25 Equilibria

Buffer solutions

Buffer solutions are able to resist a change in acidity or alkalinity, maintaining an almost constant pH, when a small amount of either substance is added. An important example of such a system occurs in blood, the pH of which is kept close to 7.4 by the presence of hydrogencarbonate ions, HCO_3^-.

KEY TERM

A **buffer solution** is a solution that can resist changes in acidity or alkalinity.

Buffers rely on the dissociation of weak acids. Consider the weak acid HA:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Because it is a weak acid, $[H^+(aq)]$ is about equal to $[A^-(aq)]$ and is very small. If a small amount of an alkali is added, the OH^- ions react with the H^+ ions, removing them from the solution as water molecules and this disturbs the equilibrium.

By Le Chatelier's principle, more HA will dissociate to restore the equilibrium, maintaining the pH. On the other hand, if some acid is added, the H^+ ions will react with the A^- ions, forming more HA. However $[A^-(aq)]$ is very low and it would soon be used up.

This problem is solved by adding more A^- ions in the form of a salt of the acid HA, such as Na^+A^-. Now there are more A^- ions to 'mop up' any added H^+ ions. So a buffer solution consists of a weak acid and a salt of that weak acid.

In the case of the buffer system in blood, the equilibrium is:

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons CO_2(aq) + H_2O(l)$$

Addition of H^+ ions moves the equilibrium to the right, forming more carbon dioxide and water, while the addition of OH^- ions removes H^+ ions causing the equilibrium to move to the left, releasing more H^+ ions.

To calculate the pH of a buffer you can use the expression:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{salt}]}{[\mathrm{acid}]}$$

In other words, you need to know the $\mathrm{p}K_a$ of the acid, together with the concentrations of the acid and its salt in the solution.

WORKED EXAMPLE

Calculate the pH of an ethanoate–ethanoic acid buffer made by mixing 25 cm^3 of 0.100 mol dm^{-3} sodium ethanoate solution with 25 cm^3 of 0.100 mol dm^{-3} ethanoic acid solution. K_a for ethanoic acid is 1.8×10^{-5} mol dm^{-3}.

Answer

Mixing the two solutions means that the total volume is 50 cm^3, so the concentration of each is halved. Substituting these values in the equation gives:

$$\begin{aligned}\mathrm{pH} &= -\log(1.8 \times 10^{-5}] + \log\frac{0.050}{0.050} \\ &= -\log(1.8 \times 10^{-5}) + \log 1 \\ &= -\log(1.8 \times 10^{-5}) + 0 \\ &= 4.7\end{aligned}$$

Solubility product

Another application of equilibrium involves the solubility of sparingly soluble salts. All the applications looked at so far have involved homogeneous equilibria (all the substances in the same phase). With sparingly soluble substances there are heterogeneous equilibria to consider, with one component in the solid phase and the remainder in the aqueous phase.

For example, in a saturated solution of silver chloride this equilibrium exists:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

The equilibrium constant for this system can be written as

$$K_c = \frac{[Ag^{+}(aq)][Cl^{-}(aq)]}{[AgCl(s)]}$$

However, it is not possible to change the concentration of a solid, so a new equilibrium constant is defined that allows for this. This is called the solubility product, K_{sp}, and is the product of the concentrations of the ions present in solution:

$$K_{sp} = [Ag^{+}(aq)][Cl^{-}(aq)]$$

In this case, the units of K_{sp} are mol^{2} dm^{-6}.

WORKED EXAMPLE

Suppose you want to know if a precipitate will form when you mix equal quantities of solutions of silver nitrate and potassium chloride. Let us assume that the concentration of potassium chloride is 1.0×10^{-3} mol dm^{-3} and that of silver nitrate is 1.0×10^{-5} mol dm^{-3}. K_{sp} for silver chloride at 298 K is 1.8×10^{-10} mol^{2} dm^{-6}.

Answer

On mixing equal quantities of the two solutions, each concentration is halved. Substituting the numbers into the expression for K_{sp} gives:

$$K_{sp} = [Ag^{+}(aq)][Cl^{-}(aq)]$$

$$[Ag^{+}(aq)][Cl^{-}(aq)] = (5.0 \times 10^{-6}) \times (5.0 \times 10^{-4})$$

$$= 2.5 \times 10^{-9}\,\text{mol}^{2}\,\text{dm}^{-6}$$

This is higher than 1.8×10^{-10} mol^{2} dm^{-6} so a precipitate will form.

This same method can be used to calculate the concentration of one ion if you know that of the other ion along with the relevant K_{sp}. It is also important to remember to write out the equilibrium equation and expression because not all salts have a 1 : 1 ratio of ions.

