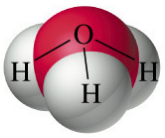
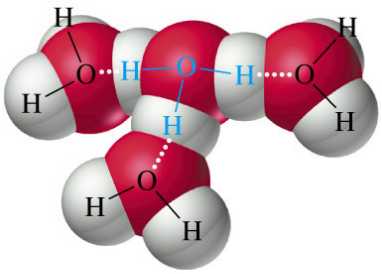
Advanced Higher Chemistry (Revised)

Unit 2 - Physical Chemistry

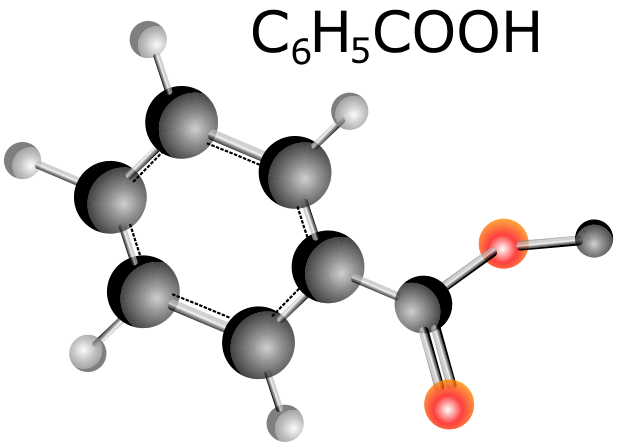
CHEMICAL EQUILIBRIUM



Hydronium ion
H_3O^+



A hydrated proton
$H_9O_4^+$



A carboxylic acid molecule.
Benzoic Acid.

Pupil Notes Learning Outcomes & Questions

2. CHEMICAL EQUILIBRIUM

Reactions at equilibrium

2.1 *A chemical reaction is at equilibrium when the composition of the reactants and products remains constant indefinitely*

2.2 *The **equilibrium constant** (**K**) characterises the equilibrium composition of the reaction mixture*

2.3 *The equilibrium constant can be measured in terms of **concentration** or, for gases, in terms of **pressure***

2.4 *For the general reaction* $aA + bB \rightarrow cC + dD$

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

*where [A], [B], [C] and [D] are the equilibrium concentrations of A, B, C and D, respectively, and **a**, **b**, **c** and **d** are the stoichiometric coefficients in a balanced reaction equation.*

2.5 *In a **homogeneous** equilibrium all the species are in the same phase*

2.6 *In a **heterogeneous** equilibrium the species are in more than one phase*

2.7 *The concentration of **pure solids or pure liquids** are constant and are given the **value 1** in the equilibrium equation*

2.8 *Equilibrium constants are **independent** of the particular concentrations or pressures of species in a given reaction.*

2.9 *Equilibrium constants depend on the reaction temperature*

2.10 ***Le Chatelier's principle** states that when a reaction is subject to change the composition alters in such a way as to minimise the effects of that change.*

2.11 *For **endothermic reactions** a rise in temperature causes an increase in K, i.e. the yield of product is increased.*

2.12 *For **exothermic reactions** a rise in temperature causes a decrease in K, i.e. the yield of product is decreased.*

2.13 *The effects of changes in concentration or pressure on the position of equilibrium can be explained quantitatively in terms of a fixed equilibrium constant.*

2.14 *The presence of a **catalyst** does not effect the equilibrium constant.*

Equilibria involving ions

2.15 *The **Bronsted-Lowry** definitions of acid and base state that an acid is a proton donor and a base is a proton acceptor*

2.16 *For every acid there is a **conjugate base**, formed by loss of a proton.*

2.17 *For every base there is a **conjugate acid**, formed by gain of a proton.*

2.18 *The ionisation of water can be represented by:*

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

2.19 *Water is **amphoteric**.*

2.20 *The equilibrium constant for the ionisation of water is known as the **ionic product** and is represented by:*

$$K_w = [H_3O^+] \; [OH^-]$$

2.21 *The value of the ionic product varies with temperature.*

2.22 *At 25°C the value of K_w is approximately 1×10^{-14} mol^2 l^{-2}*

2.23 *A shorthand representation of H_3O^+ is H^+. **Stoichiometric equations and equilibrium expressions can be written using H^+ instead of H_3O^+ where meaning is clear.***

2.24 *The dissociation in aqueous solution of an acid of general formula HA can be represented as:*

$$HA_{(aq} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

2.25 *The acid dissociation constant of acid HA is given by:*

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

2.26 *The conjugate base of an acid of general formula HA is A^-.*

2.27 *The pH of a weak acid can be calculated from the dissociation constant.*

2.28 *The dissociation constant of an acid can be represented by pKa where*

$$pK_a = -\log K_a$$

Indicators

2.29 *Indicators are weak acids for which the dissociation can be represented as*

$$HIn_{(aq} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}$$

2.30 *The acid dissociation constant is represented as K_{In} and is given by the following expression*

$$K_{In} = \frac{[H_3O^+]\,[In^-]}{[HIn]}$$

2.31 *In aqueous solution the colour of the acid (HIn) is distinctly different from that of its conjugate base (In^-).*

2.32 *The colour of the indicator is determined by the ratio of [Hln] to [In^-].*

2.33 *The theoretical mid-point at which colour changes occurs when*

$$[H^+] = K_{In} \quad or \quad pH = pK_{In}$$

2.34 *The colour change is assumed to be distinguishable when [Hln] and [In^-] differ by a factor of 10.*

2.35 *The pH range over which a colour change occurs can be estimated by the expression*

$$pH = pK_{In} \pm 1$$

Buffer solutions

2.36 *A buffer solution is one in which the pH remains approximately constant when small amounts of acid or base are added.*

2.37 *An acid buffer consists of a solution a weak acid and one of its salts.*

2.38 *In an acid buffer solution the weak acid can supply hydrogen ions when these are removed by the addition of a small amount of base. The salt of the weak acid provides the conjugate base, which can absorb excess hydrogen ions produced by the addition of a small amount of acid.*

2.39 *A basic buffer consists of a solution of a weak base and one of its salts.*

2.40 *In a basic buffer solution the weak base removes excess hydrogen ions and the conjugate acid provided by the salt supplies hydrogen ions when these are removed.*

2.41 *The pH of an acid buffer solution can be calculated from its composition and from the acid dissociation constant.*

2.42 *The required compositions of an acid buffer solution can be calculated from the desired pH and from the acid dissociation constant.*

$$pH = pK_a - \log\left(\frac{Acid}{Salt}\right)$$

2.1 EQUILIBRIUM

Reactions at equilibrium

Introduction

Often in Chemistry, particularly when doing calculations, it is convenient to assume that reactions go to completion. This means that the reactants ultimately form the products and no reactants (unless some are present in excess) are left.

Many reactions, however, never go to completion but are in a state of ***equilibrium***, with reactants and products always present. A chemical reaction is said to be in equilibrium when the composition of the reactants and products remains constant over time. In other words, at equilibrium the concentration of the reactants and products remains constant.

For an equilibrium to be established the reaction must take place in a ***closed system***. A closed system is one that allows energy to be transferred to or from the surroundings but not the reactants or products. Reactants and products are trapped in the reaction vessel and reactant molecules form the products and product molecules react to reform the starting materials. The concept of a closed system can be illustrated using the following examples.

