BUFFER SOLUTIONS

When an acid is added to a neutral solution, the pH of the solution falls, and when an alkali is added to such a solution, its pH rises.

Some solutions resist pH changes when small quantities of an acid or alkali are added to them such solutions are known as buffer solutions.

A buffer solution is a solution that resists pH changes, when a small amount of acid or alkali is added to it.

There are two types of buffer solutions

Acidic buffer (a buffer solution with pH less than seven)

This is a solution which contains a weak acid and its salt from a strong base. e.g

- Ethanoic acid(CH_3COOH) and sodium ethanoate(CH_3COONa)
- Benzoic acid(C_6H_5COOH) and sodium benzoate(C_6H_5COONa)
- Phosphoric acid(H_3PO_4) and sodium phosphate(Na_2HPO_4)

Basic buffer (a buffer solution with pH greater than seven)

This is solution which contains a weak base and its salt from a strong acid.eg

- Aqueous ammonia(NH_3) and ammonium chloride(NH_4Cl)
- Aqueous ammonia(NH_3) and ammonium sulphate($(NH_4)_2SO_4$)
- Phnylamine and phenyl ammonium chloride

Action of acidic buffer solution

We will take ethanoic acid and sodium ethanoate as a typical example. The ethanoic acid is a weak acid, and so it partially ionizes as

$$CH_3COOH\ (aq) \rightleftharpoons CH_3CO\bar{O}\ (aq) + H^+\ (aq)$$

Sodium ethanoate is an ionic salt, and in solution consists of free sodium and ethanoate ions.

$$CH_3COONa\ (aq) \longrightarrow CH_3CO\bar{O}\ (aq) + Na^+\ (aq)$$

This mixture therefore contains a relatively high concentration of undissociated acid molecules, excess ethanoate ions and a small amount of hydrogen ions formed by the original ionization of ethanoic acid.

When small amount of hydrogen ions from acid is added to such a solution, these will nearly all combine with the ethanoate ions to form ethanoic acid molecules and so the pH will hardly change at all.

$$CH_3CO\bar{O}(aq) + H^+(aq) \longrightarrow CH_3COOH\ (aq)$$

When small amount of hydroxyl ions from an alkali are added to this solution, almost all of these will react with the un- ionised ethanoic acid to make ethanoate ions and water. So the pH will hardly change at all.

$$CH_3COOH\ (aq) + \bar{O}H\ (aq) \longrightarrow CH_3CO\bar{O}\ (aq) + H_2O(l)$$

In other words, trying to alter the pH of the solution by increasing the concentration of H^+ or $\bar{O}H$ largely fails.

Action of basic buffer solution

We will take aqueous ammonia solution and ammonium chloride as a typical example. The ammonia is a weak base and so it partially ionises as

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

Ammonium chloride is an ionic salt, and so its solution consist of free ammonium and chloride ions:

$$NH_4Cl\ (aq) \longrightarrow NH_4^+\ (aq) + Cl^-\ (aq)$$

The mixture therefore contains a relatively high concentration of undissociated ammonia molecules and excess ammonium ions and enough hydroxyl ions to make the solution alkaline.

When a small amount of hydrogen ions are added to such a solution, these will nearly all combine with the ammonia present to make more ammonium ions, and so the pH hardly changes at all.

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$

When a small amount of hydroxyl ions are added to such a solution, most of them react with ammonium ions to produce ammonia molecules and water.

$$NH_4^+(aq + \bar{O}H\ (aq) \longrightarrow NH_3(aq) + H_2O(l)$$

Once again, trying to change the pH by increasing the concentration of H^+ or $\bar{O}H$ largely fails.

CALCULATING pH OF A BUFFER SOLUTION

The pH of a buffer solution can be calculated using the dissociation constant of the weak acid or base

For an acidic buffer containing ethanoic acid and its salt with a strong base, the dissociation of ethanoic acid is considered.

$$CH_3COOH\,(aq) \rightleftharpoons CH_3CO\bar{O}\,(aq) + H^+\,(aq)$$

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

Assumption: ethanoate ions are produced by the dissociation of the salt, sodium ethanoate. Therefore $[CH_3COO^-]$ = $[CH_3COONa]$ = $[salt]$

$[CH_3COOH]$= $[acid]$ since it partially ionises

$$[H^+]= \frac{K_a\,x[CH_3COOH]}{[CH_3COO\,^-]}$$

$$pH = -\log[H^+] = -\log(\frac{K_a\,x[CH_3COOH]}{[CH_3COO\,^-]})$$

$$pH = pKa+\log\frac{[salt\,]}{[acid\,]}$$

The pH of acidic buffer solution will depend on the value of pKa of weak acid and the proportion of concentration of a salt to the concentration of acid.