If a substance is added that has an ion in common with the sparingly soluble salt, the concentration of that ion affects the equilibrium. This is known as the **common ion effect**.

So, if sodium chloride solution is added to a saturated solution of silver chloride:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

more solid is precipitated. This is because the added chloride ions push the equilibrium backwards, according to Le Chatelier's principle.

NOW TEST YOURSELF

1 Magnesium fluoride is sparingly soluble in water.

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^{-}(aq)$$

a Write an expression for the solubility product, K_{sp}, for magnesium fluoride.

b What are the units for K_{sp} in this case?

Partition coefficients

You are familiar with water as a solvent, but many other liquids also act as solvents:

- In general, substances dissolve when the energy of the solute–solvent system is lower when the solute is dissolved than when the solute is not dissolved.
- This is usually the case if the interactions between the solute particles and the solvent molecules are similar to those between the solvent molecules themselves.

Molecules can attract each other in a variety of ways:

- ionic attractions
- ion–dipole attractions
- hydrogen bonding
- van der Waals' forces

As a general rule:

- Polar solvents are more likely to dissolve ionic compounds, substances that form hydrogen bonds and/or molecules with dipoles.
- Non-polar solvents dissolve solutes that have molecules attracted to each other by only van der Waals' forces.

Partition for a non-polar solvent

Iodine is a molecular solid and is unlikely to be as soluble in water (polar solvent) as it is in hexane (non-polar solvent). If some iodine crystals are shaken with a mixture of water and hexane until no further change occurs, the iodine distributes itself between the two solvents according to its solubility in each.

On measuring the amount of iodine dissolved in each solvent, you find that the ratio of the concentrations is constant, no matter how much iodine is used. This constant is known as the **partition coefficient**, $\boldsymbol{K_{pc}}$:

$$K_{pc} = \frac{[I_2(\text{hexane})]}{[I_2(\text{water})]}$$

Here, K_{pc} is an equilibrium constant for the dissolving of iodine in the two solvents. Partition coefficients have no units.

WORKED EXAMPLE

0.95 g of iodine (M_r = 254) was shaken with a mixture of 50 cm^3 of water and 50 cm^3 of tetrachloromethane. The organic layer was run off, and the aqueous layer titrated with standard 0.01 mol dm^{-3} sodium thiosulfate solution. 25.0 cm^3 of the aqueous layer required 4.30 cm^3 of thiosulfate for complete reaction. Calculate the partition coefficient of iodine between water and tetrachloromethane.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightleftharpoons S_4O_6^{2-}(aq) + 2I^-(aq)$$

Answer

$$\text{Concentration of } I_2 \text{ in the aqueous layer} = \frac{0.5 \times 4.30 \times 10^{-5}}{25 \times 10^{-3}}$$

$$= 8.6 \times 10^{-4}\,\text{mol dm}^{-3}$$

$$\text{Mass of } I_2 \text{ in the aqueous layer} = 8.6 \times 10^{-4} \times 254 \times 50 \times 10^{-3}$$

$$= 0.0109\,\text{g}$$

So the mass of iodine in the CCl_4 layer was $(0.95 - 0.0109) = 0.9391\,\text{g}$

The partition coefficient of I_2 between water and CCl_4 is $\dfrac{0.0109}{0.9391}$ or 1.16×10^{-2}.

REVISION ACTIVITY

a Assuming that the dissociation of carbonic acid, H_2CO_3, to form HCO_3^- is the major contributor to the pH of the solution, and that K_a for this reaction is 4.4×10^{-7}, calculate the pH of a solution containing 0.01 mol dm^{-3} of H_2CO_3.

b Calculate the pH of an ethanoate–ethanoic acid buffer solution made by mixing 50 cm^3 of 0.200 mol dm^{-3} sodium ethanoate solution with 25 cm^3 of 0.200 mol dm^{-3} ethanoic acid solution. K_a for ethanoic acid is 1.8×10^{-5} mol dm^{-3}.

END OF CHAPTER CHECK

By now you should be able to:

- define mathematically the terms pH, K_a, pK_a and K_w and use them in calculations; calculate [$H^+(aq)$] and pH value for strong and weak acids and strong alkalis
- define a buffer solution; explain how one can be made and explain how it controls pH using chemical equations; calculate the pH of a buffer solution from data provided

- understand, use and write an expression for the term solubility product, K_{sp}; calculate K_{sp} from concentrations and vice versa
- understand and use the common ion effect to explain the different solubility of a compound in a solution containing a common ion; perform calculations using K_{sp} and the concentration of a common ion
- state what is meant by the term partition coefficient, K_{pc}, and calculate and use a partition coefficient for a system in which the solute is in the same physical state as the two solvents
- understand the factors that affect the numerical value of K_{pc} in terms of the polarities of the solute and solvents used