Ethanoic acid is a weak acid and shows little tendency to dissociate:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

All the species are in solution and cannot 'escape', therefore this is a closed system. On the other hand, sodium carbonate reacts with dilute acid to give a salt, water and carbon dioxide, which escapes from solution and therefore this is not a closed system and equilibrium is never established. The reaction goes to completion:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

If this reaction was to be carried out in a sealed container (do not attempt this in the laboratory) then equilibrium would be established since no carbon dioxide could escape:

$$Na_2CO_3(aq) + 2HCl(aq) \rightleftharpoons 2NaCl(aq) + H_2O(l) + CO_2(g)$$

When a system is in equilibrium and the concentration of reactants and products is constant, the forward reaction (reactants to products) and the reverse reaction (products to reactants) do not stop. At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction. This means that there is no overall change in the composition of the reaction mixture when equilibrium has been established.

The equilibrium constant

Every equilibrium is described by an equilibrium constant (K), which is normally measured in terms of the concentrations of the species at equilibrium but can in the case of gaseous reactions be measured in terms of pressure (more strictly by the partial pressures of the gases involved).

The same equilibrium position is always reached whether starting with the reactants or with the products at a given temperature. This means that K is independent of concentrations or pressures of the species in the equilibrium. For the general reaction:

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

K is given by the equation:

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

where [ ] indicates the equilibrium concentration of the species present and these concentrations are raised to the power of the number of moles of the species in the balanced equation. Equilibrium can be described as homogeneous, i.e. all the species are in one state, or heterogeneous, i.e. the species are in more than one state.

Units

Equilibrium constants have no units, they are dimensionless. The reasons for this are beyond the Advanced Higher syllabus and in fact many textbooks show no units but do not explain the reasons why. A very brief and simplistic explanation is given below.

Equilibrium constants should be calculated using activity (relative concentration) not actual concentration. Simply, the concentration terms in the equilibrium constant equation shown above should be relative concentrations, i.e. a concentration C with respect to a standard concentration C_o. As both C and C_o have the same units, the units cancel out and the value obtained, the activity, has no units. Thus, using these values to calculate K means that K is dimensionless.

Pure solids and solvents

When a pure solid is present in an equilibrium reaction or a liquid is used as a solvent the concentration, at a given temperature, does not vary to a measurable extent and it is given the concentration value of 1 in the equilibrium equation. (This again comes from using activity and not

concentration.)

The effect of changing concentration

The effect of a change of concentration of one of the species in an equilibrium can be demonstrated using the following experiments.

(1) Dilute ethanoic acid has a pH of 3.0. When a spatula of solid sodium ethanoate is dissolved in the acid the pH rises to 3.5. This process is repeated four times and the results show that with each addition of sodium ethanoate the pH gradually increases:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$
$$CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

As the pH increases on the addition of $CH_3COO^-(aq)$, the concentration of H^+ must be falling. In other words, $H^+(aq)$ ions are reacting with the increased concentration of $CH_3COO^-(aq)$ ions to produce more $CH_3COOH(aq)$ compared to the forward reaction. This happens because the rate of the reverse reaction increases because of the increased concentration of $CH_3COO^-(aq)$. This continues until the rates of the forward and reverse reactions are again equal and equilibrium is re-established. The position of the equilibrium has moved to the left, but the value of *K* remains constant.

Overall, the increase in the concentration of $CH_3COO^-(aq)$ is compensated for by an increase in the concentration of $CH_3COOH(aq)$ molecules and a decrease in the concentration of $H^+(aq)$ ions (therefore a rise in pH), thus keeping the value of *K* the same:

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

(2) Dilute ammonia solution has a pH of 10.0. When a spatula of solid ammonium chloride is dissolved in the acid the pH falls to 9.5. This process is repeated four times and the results show that with each addition of ammonium chloride the pH decreases:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

In this case the concentration of $OH^-(aq)$ falls because of its reaction with the increased concentration of $NH_4^+(aq)$ ions to produce $NH_3(aq)$ and $H_2O(l)$. As before, this change occurs because the rate of the reverse reaction, compared to the forward reaction, increases because of the increased concentration of $NH_4^+(aq)$. This continues until the rates of the forward and reverse reactions are again equal and equilibrium is

re-established. The position of the equilibrium has moved to the left, but the value of *K* remains the same.

Overall the increase in the concentration of $NH_4^+(aq)$ is compensated for by a decrease in the concentration of the $OH^-(aq)$ ion (therefore a fall in pH) and an increase in the concentration of $NH_3(aq)$ and $H_2O(l)$ molecules, thus keeping the value of *K* the same:

$$K = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

(3) When dilute hydrochloric acid is added to a yellow solution of sodium chromate the solution turns orange:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$
yellow orange

The added $H^+(aq)$ ions increase the rate of the forward reaction compared to the reverse reaction. This continues until the rates of the forward and reverse reactions are the same and equilibrium is re-established. The position of the equilibrium has moved to the right.

Overall the increase in the concentration of $H^+(aq)$ is compensated for by a decrease in the concentration of $CrO_4^{2-}(aq)$ ions and an increase in the concentration of $Cr_2O_7^{2-}(aq)$ ions and $H_2O(l)$ molecules, thus keeping the value of *K* the same:

$$K = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}$$

These three experiments show that changes in the concentration of one of the species in a reaction at equilibrium will bring about a shift in the equilibrium position to maintain the value of *K* as a constant (at constant temperature).

This fact is stated formally in **Le Chatelier's principle**, which states that 'when a reaction at equilibrium is subjected to change, the composition alters in such a way as to minimise the effects of the change'.

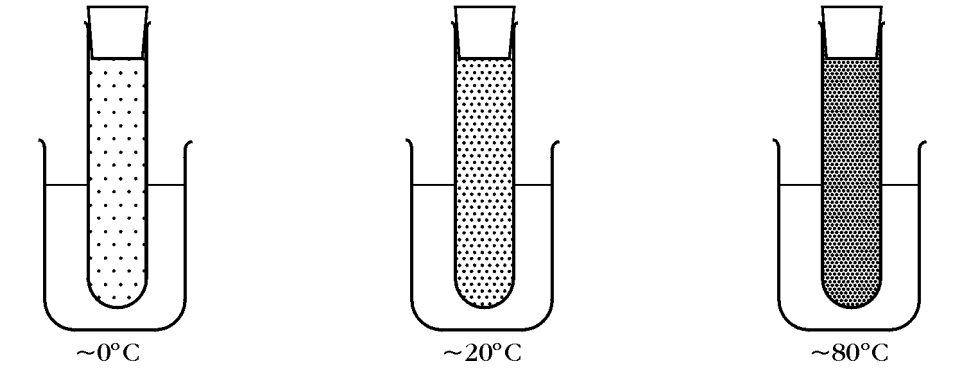
The effect of changing temperature

The effect of a temperature change on a reaction in equilibrium can be demonstrated in the laboratory using the following example:

$$\underset{\text{yellow}}{N_2O_4\ (g)} \rightleftharpoons \underset{\text{brown}}{2NO_2\ (g)} \qquad \Delta H = +\text{ve}$$

The reaction of concentrated nitric acid with copper turnings produces a mixture of N_2O_4 and NO_2. Three boiling tubes filled to an equal colour intensity with this gas mixture are collected at room temperature. One is placed in ice water (~0°C) and one in hot water (~80°C) while the third is kept, as a control, at room temperature (Figure 3). The three tubes are left for about five minutes and the colour intensities are then compared.

Figure 3



From the colour changes that have taken place, it is evident that the relative concentrations of N_2O_4 and NO_2 have been changed by a change in temperature. This means that the actual value of *K* has changed. Equilibria are therefore temperature dependent. In fact most equilibrium constants are quoted at a specific temperature.

The reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +ve$$

is endothermic for the forward reaction and exothermic for the reverse. The equilibrium constant is:

$$K = \frac{[NO_2]^2}{[N_2O_4]}$$

The colour change from 20°C to 0°C shows that more N_2O_4 is formed at 0°C and therefore $[N_2O_4]$ increases and $[NO_2]$ decreases. This leads to a fall in the value of *K*.

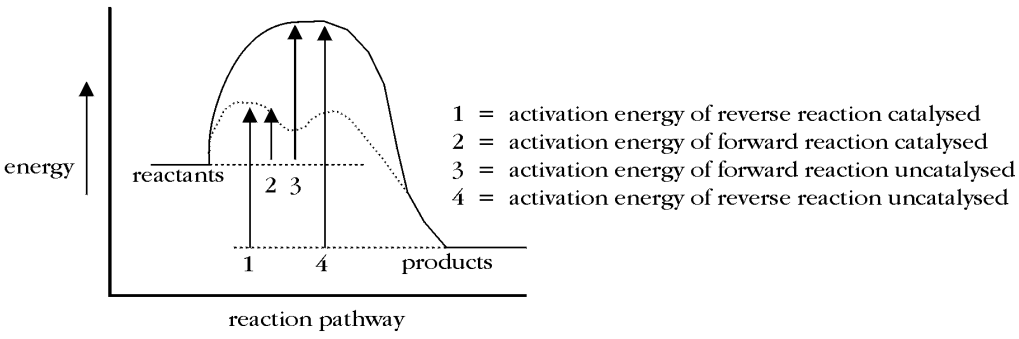
Similarly, the colour change from 20°C to 80°C shows that more NO_2 is formed at 80°C and therefore $[NO_2]$ increases and $[N_2O_4]$ decreases. This leads to a rise in the value of *K*. These observations can be related to the ΔH value and are summarised in the following way.

For endothermic reactions a rise in temperature causes an increase in K while for exothermic reactions a rise in temperature causes a decrease in K.

The effect of a catalyst

The effect of a catalyst on an equilibrium at constant temperature is best looked at in terms of a potential energy diagram (Figure 4).

Figure 4



The catalyst lowers the activation energy of both the forward and reverse reactions by the same amount and there is no change in the equilibrium concentrations. The position of the equilibrium is therefore unaltered and the value of *K* at a specific temperature remains unchanged.

All a catalyst does is to speed up the rate at which equilibrium is established.

K and the position of the equilibrium

The value of *K* gives an indication of how far the equilibrium lies to one side of a reaction or the other.

It is important to note that the value of *K* gives no indication about the rate at which the state of dynamic equilibrium is established. Also, a catalyst does not increase the percentage conversion of reactants into products, it only speeds up the rate of attainment of equilibrium.

Table 1 illustrates how the value of *K* gives an indication of the position of the equilibrium.

Table 1

System	**Value of *K***	**Position of equilibrium**
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$	1.7×10^7 at 25°C	Because $K>>1$ the equilibrium lies to the right
$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$	1.8×10^{-5} at 25°C	Because $K<<1$ the equilibrium lies to the left
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	0.87 at 55°C	Because $K\approx1$ the equilibrium lies to neither the left nor the right

Equilibria involving ions

Acid/base equilibria

Historically acids were defined as producing hydrogen ions in solution and bases as producing hydroxide ions in solution. These two ions combine in the neutralisation equation:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

As research continued throughout the nineteenth and early twentieth centuries, the definitions had to be refined. For example, pure hydrogen chloride is a gas that contains no H^+ ions and ammonia has no OH^- ions but can neutralise an acid. It was also discovered that the H^+ ion could not exist in aqueous solution. The H^+ ion is so small (10^{-3} pm compared to other cations at 10^2 pm) that the electric field it creates is huge and in water it attracts a lone pair of electrons to form H_3O^+, which is called the hydronium ion (or the oxonium ion or the hydroxonium ion):

$$H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)$$

The shorthand $H^+(aq)$ is always used in stoichiometric and equilibrium equations, although this is not strictly accurate.

In 1923 the new discoveries led two chemists, Brønsted and Lowry, to define acids and bases in a different way:

An acid is any substance capable of donating a proton.
A base is any substance capable of accepting a proton.

When an acid donates a proton the species left is called the conjugate base of that acid. When a base accepts a proton the species formed is called the conjugate acid of that base.

Table 2 gives examples of these relationships.

Table 2

acid	+	**base**	⇌	**conjugate base**	+	**conjugate acid**
HCl	+	H_2O	⇌	Cl^-	+	H_3O^+
CH_3COOH	+	H_2O	⇌	CH_3COO^-	+	H_3O^+
H_2O	+	NH_3	⇌	OH^-	+	NH_4^+
H_2O	+	CH_3COO^-	⇌	OH^-	+	CH_3COOH

Table 2 also illustrates the **amphoteric** nature of water since it can act both as a proton acceptor and a proton donor.

The dissociation of water

In Brønsted–Lowry terms the ionisation of water is represented by:

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

The equilibrium constant is $K = \dfrac{[H_3O^+][OH^-]}{[H_2O]^2}$

Since water is a liquid, $[H_2O] = 1$ (see page 11), giving:

$$K = [H_3O^+][OH^-]$$

This particular equilibrium constant is known as the **ionic product** (K_w) for water and has the value of 1.0×10^{-14} at 25°C.

The water equilibrium is more usually written as:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = [H^+][OH^-]$$

In **pure** water, for every molecule which ionises, one H^+ and one OH^- ion are produced, hence the $[H^+]$ in mol l^{-1} must equal the $[OH^-]$ in mol l^{-1}, i.e. the number of H^+ and OH^- ions in water are equal.

Substitution of $[OH^-]$ by $[H^+]$ in the above equilibrium expression gives:

$$\begin{aligned} [H^+]^2 &= 10^{-14}\ \text{mol}^2\ l^{-2} \\ \text{taking square roots } [H^+] &= 10^{-7}\ \text{mol}\ l^{-1} \\ \text{also } [OH^-] &= 10^{-7}\ \text{mol}\ l^{-1} \end{aligned}$$

Note also that $[H_2O]$ in pure water = $\dfrac{1000}{18}$ mol l^{-1} (neglecting the slight ionisation) = 55.5 mol l^{-1}, therefore the ratio of hydrogen ions to water molecules, in water is:

$$\frac{H^+}{H_2O} = \frac{10^{-7} \times 6.02 \times 10^{23}}{55.5 \times 6.02 \times 10^{23}} = \frac{1}{55.5 \times 10^7}$$

On average there is one H^+ ion and one OH^- ion for every 555 million H_2O molecules!

K_w is always quoted as 1.0×10^{-14} at 25°C since the value varies with temperature:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H \text{ +ve}$$

As the reaction is endothermic, an increase in temperature moves the equilibrium to the right and a decrease moves it to the left.

Table 3 shows the values of K_w at different temperatures.