This equation can be used to determine the amount of acid and conjugate base needed to make a buffer solution of a certain pH

For an alkaline buffer containing ammonia and ammonium chloride, the ionization of ammonia molecules is considered

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH(aq)$$

$$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3]}$$

Assumption: ammonium ions are produced by the dissociation of the salt, ammonium chloride. Therefore $[NH_4^+]$ = $[NH_4Cl]$ = $[salt]$

$[NH_3]$ = $[base]$ since the base partially ionises

$[\bar{O}H]= \frac{k_b\ x[NH_3]}{[NH_4Cl]}$

From Kw = $[H^+][\bar{O}H]$

$[\bar{O}H]=\frac{K_w}{[H^+]}$

$\frac{K_w}{[H^+]}$ = K_b x $\frac{[NH_3]}{[NH_4{}^+]}$

$[H^+]=\frac{K_w}{K_b}$ x $\frac{[NH_4{}^+]}{[NH_3]}$

pH = (pK_w-pK_b)+ log$\frac{[NH_3]}{[NH_4{}^+]}$

The pH of basic buffer will depend on ionic product of water, base ionization constant of weak bases and the proportion of weak bases and its salt of a strong acid in the solution.

Worked examples

Example one

A buffer solution was made by dissolving 18.5g propanoic acid,CH_3CH_2COOH, and 12.0g of sodium propanoate,CH_3CH_2COONa,in water and then making the volume up to 250cm^3.

(pKa for propanoic acid=4.87,C=12,O=16,Na=23,H=1)

a)calculate the pH of a buffer solution

b)calculate the change in pH when;

i)1.00cm^3 of 10moldm^{-3} hydrochloric acid.

ii)1.00cm^3 of10moldm^{-3} sodium hydroxide solution to 1000cm^3 of the buffer solution.

Solution:

Molar mass of CH_3CH_2COOH =12x3+6x1+16x2 = 74g

Moles of CH_3CH_2COOH in 250cm^3 = $\frac{18.5}{74}$

Moles of CH_3CH_2COOH in 1000cm^3 = $\frac{18.5\ x\ 1000}{74\ x\ 250}$ = 1.00moldm^{-3}

Molar mass of CH_3CH_2COONa = 12x3+5x1+16x2+23x1= 96g

Moles of CH_3CH_2COONa in 250cm^3 = $\frac{12}{96}$

Moles of CH_3CH_2COONa in 1000cm^3= $\frac{12\ x\ 1000}{96\ x\ 250}$ = 0.50moldm^{-3}

pKa = 4.87

Ka = $10^{-4.87}$

Ka = 1.35 x 10^{-5} moldm^3

Ka = $\frac{[CH_3CH_2CO\overline{O}][H^+]}{[CH_3CH_2COOH]}$

Assumption:

Because virtually all the propanoate ions $CH_3CH_2COO^-$, are coming from the sodium propanoate, and almost none from propanoic acid, the propanoate concentration is also equal to 0.50moldm^{-3} and that so little of propanoic acid ionizes that its equilibrium concentration is 1.00moldm^{-3}.

1.35x 10^{-5} = $\frac{0.500x[H^+]}{1.00}$

$[H^+]$ = 2.70 x10^{-5} moldm^{-3}

pH= 4.57

b i)the buffer solution works by combining the hydrogen ions from the added acid with propanoate ions from the sodium propanoate, turning them into propanoic acid. This means that the concentration of the propanoate ions will fall, while that of the propanoic acid will rise.

