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, $\rightleftarrows$. [e.g. $PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$ 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:

$$a\text{A} + b\text{B} \rightleftarrows c\text{C} + d\text{D}$$
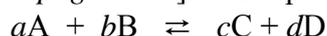
Reaction Quotient: Symbol Q, a mathematical expression relating the concentrations of reactants and products at any stage of a reaction:

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

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. [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:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$
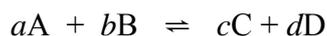
Equilibrium constant: Symbol K, a quantitative expression for the equilibrium composition of a chemical reaction. It is the value of the reaction quotient, Q, at equilibrium. Thus for the general reaction above

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

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

where [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, $c(HCl) = 0.1$ mol L^{-1}, but the concentration of hydrogen chloride molecules actually present in the solution, [HCl], is very low. For an aqueous 0.1 mol L^{-1} phosphoric acid solution, for which we would write $c(H_3PO_4) = 0.1$ mol L^{-1}, the equilibrium actually existing in solution is given by the equation:
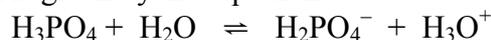
$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$$

In this solution $[H_3PO_4] < 0.1$ mol L^{-1} because some of the phosphoric acid been converted to dihydrogen phosphate. $c(H_3PO_4) = [H_3PO_4] + [H_2PO_4^-].$]

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 $pV = nRT$, $p = \dfrac{nRT}{V} = cRT$.)

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 $[H_2O]$ to put into the expression for *K* is one ($[H_2O] = c(H_2O)/c(H_2O) = 1$). Thus

$$K = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$$

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,

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$$
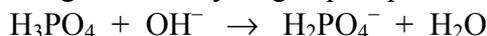
but the equilibrium concentrations of the species in this solution still obey the nett expression

$$K = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$$

pK $pK = -\log_{10}K$. 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 $K = 1.0 \times 10^{-8}$, $pK = 8.0$; if $K = 5 \times 10^{-8}$, $pK = 7.30$]

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

Percentage chemical yield: The chemical yield x 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 $K_{reverse} = 1/K_{forward}$.

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:

Reaction (1) $\quad\quad\quad\quad aA + bB \rightleftharpoons cC$
Reaction (2) $\quad\quad\quad\quad cC + dD \rightleftharpoons pP + qQ$
Overall $\quad\quad\quad\quad\quad aA + bB + dD \rightleftharpoons pP + qQ$

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

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.

(a)   *A gas dissolved in a solvent*

$$X(solv) \rightleftharpoons X(g)$$
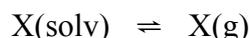
$K = \dfrac{p(X(g))}{[X(solv)]}$ Rearranging, $p(X(g)) = K[X(solv)]$ This is a form of **Henry's law**

which states that for dilute solutions or sparingly soluble gases the concentration in a saturated solution is proportional to the partial pressure of the gas above the solution.

(b)   *A molecular solid or liquid substance dissolved in a solvent.*

$$X(s) \rightleftharpoons X(solv) \quad or \quad X(l) \rightleftharpoons X(solv)$$

The concentration of X in solution is independent of the excess amount of X(s) or X(l) present, and the ratio of [X(s)] or [X(l)] to the standard states of the pure solid or liquid is one (as explained under units of K), and the expression for K is: $K = $ [X(solv)]. In this case K is the solubility of X in the solvent, $K = s$.

(c)   *An ionic solid dissolving in water*

Solubility constant: Symbol K_s (older term **solubility product**, symbol K_{sp}), the equilibrium constant for the dissolution of an ionic compound in water.

(i) $MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$
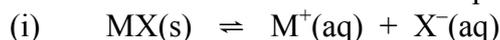
$$K_s = [M^+(aq)][X^-(aq)].$$

In this case it can be seen from the stoichiometry that:

$s(MX) = [M^+(aq)] = [X^-(aq)]$ and $s = K_s^{1/2}$ because $K_s = s^2$.

(ii) $MX_2(s) \rightleftharpoons M^{2+}(aq) + 2X^-(aq)$
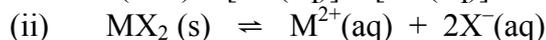
Here $K_s = [M^{2+}(aq)][X^-(aq)]^2$, and $s(MX_2) = [M^{2+}(aq)] = [X^-(aq)]/2$.