Table 3

Temperature (°C)	K_w ($\times 10^{-14}$)
18	0.6
25	1.0
40	2.9
75	16.9

The pH scale

From the Higher course it will be remembered that the pH of an aqueous solution is a measure of the concentration of hydrogen ions in the solution. In fact the pH of any aqueous solution can be calculated using the expression:

$$pH = -\log[H_3O^+] \qquad \text{or} \qquad pH = -\log[H^+]$$

The following examples illustrate its use:

pure water $[H^+] = 10^{-7}$ pH = 7
1.0 mol l^{-1} HCl $[H^+] = 1.0\ (10^0)$ pH = 0
0.2 mol l^{-1} HCl $[H^+] = 0.2\ (2 \times 10^{-1})$ $pH = -\log 2 - \log(10^{-1})$
$= -0.3 + 1.0 = 0.7$
0.01 mol l^{-1} NaOH $[OH^-] = 10^{-2}$, $[H^+] = 10^{-12}$, pH = 12
0.5 mol l^{-1} NaOH $[H^+] = 2 \times 10^{-14}$ $pH = -\log 2 - \log(10^{-14})$
$= -0.3 + 14 = 13.7$

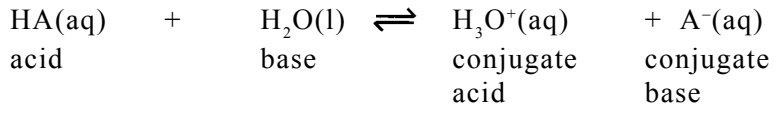
For calculations involving strong acids and alkalis it can be assumed that they are 100% dissociated and that the small number of hydrogen ions supplied by the water can be ignored.

Question

Calculate the pH of the following solutions:
(a) 0.35 mol l^{-1} HNO_3
(b) 0.14 mol l^{-1} H_2SO_4 (assume fully ionised)
(c) 0.78 mol l^{-1} NaOH

The dissociation of acids

The dissociation of any acid, HA, in aqueous solution can be represented by the equation:



The dissociation constant of acid HA from the above equation is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

and is a measure of the strength of the acid.

The $[H_2O]$ has been omitted as it is the solvent and taken to be 1.

In **strong acids** the above equilibrium lies to the right with effectively complete dissociation so that K_a has no meaning. However, some acids do not dissociate well (less than 5%) in aqueous solution and these are called **weak acids**.

Conveniently, nearly all acids fall into one of these two categories. Within the weak acids, the value of K_a gives a measure of how weak (or how dissociated) the acid is: the smaller the value of K_a, the weaker the acid.

Calculation of pH of a weak monobasic acid

Using the dissociation constant from the previous page, the pH of a weak monobasic acid can be calculated.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Since $[H_3O^+] = [A^-]$:

$$K_a = \frac{[H_3O^+]^2}{[HA]}$$

Taking logs of both sides:

$$\log K_a = \log[H_3O^+]^2 - \log[HA]$$
$$= 2\log[H_3O^+] - \log[HA]$$

but $-\log[H_3O^+]$ = pH, and assigning $-\log K_a$ as pK_a we get:

$-pK_a = -2pH - \log[HA]$

$pK_a = 2pH + \log[HA]$

For a weak acid HA of concentration c mol l^{-1}, [HA] at equilibrium will be approximately equal to the original concentration c mol l^{-1}, so:

$$pK_a = 2pH + \log c$$

which can be rearranged to give the expression:

$$pH = \tfrac{1}{2}pK_a - \tfrac{1}{2}\log c$$

This equation is only valid for weak acids in which the concentration of HA at equilibrium is almost the same as the original concentration.

The weaker the acid is, the more closely the calculated pH will approach the actual pH of the solution. The stronger the acid, the more inaccurate the calculated pH will be.

Questions

1. Calculate the pH of a 0.2 mol l^{-1} solution of ethanoic acid if $K_a = 1.7 \times 10^{-5}$.

2. 0.02 mol l^{-1} benzoic acid C_6H_5COOH, a monobasic acid, was found to have a pH of 2.94. Calculate the K_a of this weak acid.

Indicators

Indicators are used to determine the end-point in an acid–alkali titration. A suitable indicator must be chosen for any given reaction. Indicators are dyes whose colours are sensitive to pH. An indicator is usually a weak acid that dissociates as shown:

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

The unionised form of the indicator (HIn) has a different colour from its conjugate base (In^-). The equilibrium constant (K_{In}) for the above equation is:

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

Rearranging this expression gives:

$$\frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H_3O^+]}$$

This shows that the relative concentrations of the two coloured forms is a function of the H_3O^+ concentration, i.e. the pH of the solution. It follows therefore that the colour of the indicator in any given solution depends on the relative concentrations of the two coloured forms, which in turn is determined by the pH. The theoretical point at which the colour change occurs is when [HIn] = [In^-] and therefore $K_{In} = [H_3O^+]$. In other words, the colour change occurs when pK_{In} = pH. In practice the colour change cannot be seen when [HIn] = [In^-] and it is only distinguishable when [HIn] and [In^-] differ by a factor of 10.

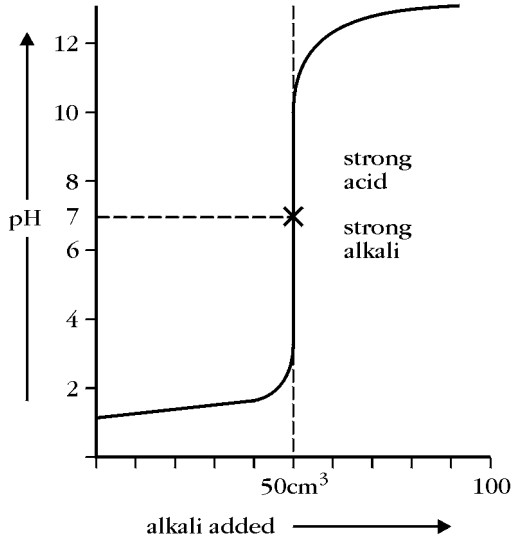
The pH range over which a colour change can be seen is therefore established using the expression:

$$pH = pK_{In} \pm 1 \qquad (\log 10 = 1)$$

The appropriate indicator for any titration must be chosen such that the colour change occurs over the pH range when the pH is changing very rapidly. This means that the indicator must change colour during the addition of, say, half a drop of reagent. The indicator for a reaction can therefore be chosen by reference to titration curves, which are drawn from data obtained by measuring the pH of an acid continuously against the volume of alkali added during and after neutralisation (Figures 9–12).

Consider the titration of a strong acid with a strong alkali (Figure 9), e.g. the addition of 0.01 mol l^{-1} NaOH solution to 50 cm^3 of 0.01 mol l^{-1} HCl. The pH of the original acid solution will be 2 ($[H^+] = 10^{-2}$ mol l^{-1}). When 49 cm^3 of NaOH solution has been added there will be only 1 cm^3 of the original 0.01 mol l^{-1} HCl left un-neutralised. This amount is now in an overall volume of 50 + 49 cm^3 ~ 100 cm^3, i.e. the solution is now 0.0001 mol l^{-1} with respect to $H^+(aq)$, thus $[H^+] = 10^{-4}$ mol l^{-1} and pH = 4.

Figure 9



On adding 49.9 cm^3 alkali, only 0.1 cm^3 of acid will remain in ~100 cm^3 solution and therefore $[H^+] = 10^{-5}$ mol l^{-1} and pH = 5. When 49.99 cm^3 alkali has been added the pH of the solution is 6 and at 50 cm^3 the pH rises to 7 and neutralisation is complete.

Note the rapid rise in pH as the end-point of the titration is approached. Thereafter the alkali added has nothing to react with and the pH continues to rise to a final value of 12.

The titration curves in Figures 10 and 11 show the pH changes that occur on titrating weak and strong alkalis (50 cm^3) with equimolar solutions of strong and weak acids (50 cm^3) respectively.

