

## 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( $\text{CH}_3\text{COOH}$ ) and sodium ethanoate( $\text{CH}_3\text{COONa}$ )
- Benzoic acid( $\text{C}_6\text{H}_5\text{COOH}$ ) and sodium benzoate( $\text{C}_6\text{H}_5\text{COONa}$ )
- Phosphoric acid( $\text{H}_3\text{PO}_4$ ) and sodium phosphate( $\text{Na}_2\text{HPO}_4$ )

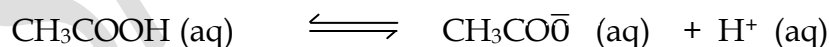
**Basic buffer** ( a buffer solution with pH greater than seven)

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

- Aqueous ammonia( $\text{NH}_3$ ) and ammonium chloride( $\text{NH}_4\text{Cl}$ )
- Aqueous ammonia( $\text{NH}_3$ ) and ammonium sulphate( $(\text{NH}_4)_2\text{SO}_4$ )
- 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

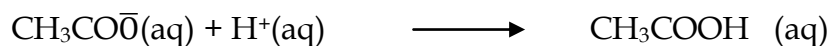


Sodium ethanoate is an ionic salt, and in solution consists of free sodium and ethanoate ions.

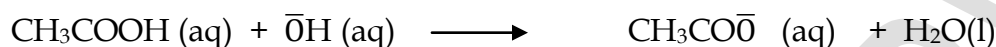


This mixture therefore contains a relatively high concentration of undissociated acid molecules, excess ethanoate ions and a small amount of hydrogen ions formed by the original ionization of ethanoic acid.

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.



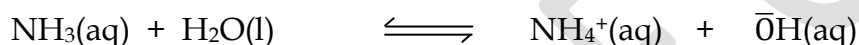
When small amount of hydroxyl ions from an alkali are added to this solution, almost all of these will react with the un-ionised ethanoic acid to make ethanoate ions and water. So the pH will hardly change at all.



In other words, trying to alter the pH of the solution by increasing the concentration of  $\text{H}^+$  or  $\text{OH}^-$  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

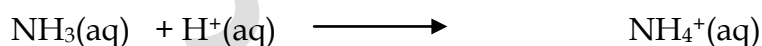


Ammonium chloride is an ionic salt, and so its solution consist of free ammonium and chloride ions:

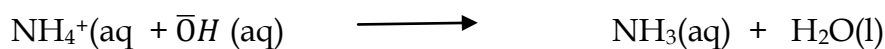


The mixture therefore contains a relatively high concentration of undissociated ammonia molecules and excess ammonium ions and enough hydroxyl ions to make the solution alkaline.

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.



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.

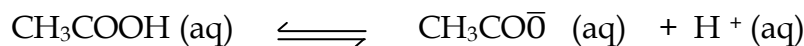


Once again, trying to change the pH by increasing the concentration of  $\text{H}^+$  or  $\text{OH}^-$  largely fails.

## 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.



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

**Assumption:** ethanoate ions are produced by the dissociation of the salt, sodium ethanoate. Therefore  $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COONa}] = [\text{salt}]$

$[\text{CH}_3\text{COOH}] = [\text{acid}]$  since it partially ionises

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

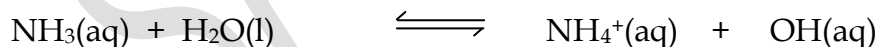
$$\text{pH} = -\log[\text{H}^+] = -\log\left(\frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}\right)$$

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

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



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

**Assumption:** ammonium ions are produced by the dissociation of the salt, ammonium chloride. Therefore  $[\text{NH}_4^+] = [\text{NH}_4\text{Cl}] = [\text{salt}]$

$[\text{NH}_3] = [\text{base}]$  since the base partially ionises

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

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

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

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

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

$$\text{pH} = (\text{p}K_w - \text{p}K_b) + \log \frac{[NH_3]}{[NH_4^+]}$$

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,  $\text{CH}_3\text{CH}_2\text{COOH}$ , and 12.0g of sodium propanoate,  $\text{CH}_3\text{CH}_2\text{COONa}$ , in water and then making the volume up to  $250\text{cm}^3$ .