Number of moles of H+ ions added = $\frac{1\ x\ 10}{1000}$ = 0.010mol

$CH_3CH_2COO^-\ (aq) + H^+\ (aq) \longrightarrow CH_3CH_2COOH\ (aq)$

New moles of $CH_3CH_2COO^-$ = 0.5 – 0.01 =0.49

New moles of CH_3CH_2COOH = 1.00 + 0.01 =1.01

Ka = $\frac{[CH_3CH_2CO\overline{O}][H^+]}{[CH_3CH_2COOH]}$

$1.35\text{x } 10^{-5} = \frac{0.49.\ x\ [H^+]}{1.01}$

$[H^+] = 2.78\text{x}10^{-5}$

pH = 4.56

change in pH 0.01

ii) The buffer solution works by reacting the hydroxide ions from the sodium hydroxide with propanoic acid, producing more propanoate ions. This means that the concentration of the propanoate ions will rise, while that of the propanoic acid will fall.

Number of moles of ^-OH ions added = $\frac{1\ x\ 10}{1000}$ = 0.010moles

$CH_3CH_2COOH\ (aq) + {}^-OH\ (aq) \longrightarrow CH_3CH_2COO^-\ (aq) + H_2O(\ l)$

New moles of $CH_3CH_2COO^-$ = 0.5 + 0.01 = 0.51

New moles of CH_3CH_2COOH = 1.00 - 0.01 = 0.99

$Ka = \frac{[CH_3CH_2CO\overline{O}][H^+]}{[CH_3CH_2COOH]}$

$1.35\text{x } 10^{-5} = \frac{0.51.x[H^+]}{0.99}$

$[H^+] = 2.62\text{x}10^{-5}$

pH = - log$[H^+]$ = -log(2.62x10^{-5}) = 4.58

change in pH is 0.01

Example two

Calculate the pH of a buffer solution made by mixing 50cm^3 of 0.300moldm^{-3} ethanoic acid with 100cm^3 of 0.600 moldm^{-3} sodium ethanoate.
(Ka for ethanoic acid = 1.75 x 10^{-5} moldm^{-3})

Total volume 100 +50 =150cm^3

Moles of ethanoic acid in the total volume of 150cm^3 = $\frac{0.300x50}{1000}$ = 0.015

Moles of ethanoic acid in 1000cm^3 = $\frac{0.015x1000}{150}$ = 0.100moldm^{-3}

Moles of sodium ethanoate in the total volume of 150cm^3 = $\frac{0.600\ x\ 100}{1000}$ = 0.0600

Moles of sodium ethanoate in 1000cm^3 $= \frac{0.0600\,x\,1000}{150}$ = 0.400moldm^{-3}

$Ka = \frac{[CH_3CO\bar{O}][H^+]}{[CH_3COOH]}$

$[H^+] = \frac{K_a\ x[CH_3COOH]}{[CH_3CO\bar{O}]}$

$[H^+] = \frac{K_a\ x[CH_3COOH]}{[CH_3CO\bar{O}]} = \frac{1.75\ x\ 10^{-5}\ x\ 0.100}{0.400}$ = 4.375 x 10^{-6} moldm^{-3}

pH = -log(4.375x10^{-6})

= 5.36

Example three

A solution was made by mixing 30cm^3 of a 0.1M ethanoic acid and 20cm^3 of 0.1M sodium hydroxide solution. Calculate the pH of the resultant solution.

State any assumption made. (K_a for ethanoic acid = 1.8 x 10^{-5} moldm^{-3})

Solution

1000cm^3 of ethanoic acid solution contains 0.1 moles

30cm^3 of ethanoic acid solution contains $\frac{0.1\ x\ 30}{1000}$ = 3 x10^{-3} moles

1000cm^3 of sodium hydroxide solution contains 0.1 moles

20cm^3 of sodium hydroxide solution contains $\frac{0.1\ x\ 20}{1000}$ = 2 x10^{-3} moles

$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa\ (aq) + H_2O(l)$

One mole of sodium hydroxide reacts with one mole of ethanoic acid

Therefore moles of ethanoic acid reacting = 2 x10^{-3} moles

Excess moles of ethanoic acid in solution = 3 x10^{-3} – 2 x10^{-3} =1 x10^{-3} moles

The resultant solution is a buffer containing excess ethanoic acid and the salt sodium ethanoate formed

Total volume of the mixture (30+20) = 50cm^3

Concentration of ethanoate ions in the mixture = $\frac{2x\ 10^{-3}\ \ x\ 1000}{50}$ = 0.04moldm^{-3}

Concentration of ethanoic acid in the mixture = $\frac{1x\ 10^{-3}\ \ x\ 1000}{50}$ = 0.02moldm^{-3}

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

Assumption: ethanoate ions are produced by the dissociation of the salt, sodium ethanoate. Therefore $[CH_3COO^-]$ = $[CH_3COONa]$.