Figure 10

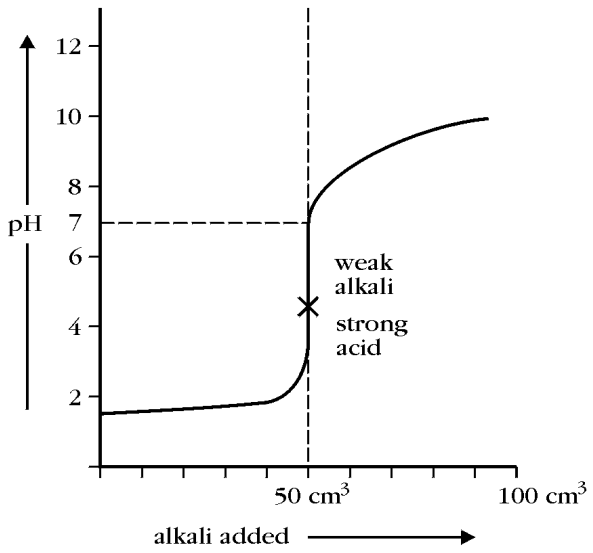
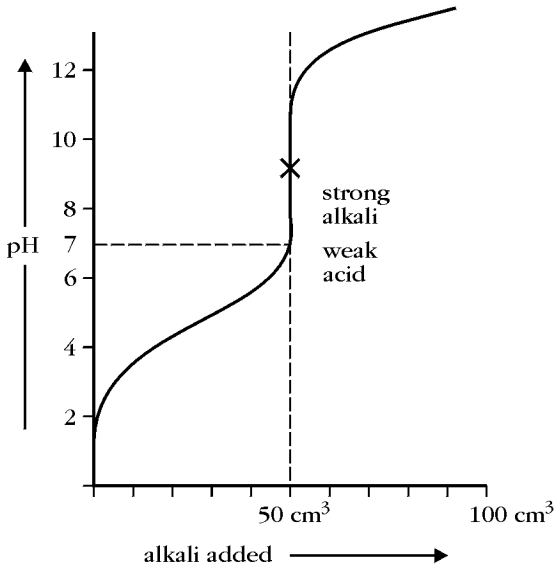


Figure 11



It can be seen from Figures 9, 10 and 11 that there is a region of rapid pH change around the end-point. For an indicator to be suitable, its pH range must fall within this region. From Figure 9 it can be seen that for a strong acid and strong alkali a suitable indicator can have a colour change within the pH range 3–10. From Figure 10 an indicator for a strong acid and weak alkali would change somewhere in the range 3–7. Similarly, from Figure 11, for a weak acid and strong alkali, a suitable indicator must change colour within the pH range 7–10.

It is not possible to select any suitable indicator for a weak acid/weak alkali combination (Figure 12), since the pH does not change rapidly enough at the end-point, i.e. the titration curve does not have an almost vertical section like the others.

Figure 12

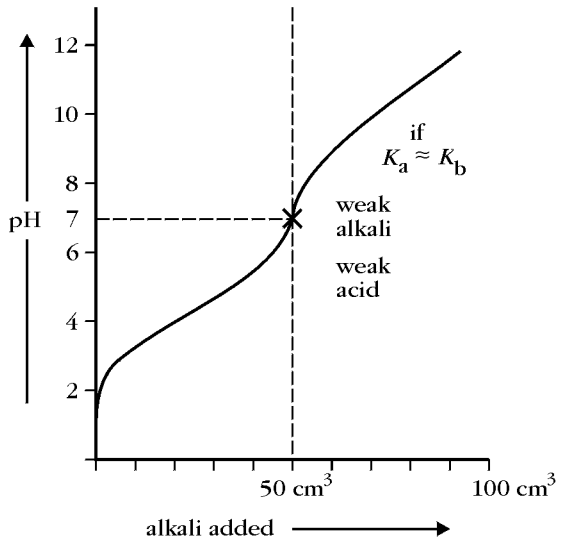


Table 4 shows some common indicators, their pH range and colours.

Table 4

Name of indicator	pH of colour change	Colour (HIn)	Colour (In)
Methyl orange	3.0–4.4	Orange	Yellow
Methyl red	4.2–6.3	Red	Yellow
Bromothymol blue	6.0–7.6	Yellow	Blue
Phenolphthalein	8.0–9.8	Colourless	Red

Question

From Table 4 above, calculate the pK_a and K_a for the four indicators.

Buffer solutions

A buffer solution is one in which the pH of the solution remains approximately constant when small amounts of acid or base are added or the solution is diluted with water.

An **acidic buffer** consists of a solution of a weak acid and one of its salts with a strong alkali. A **basic buffer** consists of a solution of a weak base and one of its salts with a strong acid.

Both types of buffer solution work in the same way.

In an acid buffer solution, the weak acid supplies more hydrogen ions when the existing ones are removed by a base being added, while the salt of the weak acid provides the conjugate base to react with the hydrogen ions when small amounts of acid are added.

In a basic buffer solution, the weak base reacts with the hydrogen ions when acid is added and the salt provides the conjugate acid, which dissociates to replace the hydrogen ions when these are removed by addition of small amounts of base.

In consequence, the pH hardly changes in both cases.

This principle is illustrated by an acid buffer of weak acid HA and the sodium salt of that acid NaA. In solution the following occurs:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \quad \text{equilibrium}$$

$$\text{and} \quad NaA(aq) \rightarrow Na^+(aq) + A^-(aq) \quad \text{fully ionised}$$

NaA is fully ionised in solution and therefore the $[A^-]$ is very large, forcing the equilibrium to the left.

Addition of small volumes of H^+ does not alter the pH greatly since an increase in $[H^+]$ favours the reverse reaction (HA formation) to maintain K_a. Since $[A^-]$ is high compared to $[H^+]$ in the original buffer solution, its ability to remove H^+ ions is substantial (but not infinite) and the pH of the solution is maintained.

In the same way, addition of OH^- does not alter the pH greatly since the OH^- ions combine with the H^+ of the weak acid until K_w is attained. Removal of H^+ means that more HA ionises, giving $H^+ + A^-$ until equilibrium is re-established, and the pH of the solution is maintained:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$[H_3O^+] = \frac{[K_a][HA]}{[A^-]}$$

where [HA] is the concentration of the acid as it is a weak acid and [A^-] is the concentration of the salt as it is fully ionised and very little comes from the acid dissociating. Therefore:

$$[H_3O^+] = \frac{K_a[\text{acid}]}{[\text{salt}]}$$

If the buffer solution has water added to it, i.e. it is diluted, both [acid] and [salt] are equally affected and therefore [H_3O^+] and the pH remain unaltered.

An efficient buffer must have a reasonable reserve of HA and A^- as the H^+ from HA removes added OH^- and the A^- removes added H^+, therefore since:

$$[H_3O^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

if [acid] = [salt] the buffer will have the same ability to resist addition of H^+ and OH^-.

Similar reasoning can be used to show how a basic buffer solution operates.

The pH of an acid buffer solution can be calculated by conversion of the above equation:

$$[H_3O^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

to $$\text{pH} = \text{p}K_a - \log\frac{[\text{acid}]}{[\text{salt}]}$$

Questions

1. Calculate the pH of the buffer solution made from 1.0 mol l^{-1} methanoic acid and 1.78 mol l^{-1} sodium methanoate solution. The pK_a of methanoic acid is 3.8.