( $\text{p}K_a$  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)  $1.00\text{cm}^3$  of  $10\text{mol dm}^{-3}$  hydrochloric acid.

ii)  $1.00\text{cm}^3$  of  $10\text{mol dm}^{-3}$  sodium hydroxide solution to  $1000\text{cm}^3$  of the buffer solution.

#### Solution:

Molar mass of  $\text{CH}_3\text{CH}_2\text{COOH} = 12 \times 3 + 6 \times 1 + 16 \times 2 = 74\text{g}$

$$\text{Moles of } \text{CH}_3\text{CH}_2\text{COOH in } 250\text{cm}^3 = \frac{18.5}{74}$$

$$\text{Moles of } \text{CH}_3\text{CH}_2\text{COOH in } 1000\text{cm}^3 = \frac{18.5 \times 1000}{74 \times 250} = 1.00\text{mol dm}^{-3}$$

$$\text{Molar mass of CH}_3\text{CH}_2\text{COONa} = 12 \times 3 + 5 \times 1 + 16 \times 2 + 23 \times 1 = 96 \text{ g}$$

$$\text{Moles of CH}_3\text{CH}_2\text{COONa in } 250 \text{ cm}^3 = \frac{12}{96}$$

$$\text{Moles of CH}_3\text{CH}_2\text{COONa in } 1000 \text{ cm}^3 = \frac{12 \times 1000}{96 \times 250} = 0.50 \text{ mol dm}^{-3}$$

$$\text{pK}_a = 4.87$$

$$\text{K}_a = 10^{-4.87}$$

$$\text{K}_a = 1.35 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{K}_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

### Assumption:

Because virtually all the propanoate ions  $\text{CH}_3\text{CH}_2\text{COO}^-$ , are coming from the sodium propanoate, and almost none from propanoic acid, the propanoate concentration is also equal to  $0.50 \text{ mol dm}^{-3}$  and that so little of propanoic acid ionizes that its equilibrium concentration is  $1.00 \text{ mol dm}^{-3}$ .

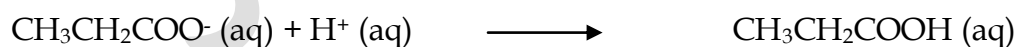
$$1.35 \times 10^{-5} = \frac{0.500 \times [\text{H}^+]}{1.00}$$

$$[\text{H}^+] = 2.70 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH} = 4.57$$

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.

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



$$\text{New moles of CH}_3\text{CH}_2\text{COO}^- = 0.5 - 0.01 = 0.49$$

$$\text{New moles of CH}_3\text{CH}_2\text{COOH} = 1.00 + 0.01 = 1.01$$

$$\text{K}_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

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

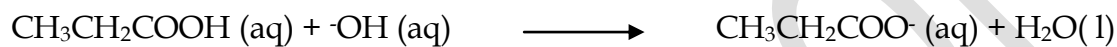
$$[H^+] = 2.78 \times 10^{-5}$$

$$\text{pH} = 4.56$$

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.

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



$$\text{New moles of } \text{CH}_3\text{CH}_2\text{COO}^- = 0.5 + 0.01 = 0.51$$

$$\text{New moles of } \text{CH}_3\text{CH}_2\text{COOH} = 1.00 - 0.01 = 0.99$$

$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][H^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

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

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

$$\text{pH} = -\log[H^+] = -\log(2.62 \times 10^{-5}) = 4.58$$

change in pH is 0.01

### Example two

Calculate the pH of a buffer solution made by mixing  $50\text{cm}^3$  of  $0.300\text{mol dm}^{-3}$  ethanoic acid with  $100\text{cm}^3$  of  $0.600\text{mol dm}^{-3}$  sodium ethanoate.

( $K_a$  for ethanoic acid =  $1.75 \times 10^{-5}\text{mol dm}^{-3}$ )

$$\text{Total volume } 100 + 50 = 150\text{cm}^3$$

$$\text{Moles of ethanoic acid in the total volume of } 150\text{cm}^3 = \frac{0.300 \times 50}{1000} = 0.015$$

$$\text{Moles of ethanoic acid in } 1000\text{cm}^3 = \frac{0.015 \times 1000}{150} = 0.100\text{mol dm}^{-3}$$