Thus $K_s = s \times (2s)^2 = 4s^3$ and $s = (K_s/4)$

(d)   *Distribution of a solute between two immiscible liquids A and B*

Distribution coefficient: The equilibrium for the distribution of a substance between two immiscible liquids (i.e. liquids of low solubility in each other) A and B.

$$X(A) \rightleftharpoons X(B)$$
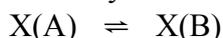
$$K = \frac{[X(B)]}{[X(A)]}$$

(2) **Decomposition of a substance**

[e.g. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
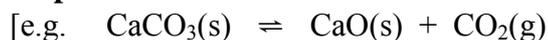
Decomposition of limestone on heating (calcining). $K = p(CO_2)$

or $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
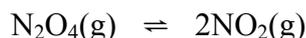
Dissociation of N_2O_4. $K = \dfrac{p(NO_2)^2}{p(N_2O_4)}$]

(3) **Acid-base**

pH: pH = $-\log_{10}([H_3O^+]/1\,\text{mol L}^{-1})$. The quantity most measured in aqueous acid-base equilibrium is the oxonium (hydronium) ion concentration (but usually called the hydrogen ion concentration in this context) $[H_3O^+(aq)]$. As this is often very small it is common to take the logarithm of the hydrogen ion concentration and express it as pH. [e.g. If the pH of a solution is 6, $[H_3O^+] = 1 \times 10^{-6}$ mol L^{-1}] The operation of taking a logarithm can only be performed on a pure number. Thus $[H_3O^+]$ is divided by the standard unit of concentration, 1 mol L^{-1}.

K_w: $K_w = [H_3O^+][OH^-]$. In water the very important equilibrium
$$H_2O + H_2O \;\rightleftharpoons\; H_3O^+(aq) + OH^-(aq)$$
always exists, with the equilibrium constant $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ at 25 °C and. $pK_w = 14$. In very pure water at 25 °C $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ mol L^{-1}.
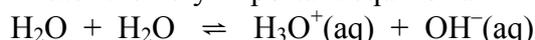
Neutral solution: An aqueous solution with $[H_3O^+] = [OH^-]$; at 25 °C pH = 7.

Acidic solution: An aqueous solution with pH < 7.

Basic or **alkaline solution**: An aqueous solution with pH > 7.

Acidity constant: symbol K_a, the equilibrium constant for the reaction
$$HA(aq) + H_2O \;\rightleftharpoons\; H_3O^+(aq) + A^-(aq)$$
(older term, the **acid dissociation constant**.):
$$K_a(HA) = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$
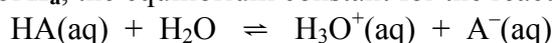
Weak acids: Acids with small values of K_a. ($K_a < 1$, pK_a positive, position of equilibrium well to left, only a small fraction of acid molecules reacted.) [e.g. In 1.0 mol L^{-1} acetic acid, $pK_a = 4.76$, $[CH_3CO_2^-] = [H_3O^+] = 4.2 \times 10^{-3}$ mol L^{-1}, pH = 2.4.]

Strong acids: Acids with large values of K_a ($K_a \gg 1$, pK_a negative, equilibrium well to right, almost all acid molecules reacted). [e.g. in 1.0 mol L^{-1} nitric acid, $pK_a = -1.3$, $[H_3O^+] = 1.0$ mol L^{-1}, pH = 0 ([HNO$_3$] very small).]

Weak base: A base for which the equilibrium position for the reaction
$$B(aq) + H_2O \;\rightleftharpoons\; BH^+(aq) + OH^-(aq)$$
lies well to the left, only a small fraction of molecules have accepted a proton from water.

Strong base: A base for which the equilibrium position for the above reaction lies well to the right, only a small fraction of molecules remain in the solution.

Basicity constant: symbol K_b the equilibrium constant for the reaction
$$B(aq) + H_2O \;\rightleftharpoons\; BH^+(aq) + OH^-(aq)$$
$$K_b = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

It is easily shown that $K_b = \dfrac{K_w}{K_a(\text{conjugate acid})}$. Qualitatively, this expression says that the stronger an acid the weaker its conjugate base. Strong acids have very weak conjugate bases and very weak acids have strong conjugate bases. [e.g. HNO_3 is a strong acid, ($pK_a -1.3$), NO_3^- is a very very weak base; HS^- is a very weak acid (pK_a 19), S^{2-} is a strong base.] Tables of K_b are unnecessary, tables of K_a or pK_a of the corresponding conjugate acids being sufficient to state base strength. For an acid HA, where $pK_a(HA) = 7$, $pK_b(A^-)$ is also 7, and it can be said that the strengths of the acid and its conjugate base are the same.