2. Calculate the pH of the buffer solution made from 0.1 mol l^{-1} solution of ethanoic acid and potassium ethanoate. The pK_a of ethanoic acid is 4.8.

The composition of an acid buffer solution can be calculated from the same equation as long as the required pH and the pK_a of the acid are known, e.g. to make an acidic buffer of pH 5.0, using propanoic acid pK_a 4.9.

$$\text{pH} = \text{p}K_a - \log\frac{[\text{acid}]}{[\text{salt}]}$$

$$5.0 = 4.9 - \log\frac{[\text{acid}]}{[\text{salt}]}$$

$$\log\frac{[\text{acid}]}{[\text{salt}]} = -0.1$$

$$\log\frac{[\text{salt}]}{[\text{acid}]} = 0.1$$

$$\frac{[\text{salt}]}{[\text{acid}]} = 1.26, \text{which is a ratio of } \frac{1.26}{1}$$

The buffer is therefore made by mixing 1.26 moles of sodium propanoate with 1.0 mole of propanoic acid per litre of solution required.

Question

Calculate the concentrations of acid and salt solutions required to make:

(a) a buffer of pH 6.0 from carbonic acid and sodium hydrogen carbonate (pK_a of carbonic acid is 6.4)

(b) a buffer of pH 3.1 from chloroethanoic acid and its potassium salt (pK_a of chloroethanoic acid is 2.9).

Buffer solutions are important in biological systems, especially those where enzymes work within narrow pH ranges, e.g. blood is a buffered solution of pH around 7.4 (CO_2/bicarbonate equilibrium is maintained by respiration and excretion of bicarbonate into the urine).

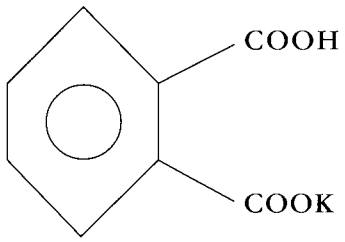
The sea is also a buffer because it contains significant concentrations of carbonate and hydrogencarbonate ions. These act as a buffer, maintaining the pH of the sea within certain limits, and this allows marine life to exist:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

Phosphate solutions can act as buffers because the second and third dissociations of phosphoric acid are weak:

$$H_3PO_4 \rightarrow H^+ + H_2PO_4$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

Another useful buffer in the laboratory is potassium hydrogenphthalate, which is a weak acid and its salt all in one molecule:



Q1 The value for the equilibrium constant, K, for a specific example of the following reaction is equal to 1:

$$\text{acid} + \text{alcohol} \rightleftharpoons \text{ester} + \text{water}$$

a) ***i)*** Predict the maximum yield of ester, given this value of K. **1**

ii) Give ***one*** reason why this yield might not be achieved in practice. **1**

b) A student suggested that a careful choice of catalyst could increase the yield of ester. Comment on this suggestion. **2**

b) Another student suggested that increasing the concentration of the alcohol in the reaction mixture would increase the yield of ester by altering the value of K. Comment on this suggestion. **2**

(6)

Q2 The balanced equation for the principle reaction in the contact process is:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = \text{-ve}$$

a) Write an expression for K, the equilibrium constant for this reaction, when the system has reached equilibrium. **1**

b) ***i)*** State Le Chatelier's Principle. **2**

ii) Use this generalisation to predict how an increase in temperature would affect the position of equilibrium. **1**

iii) Explain the effect this increase in temperature would have on the value of K. **1**

(5)

Q3 Write the formula for the conjugate base of each of the following acids:

a) H_3O^+ **1**

b) H_2O **1**

c) NH_4^+ **1**

(3)

Q4 In the Data Booklet, the solubility of barium sulphate, shown by the equation:

$$BaSO_{4(s)} + \text{water} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

is given as less than 1 g l^{-1}. In a more advanced text book, it is noticed that an equilibrium constant, known as the solubility product K_{sp}, can be written to represent the dissolving process. K_{sp} is equal to the product of the concentrations of the ions in the solution:

$$K_{sp} = [Ba^{2+}] \; x \; [SO_4^{2-}]$$

a) At 298K, K_{sp} for barium sulphate is equal to $1 \; x \; 10^{-10}$ mol^2 l^{-2}

For a saturated solution of barium sulphate at 298K, calculate

i) the concentration of barium ions dissolved in the solution. **1**

ii) the mass of barium sulphate dissolved in 1 litre of solution. **3**

b) A small quantity of very soluble sodium sulphate is now added to the saturated solution of barium sulphate.

i) What will happen to the value of K_{sp} ? **1**

ii) What will happen to the concentration of barium ions? **1**

SYS 96 (6)

Q5 Substance X is distributed between equal volumes of two immiscible liquids as shown in the diagram. The number of dots represents the relative distribution of X in the two liquids at equilibrium.

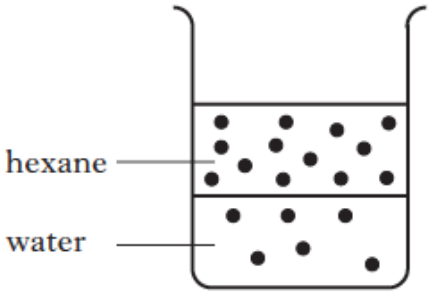
The value of the equilibrium constant for this system is

A 0·46

B 0·50

C 2·00

D 2·17.



$\mathbf{X}(aq) \rightleftharpoons \mathbf{X}(hexane)$

RevAdV 13 (1)

Q6 ***a)*** Calculate the pH of a solution of ethanoic acid with a concentration of 0.01 mol l^{-1}. (K_a ethanoic acid = 1.7 x 10^{-5}). **3**

b) A mixture of ethanoic acid and sodium ethanoate solution constitutes a buffer solution. Show how this buffer solution is able to resist change in pH when small quantities of each of the following are added.

i) hydrochloric acid **2**

ii) sodium hydroxide solution **2**

c) The simplified equation for the pH of a buffer solution is:

$$\text{pH} = \text{pK}_\text{a} - \log\left(\frac{[\text{acid}]}{[\text{salt}]}\right)$$

A buffer solution was prepared from ethanoic acid (0.25 mol l^{-1}) and sodium ethanoate solution (0.15 mol l^{-1}).

Calculate the pH of the buffer solution. **2**

SYS 94 ***(9)***

Q7 Propanoic acid is a weak acid. Sodium propanoate is a salt which can be formed from it. Both propanoic acid and sodium propanoate can be used as mould inhibitors.

a) Calculate the pH of 0·10 mol l^{-1} propanoic acid solution. **2**

b) 0·20 moles of sodium propanoate are added to 100 cm^3 of the 0·10 mol l^{-1} solution of propanoic acid.