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

$[H^+]$ = $\frac{K_a\ x[CH_3COOH]}{[CH_3COO\ ^-]}$ = $\frac{1.8\ x\ 10^{-5}\ \ x\ 0.02}{0.04}$ = 9.0 x 10^{-6}moldm^{-3}

pH = -log(9.0 x 10^{-6}) = 5.0

Example four

Calculate the mass of sodium ethanoate that should be added to 1dm^3 of 0.1 M ethanoic acid at 25^0 C to give a solution whose pH is 5.5 State any assumption made.

(Ka for ethanoic acid =1.8 x 10 $^{-5}$ mol dm^{-3})

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

Assumption: ethanoate ions are produced by the dissociation of the salt, sodium ethanoate. Therefore $[CH_3COO^-]$ = $[CH_3COONa]$

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

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

pH = -log$[H^+]$

$[H^+]$ = $10^{-5.5}$ = 3.16 x 10^{-6} moldm^{-3}

$[CH_3CO\bar{O}]$ = $\frac{K_a[CH_3COOH]}{[H^+]}$ = $\frac{1.8\ x\ 10^{-5}\ \ x\ \ 0.1}{3.16\ x\ 10^{-6}}$ = 0.5696 moldm^{-3}

Molar mass of CH_3COONa= (12x2) +(1x3) +(16x2) +(23x1) =82

0.5696 moles of CH_3COONa weighs (0.5696 x 82) = 46.71g

Example five

A buffer solution was made by mixing 0.1 M ammonia solution and 0.025M Ammonium chloride in $1.0dm^3$

a) Calculate the pH of this solution.

b) Calculate the pH of the above solution when

i)$10cm^3$ of 0.1 M NaOH was added

ii)$10cm^3$ of 0.1M HCl was added .(K_b for ammonia = 1.8×10^{-5} $moldm^{-3}$)

Solution

a)Kb = $\frac{[NH_4^+][\bar{O}H]}{[NH_3]}$

$[\bar{O}H]$= $\frac{K_b[NH_3]}{[NH_4^+]}$

Assumption: $[NH_4^+] = [NH_4Cl]$

$[\bar{O}H]$= $\frac{1.8 \ x\ 10^{-5} x\ 0.1}{0.025}$ = 7.2×10^{-5} $moldm^{-3}$

$[H^+]$= $\frac{K_W}{[\bar{O}H]}$ = $\frac{1\ x\ 10^{-14}}{7.2\ \ x\ \ 10^{-5}}$ = 1.389×10^{-10}

pH = -log (1.389×10^{-10}) = 9.857

b) Moles of NaOH in $10cm^3$ = $\frac{0.1\ x\ 10}{1000}$ = 1×10^{-3}

After the addition of sodium hydroxide concentration of NH_3 increases by 0.001 while concentration of NH_4Cl decreases by 0.001 moles.

$NH_4^+(aq) + \bar{O}H(aq) \longrightarrow NH_3(aq) + H_2O(l)$

New concentration of NH_3 = 0.1 + 0.001 = 0.101moles

New concentration of NH_4^+ = 0.025 – 0.001 = 0.024 moles

a)K_b = $\frac{[NH_4^+][\bar{O}H]}{[NH_3]}$

$[\bar{O}H]$= $\frac{K_b[NH_3]}{[NH_4^+]}$

Assumption: $[NH_4^+] = [NH_4Cl]$

$[\bar{O}H] = \frac{1.8 \ x \ 10^{-5} x \ 0.101}{0.024}$ = 7.515 x 10^{-5} moldm^{-3}

$[H^+] = \frac{K_W}{[\bar{O}H]} = \frac{1 \ x \ 10^{-14}}{7.515 \ \ x \ 10^{-5}}$ = 1.320 x $1O^{-10}$

pH = -log (1.320 x 10^{-10}) = 9.879

ii) b) moles of HCl in 10cm^3 = $\frac{0.1 \ x \ 10}{1000}$ = 1 x 10^{-3}

After the addition of hydrochloric acid concentration of NH_4Cl increases by 0.001 while concentration of NH_3 decreases by 0.001 moles.