Polyprotic acids and bases: Acids with two, three or more hydrogens which can undergo proton transfer. Polyprotic acids can be diprotic, triprotic etc. [e.g. H_2SO_4- diprotic; H_3PO_4 - triprotic] Similarly bases which can accept more than one proton are said to be polyprotic bases. [e.g. S^{2-}- diprotic; PO_4^{3-}- triprotic] For polyprotic acids successive acidity constants can be written [e.g. for phosphoric acid:

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \qquad K = K_1(H_3PO_4)$$
$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K = K_2(H_3PO_4)$$
$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+ \qquad K = K_3(H_3PO_4)$$
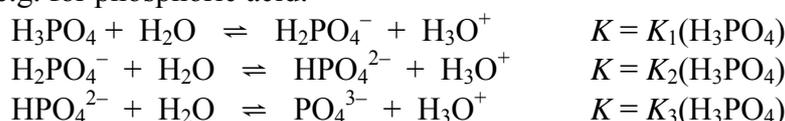
Buffer solution: A solution which is resistant to change in pH (when small amounts of acid or base are added or it is diluted). A buffer solution contains significant amounts of both an acid and its conjugate base. If H_3O^+ is added to or produced in the solution, it is removed by reaction with the base. Like wise any OH^- is removed by reaction with the conjugate acid:

$$H_3O^+ + A^- \rightleftharpoons HA + H_2O$$
$$OH^- + HA \rightleftharpoons A^- + H_2O$$
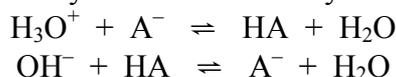
It can be seen from the expression of $K_a(HA)$ that if a buffer solution is made up with equimolar amounts of HA and A^- that the pH of the solution is equal to the $pK_a(HA)$ of the acid. The pH of a buffer solution can be controlled by taking the appropriate amounts of HA and A^-.

Brønsted acid: A proton donor; the molecule or ion must contain H [e.g. HCl and all the acids above in this section]. (See *page 12-3*)

Brønsted base: A proton acceptor; the molecule or ion must have a pair of non-bonding electrons to form a bond with a proton [e.g. $:NH_3$ and all the bases above in this section]. (See *page 12-3*)

Lewis acid: A species (molecule or ion) which can accept a pair of electrons from a base and form a bond. This is a broader definition of an acid [e.g. carbon dioxide in its reaction with the hydroxide ion to give the hydrogencarbonate ion: $CO_2 + OH^- \rightarrow HCO_3^-$]. A proton is a Lewis acid by this definition.

Lewis base: An electron pair donor. [e.g. the hydroxide ion in the above example] Brönsted bases are also Lewis bases as they donate a pair of electrons to the proton.

(4) **Complex ion formation**

Complex ion: An ionic species consisting of ligands (Lewis bases) (*page 13-1*) bonded to a metal cation (which is acting as a Lewis acid) [e.g. $Cu(NH_3)_4^{2+}$; $CrCl_6^{3-}$]. The ligands may

be neutral molecules [e.g. NH_3] or anions [e.g. Cl^-].

Stability constant (Formation constant): The equilibrium constant for the overall reaction between the aquated metal cation and the free ligands to form the complex ion. [e.g

$$Cu^{2+}(aq) + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}(aq)][NH_3]^4} \quad]$$
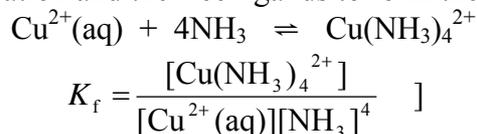
Note: The formal convention for arrows in chemical equations is that $\rightarrow$ represents a reaction in the forward direction, $\rightleftarrows$ represents a reversible reaction, and $\rightleftharpoons$ represents a reaction at equilibrium.

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EXERCISES

Write the expression for the equilibrium constant for the following reactions.

1. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

2. $N_2(g) + 3H_2(g) \rightleftharpoons 2 NH_3(g)$

3. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

4. $2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$

5. $HF(aq) + H_2O \rightleftharpoons H_3O^+(aq) + F^-(aq)$

6. $Ch_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

7. $HCO_3^-(aq) + H_2O \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

8. $CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

Calculate the solubility in pure water of the following ionic solids.

9. AgBr, $pK_s = 12.3$ 10. $CaCO_3$, $pK_s = 8.48$ 11. PbI_2, $pK_s = 8.10$

Calculate the pH of a solution if

12. $[H_3O^+] = 1.0 \times 10^{-3}$ mol L^{-1} 13. $[H_3O^+] = 2.4 \times 10^{-4}$ mol L^{-1}

14. $[OH^-] = 1.0 \times 10^{-3}$ mol L^{-1} 15. $[OH^-] = 2.4 \times 10^{-4}$ mol L^{-1}

16.   A buffer solution was made up with $H_2PO_4^-$ and HPO_4^{2-}. Calculate the pH of the solution (i) when equimolar amounts 0f each ion are used, and (ii) when the amount of $H_2PO_4^-$ is twice that of HPO_4^{2-}. $pK_2(H_3PO_4) = 7.20$

Calculate pK_a for weak acids with

17. $K_a = 1.0 \times 10^{-6}$ 18. $K_a = 5.6 \times 10^{-8}$