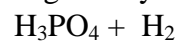


**SECTION 14****CHEMICAL EQUILIBRIUM**

**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:

*a*

equation. Again the square bracket notation is used for concentration. [e.g. For an aqueous  $0.1 \text{ mol L}^{-1}$  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  $0.1 \text{ mol L}^{-1}$  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:





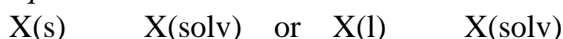
- (a)
- A gas dissolved in a solvent*



$$K = \frac{p(\text{X(g)})}{[\text{X(soln)}]} \quad \text{Rearranging, } p(\text{X(g)}) = K[\text{X(soln)}] \quad \text{This is a form of **Henry's law**}$$

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.

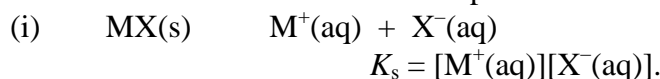
- (b)
- A molecular solid or liquid substance dissolved in a solvent.*



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:  $K = [\text{X(soln)}]$ . 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.



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

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

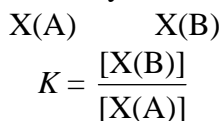


Here  $K_s = [\text{M}^{2+}(\text{aq})][\text{X}^-(\text{aq})]^2$ , and  $s(\text{MX}_2) = [\text{M}^{2+}(\text{aq})] = [\text{X}^-(\text{aq})]/2$ .

Thus  $K_s = s \times (2s)^2 = 4s^3$  and  $s = (K_s/4)^{1/3}$

- (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.



## (2) Decomposition of a substance



Decomposition of limestone on heating (calcining).  $K = p(\text{CO}_2)$



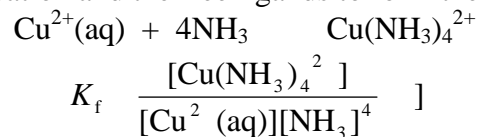
Dissociation of  $\text{N}_2$



It is easily shown that  $K_b = \frac{K_w}{K_a(\text{conjugate acid})}$ . 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.  $\text{HNO}_3$  is a strong acid, ( $\text{p}K_a -1.3$ ),  $\text{NO}_3^-$  is a very very weak base;  $\text{HS}^-$  is a very weak acid ( $\text{p}K_a 19$ ), S

be neutral molecules [e.g.  $\text{NH}_3$ ] or anions [e.g.  $\text{Cl}^-$ ].

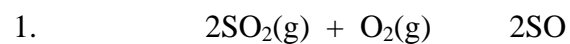
**Stability constant (Formation constant):** The equilibrium constant for the overall reaction between the aquated metal cation and the free ligands to form the complex ion. [e.g.



*Note:* The formal convention for arrows in chemical equations is that  $\rightarrow$  represents a reaction in the forward direction,  $\rightleftharpoons$  represents a reversible reaction, and  $\rightleftharpoons$  represents a reaction at equilibrium.

### EXERCISES

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



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

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