatever the composition of the system. [e.g. in an equimolar solution of aqueous H_3PO_4 and NaOH , (i.e. one made up of equal amounts of the two reactants), almost all the phosphoric acid reacts to give the dihydrogen phosphate anion,



but the equilibrium concentrations of the species in this solution still obey the nett expression

$$K = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

pK $\text{p}K = -\log_{10}K$. Many equilibrium constants have extremely small numerical values and it is often convenient, especially in tabulation, to express them in a logarithmic form. [e.g if $K = 1.0 \times 10^{-8}$, $\text{p}K = 8.0$; if $K = 5 \times 10^{-8}$, $\text{p}K = 7.30$]

Chemical yield: The fraction of the limiting reactant converted to required product.

Percentage chemical yield: The chemical yield $\times 100$; a common way of expressing chemical yield.

Temperature control of equilibrium: The magnitude of K varies with temperature, decreasing with increasing temperature for exothermic reactions, and increasing with increasing temperature for endothermic reactions. The larger the numerical value of $\Delta_r H$ the greater the change in K with change in temperature. Thus the position of equilibrium, and hence the chemical yield can be altered by changing the temperature.

K 's on reaction written in reverse direction. It follows from the definition of K that if the direction of the chemical equation is reversed $K_{\text{reverse}} = 1/K_{\text{forward}}$.

K for overall reactions: When an overall reaction can be considered as the sum of a series of reactions, K for the overall reaction is the product of the equilibrium constants of the individual reactions, as can be seen for a general case:



$$K(1) \times K(2) = \frac{[C]^c}{[A]^a[B]^b} \times \frac{[P]^p[Q]^q}{[C]^c[D]^d} = \frac{[P]^p[Q]^q}{[A]^a[B]^b[D]^d} = K(\text{overall})$$

It follows from the above discussion (and from the definition of K) that if the stoichiometry of a reaction equation is altered by multiplying by 2, the value of K is squared.

SOME CLASSES OF EQUILIBRIUM

(1) Solubility

Saturated solution: A solution in which the dissolved and undissolved solute are in dynamic equilibrium, or a solution containing the maximum amount of solid under equilibrium conditions.

Solubility: Symbol s , the amount of substance dissolved in unit volume of a saturated solution.