because its ionization will be suppressed by the presence of common acetate ions produced by complete dissociation of the sodium salt. The pH of this solution can be described by Equation 3.23, which is Equation 3.16 in which $[A^-]$ is the concentration of acetate ions and [HA] is the concentration of acetic acid in the buffer solution:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad (3.23)$$

It can be seen from Equation 3.23 that the pH will remain constant as long as the logarithm of the ratio [acetate]/[acetic acid] does not change. When a small amount of an acid is added to the solution, it will convert some of the salt into acetic acid, but if the concentrations of both acetate ion and acetic acid are reasonably large then the effect of the change will be negligible and the pH will remain constant. Similarly, the addition of a small amount of base will convert some of the acetic acid into its salt form but the pH will be virtually unaltered if the overall changes in concentrations of the two species are relatively small.

If large amounts of acid or base are added to a buffer, then changes in the ratio of ionized to unionized species become appreciable and the pH will then alter. The ability of a buffer to withstand the effects of acids and bases is an important property from a practical point of view. This ability is expressed in terms of *buffer capacity* (β). It can be defined as being equal to the amount of strong acid or strong base, expressed as moles of H^+ or OH^- ion, required to change the pH of 1 litre of the buffer by 1 pH unit. From the remarks above, it should be clear that buffer capacity increases as the concentrations of the buffer components increase. In addition, the capacity is also affected by the ratio of the concentrations of weak acid and its salt, maximum capacity (β_{max}) being obtained when the ratio of acid to salt = 1, i.e. pH equals the pK_a of the acid.

The components of various buffer systems and the concentrations required to produce different pHs are listed in several reference books, such as the pharmacopoeias. When selecting a suitable buffer, the pK_a value of the acid should be close to the required pH and the compatibility of its components with other ingredients in the system should be considered. The toxicity of buffer components must also be taken into account if the solution is to be used for medicinal purposes.

Colligative properties

When a non-volatile solute is dissolved in a solvent, certain properties of the resultant solution are largely independent of the nature of the solute and are determined by the concentration of solute particles. These properties are known as *colligative properties*. In the case of a nonelectrolyte the solute particles will be molecules,but if the solute is an electrolyte, then its degree of dissociation will determine whether the particles will be ions only or a mixture of ions and undissociated molecules.

The most important colligative property from a pharmaceutical aspect is referred to as *osmotic pressure*. However, since all colligative properties are related to each other by virtue of their common dependency on the concentration of the solute molecules, other colligative properties (which include lowering of vapour pressure of the solvent, elevation of its boiling point and depression of its freezing point) are of pharmaceutical interest. Observations of these other properties offer alternatives to osmotic pressure measurements as methods of comparing the colligative properties of different solutions.

Osmotic pressure

The osmotic pressure of a solution is the external pressure that must be applied to the solution in order to prevent it being diluted by the entry of solvent via a process that is known as *osmosis*. This is the spontaneous diffusion of solvent from a solution of low solute concentration (or a pure solvent) into a more concentrated one through a semipermeable membrane. Such a membrane separates the two solutions and is permeable only to solvent molecules (i.e. not solute ones).

Since the process occurs spontaneously at constant temperature and pressure, the laws of thermodynamics indicate that it will be accompanied by a decrease in the *free energy* (G) of the system. This free energy may be regarded as the energy available for the performance of useful work. When an equilibrium position is attained then there is no remaining difference between the energies of the states that are in equilibrium. The rate of increase in free energy of a solution caused by an increase in the number of moles of one component is termed the *partial molar free energy* ($\bar{G}$) or *chemical potential* (μ) of that component. For example, the chemical