Calculate the pH of the buffer solution formed. **2**

RevAdV 13 ***(4)***

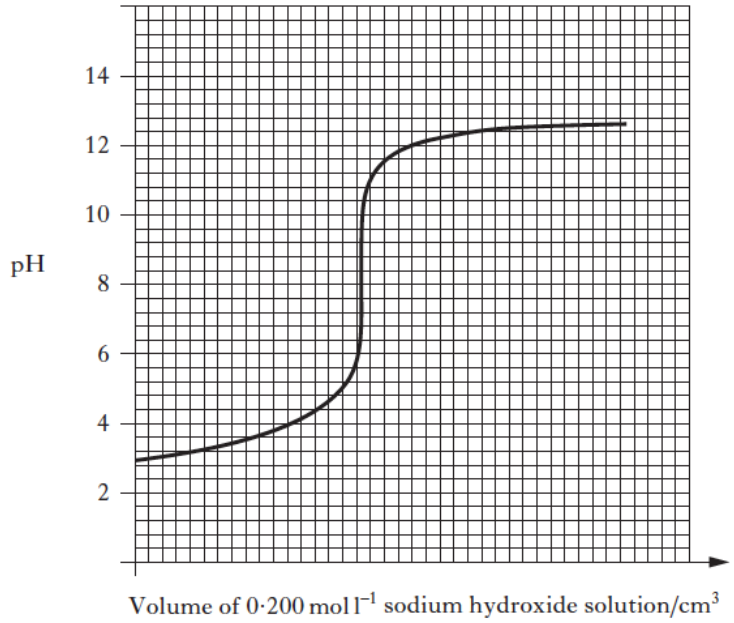
Q8 The salt sodium propanoate, $C_2H_5COO^-Na^+$, is produced when sodium hydroxide reacts with propanoic acid. When sodium propanoate is dissolved in water an alkaline solution is formed.

a) ***i)*** Write the formula for the conjugate base of propanoic acid. **1**

ii) Explain why a solution of sodium propanoate is alkaline. **2**

Q8 b) The titration of propanoic acid with sodium hydroxide can be followed using a pH meter.

The graph below was obtained when 40·0 cm^3 of an aqueous solution of propanoic acid was titrated with 0·200 mol l^{-1} sodium hydroxide.



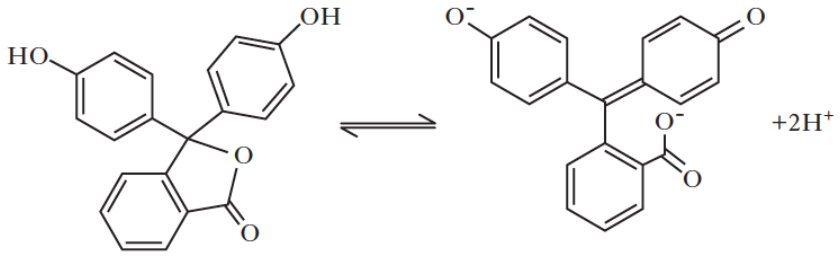
i) The initial pH was recorded as 2·93.
Calculate the initial concentration of the propanoic acid. **3**

ii) The table shows four indicators which could be used to detect the end-point of a titration.

Indicator	pH range
Phenolphthalein	8·3 – 10·0
Bromophenol red	5·2 – 6·8
Methyl orange	3·1 – 4·4
Methyl red	4·2 – 6·3

Why is phenolphthalein the most suitable indicator for ***this*** titration? **1**

c) Phenolphthalein is a weak acid. The equation shows how phenolphthalein dissociates.



unionised molecule (colourless) ion (pink)

With reference to the above equilibrium, explain why the colour changes from colourless to pink at the end-point. **1**

RevAdV 12 (8)

Q9 The ionic product of water (K_w) is usually taken to be 10^{-14} , but it varies with temperature. The following table shows this variation.

Temperature / K	K_w
273	0.114×10^{-14}
283	0.293×10^{-14}
298	1.008×10^{-14}
323	5.476×10^{-14}
373	51.3×10^{-14}

a) What is meant by the term 'ionic product of water' ? **1**

b) Since K_w varies with temperature, the pH of pure water is not always 7. Calculate the pH of pure water at 373K. **3**

c) The ionisation of water is endothermic. Explain how the information in the table supports this statement. **1**

SYS 91 ***(5)***

Q10 Phosphoric(V) acid, H_3PO_4, is triprotic. When neutralised by sodium hydroxide solution, it can form three different salts.

a) Give the formula for each of the three sodium salts of the acid. **2**

b) The first stage of the ionisation of phosphoric (V) acid has a dissociation constant of 7.08×10^{-3} .

Calculate the approximate pH of a 0.1 mol l^{-1} solution of phosphoric(V) acid. (You can assume that the other two stages in the ionisation do not significantly affect the hydrogen ion concentration). **3**

SYS 91 ***(5)***

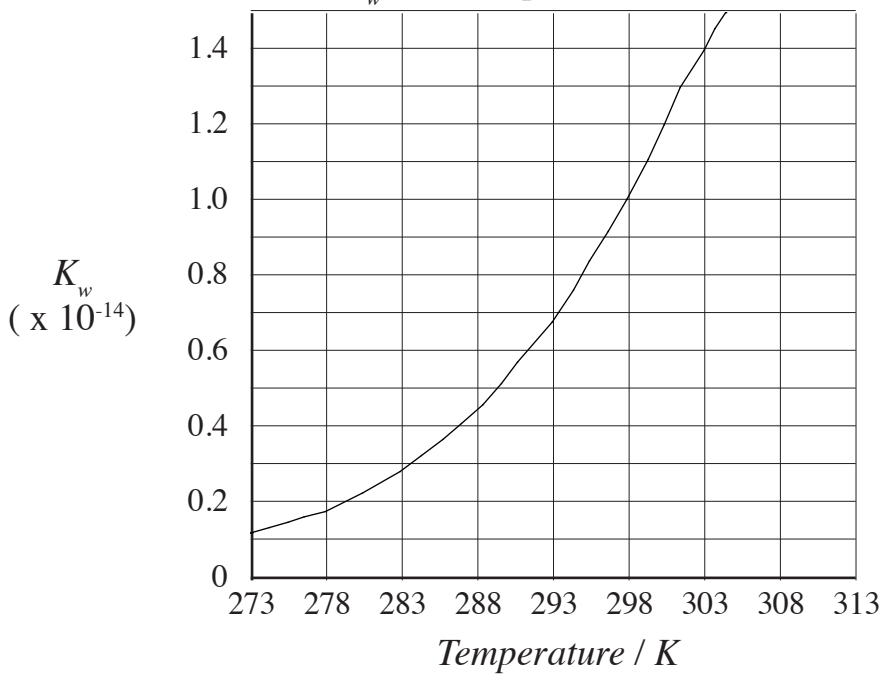
Q11 Limewater is a saturated solution of calcium hydroxide. At 20°C, 100 cm^3 of a limewater solution conatined 0.126g of calcium hydroxide.

a) Calculate the concentration of of hydroxide ions, in mol l^{-1}, in this solution. **2**

b) Using your answer to part ***a)***, calculate the pH of the solution **2**

SYS 99 ***(4)***

Q12 At 298K the dissociation constant K_w for water is 1 x 10^{-14}.
The graph shows the variation of K_w with temperature.



From the graph calculate the pH of water at 288K **3**

SYS 96 ***(3)***

Q13 Most Indicators are weak acids of general formula HIn. Their dissociation in aqueous solution can be represented as:

$$\underset{\text{colour A}}{HIn} \rightleftharpoons H^+ + \underset{\text{colour B}}{In^-}$$

$$K_{indicator} = \frac{[H^+]\,[In^-]}{[HIn]}$$

At the end point, $[In^-] = [HIn]$ and therefore $K_{indicator} = [H^+]$.

Use the above and the information in the table below to answer the questions that follow.