$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$

New concentration of NH_3 = 0.1 – 0.001 = 0.099moles

New concentration of NH_4^+ = 0.025 + 0.001 = 0.026 moles

$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3]}$

$[\bar{O}H] = \frac{K_b[NH_3]}{[NH_4^+]}$

Assumption: $[NH_4^+] = [NH_4Cl]$

$[\bar{O}H] = \frac{1.8 \ x \ 10^{-5} x \ 0.099}{0.026}$ = 6.854 x 10^{-5} moldm^{-3}

$[H^+] = \frac{K_W}{[\bar{O}H]} = \frac{1 \ x \ 10^{-14}}{6.854 \ \ x \ \ 10^{-5}}$ = 1.459 x 10^{-10}

pH = -log (1.459 x 10^{-10})

= 9.83

Example six

Calculate the pH of a solution obtained when 25cm^3 of 0.02 M HCl are added to 25cm^3 of 0.04M NH_3.(pK_b of ammonia is 4.76 at 25^{0}C).

Solution

1000cm^3 of hydrochloric acid contains 0.02 moles

25cm^3 of hydrochloric acid contains $\frac{0.02x25}{1000}$ = $5x10^{-4}$ moles

1000cm^3 of ammonia solution contains 0.04 moles

25cm^3 of ammonia solution contains $\frac{0.04x25}{1000}$ = $10x10^{-3}$ moles

$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$

One mole of HCl reacts with one mole of NH_3

Therefore moles of ammonia reacting = $5x10^{-4}$

Excess moles of ammonia = $10x10^{-3} - 5x10^{-4} = 5x10^{-4}$

The buffer formed is composed of excess NH_3 and the salt formed NH_4Cl

Total volume of the mixture =(25 +25) = 50cm^3

Concentration of ammonium ions in the mixture = $\frac{5x\ 10^{-4}\ \ x\ 1000}{50}$ = 0.01moldm^{-3}

Concentration of ammonia in the mixture = $\frac{5x\ 10^{-4}\ \ x\ 1000}{50}$ = 0.01moldm^{-3}

$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3]}$

$K_b = 10^{-4.76}$ = 1.738 x 10^{-5} moldm^{-3}

$[\bar{O}H] = \frac{K_b[NH_3]}{[NH_4^+]} = \frac{1.738\ X10^{-5}\ \ x\ \ 0.01}{0.01}$ = 1.738 x 10^{-5} moles

$K_W = [H^+][\bar{O}H]$

1 x 10^{-14} = $[H^+]$ x 1.738 x 10^{-5}

$[H^+]$ = 5.754 x 10^{-10}moldm^{-3}

pH = -log(5.754 x 10^{-10}) = 9.24

Example seven

In what proportions should ammonia and ammonium chloride be mixed in solution to give a buffer solution of pH 10.0? pK_b for NH_3 is 4.76

Solution

pH=10

$[H^+]$ = 1.00 x 10 $^{-10}$ moldm^{-3}

pK_b = 4.76

K_b =1.74 x10^{-5}moldm^{-3}

$pH = (pK_w - pK_b) + \log\frac{[NH_3]}{[NH_4{}^+]}$

$10 = (14-4.76) + \log\frac{[NH_3]}{[NH_4{}^+]}$

$0.76 = \log\frac{[NH_3]}{[NH_4{}^+]}$

$5.75 = \frac{[NH_3]}{[NH_4{}^+]}$

$\frac{5.75}{1.0} = \frac{[NH_3]}{[NH_4{}^+]}$

The concentration of ammonia to ammonium chloride should be 5.75 to 1.0

Application of buffer solutions

In medicine, injections into blood stream given for medical reasons should be buffered. The pH of living cells and blood must be maintained at its value of pH =7.4 any variation of about 0.5 in this pH could prove fatal.

In agriculture, specific plants grow in specific soil pH and therefore the pH of the soil has to be maintained. Fertilizers applied must be well buffered

In industrial processes, for example in fermentation process any change in pH would cause death of the fermenting organism's thus fermentation process must be buffered.

In Preservation of food

In Preparation of standard solutions of definite pH

In electroplating processes must be buffered