Indicator	$K_{indicator}$	***Colour change (low pH → high pH)***
Methyl yellow	5.1 x 10^{-4}	red → yellow
Bromothymol blue	1.0 x 10^{-7}	yellow → blue
Thymol Blue	1.3 x 10^{-9}	yellow → blue

Q13 contd

a) At what pH would the colour change be expected to take place in each of the indicators? **2**

b) A student is asked to carry out a titration of ethanoic acid and sodium hydroxide. Which indicator in the table is most suitable for the titration? Give a reason for your choice. **2**

SYS 95 ***(4)***

Q14 250 cm^3 of sulphurous acid solution was prepared by dissolving 1.6g of sulphur dioxide in water at 298K.

a) Calculate the concentration of the acid in mol l^{-1}. **2**

b) Using your answer to ***a)*** and your Data Booklet, calculate the pH of the acid solution. **3**

c) Why is this acid unsuitable for use as a primary standard? **1**

d) If this acid is standardised using a strong alkali, what will be the approximate pH range of the indicator needed for the titration? **1**

SYS 98 ***(7)***

Answers

Q1 ***a)*** ***i)*** Yield = 50% **1**

ii) side reactions or impurities **1**

b) The suggestion is wrong. (1)
A catalyst only brings the reaction to the same equilibrium more quickly. (1)
2

c) K is a constant at a fixed temperature and altering the alcohol concentration will not change the value of K. (1)
It will, however, increase the yield of the ester as the forward reaction will be increased. (1)
2
(6)

Q2 ***a)*** $K = [SO_3]/[SO_2]^2 [O_2]$ **1**

b) ***i)*** Le Chatelier's principle states that if a system is subjected to any change, the system readjusts itself to counteract the applied change.
2

ii) Increased temperature favours ΔH +ve. Thus the backward reaction is favoured and the equilibrium position moves to the left.
1

iii) K will decrease. **1**
(5)

Q3 ***a)*** H_2O **1**

b) OH^- **1**

c) NH_3 **1**
(3)

Q4 ***a)*** $[Ba^{2+}] = \sqrt{1 \times 10^{-10}} = 1 \times 10^{-5}$ mol l^{-1} **1**

b) $BaSO_4 = 233.4$ g mol^{-1} (1)
Mass dissolving = $233.4 \times 1 \times 10^{-5}$ (1)
= 2.334×10^{-3}g (1) **3**

c) ***i)*** K_{sp} is a constant therefore stays the same. **1**

ii) The equilibrium moves to the left therefore $[Ba^{2+}]$ decreases. **1**
(6)

Q5 ***D*** **1**
(1)

Q6 ***a)*** pH = $\frac{1}{2}pK_a - \frac{1}{2}\log c$ (1)
= $\frac{1}{2} \times 4.77 - \frac{1}{2}\log 0.01$ (1)
= $2.385 - (-1)$
= 3.4 (1)

or $K_a = [H^+]^2/[CH_3COOH]$ (1)

Therefore $[H^+] = \sqrt{(1.75 \times 10^{-5} \times 0.01)}$ (1)
= $\sqrt{1.7 \times 10^{-7}}$
= 4.12×10^{-4}

pH = $-\log [H^+] = -\log 4.12 \times 10^{-4} = 3.4$ (1) **3**

b) $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$ acid

$CH_3COO^-Na^+_{(s)} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$ salt

i) Add HCl – the $H^+_{(aq)}$ ions added react with the excess $CH_3COO^-_{(aq)}$ from the salt. (1 + 1) **2**

ii) Add NaOH – the $OH^-_{(aq)}$ added reacts with the $H^{+(aq)}$ from the acid and more CH_3COOH ionises to replace the $H^+_{(aq)}$ ions removed. (1 + 1) **2**

c) $pH = pK_a - \log[acid]/[salt]$ = $4.77 - \log 0.25/0.15$ (1)
= 4.55 (1) **2**
(9)

Q7 ***a)*** pH = ½ pKa – ½ log c (1)

= 2·935 or 2·94 or 2·9 (1) **2**

b) pH = pKa – log [acid]
[salt] (1)

= 6·171 or 6·17 or 6·2 1 (1) **2**

(4)

Q8 ***a)*** ***i)*** $C_2H_5COO^-_{(aq)}$ or $CH_3CH_2COO^-_{(aq)}$ or $C_3H_5O_2^-{}_{(aq)}$
(aq) can be omitted **1**

ii) Conjugate base removes hydrogen ions (1)
Water equilibrium shifts right and hydroxide ions are in excess (1)
(Could also use equations to explain.) **2**

b) ***i)*** pH = ½ pKa – ½ log c (1)
2·93 = ½ (4·87) – ½ log c (1)
c = 0·1 mol l^{-1} (lose mark if no unit) (1) **3**

ii) pH range is best match for equivalence point or end-point or pH range of phenolphthalein fits into "vertical" part of graph **1**

c) At the end-point the excess OH^- ions react with the H^+ ions at the right of the equilibrium equation thus shifting the position of equilibrium to the right. **1**

(8)

Q9 ***a)*** The product of $[H^+_{(aq)}] \times [OH^-_{(aq)}]$ **1**

b) $[H^+]^2 = 51.3 \times 10^{-14}$, (1)

therefore $[H^+] = 7.16 \times 10^{-7}$ and (1)

pH = 6.15 (1) 3

c) An increase in temperature favours ΔH +ve. As the temperature increases so does the value of Kw and therefore more ions form.

Thus the ionisation is endothermic. **1**

(5)

Q10 ***a)*** NaH_2PO_4; Na_2HPO_4; Na_3PO_4 (any two, 1+1) **2**

b) $K_a = [H^+][H_2PO4^-]/[H_3PO4]$ (1)

$7.08 \times 10^{-3} = [H^+]^2/0.1$

$[H^+]^2 = 7.08 \times 10^{-4}$

$[H^+] = 2.66 \times 10^{-2}$ (1)

pH = 1.6 (1) **3**

(You could also use pH = ½pKa – ½log[C].) ***(5)***

Q11 ***a)*** $[Ca(OH)_2] = 0.126/74$ moles per 100 cm^3

$= 0.017$ mol l^{-1} (1)

$[OH^-] = 2 \times 0.017 = 0.034$ mol l^{-1} (1) **2**

b) $[H^+] = 10^{-14}/0.034 = 2.94 \times 10^{-13}$ (1)

pH = – log (2.94×10^{-13}) = 12.53 (1) **2**

(4)

Q12 K_w at 288K = 0.45×10^{-14} (1)

$[H^+] = 6.71 \times 10^{-8}$ (1)

pH = $-\log (6.71 \times 10^{-8}) = 7.17$ (1) ***(3)***

Q13 ***a)*** Methyl yellow pH = 3.3;
bromothymol blue pH = 7;
thymol blue pH = 8.9 (3 correct = 2; 1 or 2 correct = 1) **2**

b) Thymol blue. (1)

The titration involves a weak acid and strong alkali therefore the salt will have a pH above 7. (1) ***2***

(4)

Q14 ***a)*** 1.6/64.1 = 0.025 mol in 250 cm^3 (1)

= 0.1 mol l^{-1} (1) **2**

b) pH = ½ pKa – ½logc (1)

= (½ × 1.8) – (½ log 0.1) (1)

= 1.4 (1)

or K_a = $[H^+][HSO^{3-}]/[H_2SO_4]$ (1)

H^+ = $\sqrt{Ka \times [H_2SO_4]} = \sqrt{(1.5 \times 10^{-2}) \times (0.1)}$ (1)

= 3.87×10^{-2}

pH = – log $[H^+]$ = 1.4 (1)

(If the wrong equation is used then zero marks.) **3**

c) It is volatile, i.e. SO_2 is given off from solution.

or It is unstable. **1**

d) Accept range within 7.5 – 10.5 but must have at least 1.5 of a difference between values. **1**

(7)