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

$$\text{Moles of sodium ethanoate in } 1000\text{cm}^3 = \frac{0.0600 \times 1000}{150} = 0.400 \text{ mol dm}^{-3}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{1.75 \times 10^{-5} \times 0.100}{0.400} = 4.375 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(4.375 \times 10^{-6})$$

$$= 5.36$$

### Example three

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

State any assumption made. ( $K_a$  for ethanoic acid =  $1.8 \times 10^{-5} \text{ mol dm}^{-3}$ )

### Solution

$1000\text{cm}^3$  of ethanoic acid solution contains  $0.1$  moles

$$30\text{cm}^3 \text{ of ethanoic acid solution contains } \frac{0.1 \times 30}{1000} = 3 \times 10^{-3} \text{ moles}$$

$1000\text{cm}^3$  of sodium hydroxide solution contains  $0.1$  moles

$$20\text{cm}^3 \text{ of sodium hydroxide solution contains } \frac{0.1 \times 20}{1000} = 2 \times 10^{-3} \text{ moles}$$



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

Therefore moles of ethanoic acid reacting =  $2 \times 10^{-3}$  moles

$$\text{Excess moles of ethanoic acid in solution} = 3 \times 10^{-3} - 2 \times 10^{-3} = 1 \times 10^{-3} \text{ moles}$$

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

Total volume of the mixture ( $30+20$ ) =  $50\text{cm}^3$

$$\text{Concentration of ethanoate ions in the mixture} = \frac{2 \times 10^{-3} \times 1000}{50} = 0.04 \text{ mol dm}^{-3}$$

$$\text{Concentration of ethanoic acid in the mixture} = \frac{1 \times 10^{-3} \times 1000}{50} = 0.02 \text{ mol dm}^{-3}$$

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

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

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

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{1.8 \times 10^{-5} \times 0.02}{0.04} = 9.0 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(9.0 \times 10^{-6}) = 5.0$$

#### Example four

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

( $K_a$  for ethanoic acid  $= 1.8 \times 10^{-5} \text{ mol dm}^{-3}$ )

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

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

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

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

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

$$[H^+] = 10^{-5.5} = 3.16 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[CH_3COO^-] = \frac{K_a [CH_3COOH]}{[H^+]} = \frac{1.8 \times 10^{-5} \times 0.1}{3.16 \times 10^{-6}} = 0.5696 \text{ mol dm}^{-3}$$

$$\text{Molar mass of } CH_3COONa = (12 \times 2) + (1 \times 3) + (16 \times 2) + (23 \times 1) = 82$$

$$0.5696 \text{ moles of } CH_3COONa \text{ weighs } (0.5696 \times 82) = 46.71 \text{ g}$$

### Example five

A buffer solution was made by mixing 0.1 M ammonia solution and 0.025M Ammonium chloride in 1.0dm<sup>3</sup>

- a) Calculate the pH of this solution.
- b) Calculate the pH of the above solution when
- i) 10cm<sup>3</sup> of 0.1 M NaOH was added
- ii) 10cm<sup>3</sup> of 0.1M HCl was added .(K<sub>b</sub> for ammonia = 1.8 × 10<sup>-5</sup> moldm<sup>-3</sup> )

### Solution

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

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

$$\text{Assumption: } [NH_4^+] = [NH_4Cl]$$

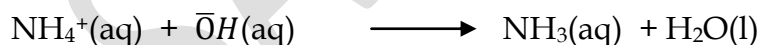
$$[\bar{O}H] = \frac{1.8 \times 10^{-5} \times 0.1}{0.025} = 7.2 \times 10^{-5} \text{ moldm}^{-3}$$

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

$$pH = -\log(1.389 \times 10^{-10}) = 9.857$$

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

After the addition of sodium hydroxide concentration of NH<sub>3</sub> increases by 0.001 while concentration of NH<sub>4</sub>Cl decreases by 0.001 moles.



New concentration of NH<sub>3</sub> = 0.1 + 0.001 = 0.101 moles

New concentration of NH<sub>4</sub><sup>+</sup> = 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:  $[NH_4^+] = [NH_4Cl]$

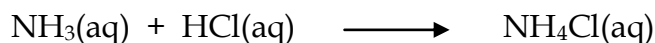
$$[\bar{O}H] = \frac{1.8 \times 10^{-5} \times 0.101}{0.024} = 7.515 \times 10^{-5} \text{ moldm}^{-3}$$

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

$$\text{pH} = -\log(1.320 \times 10^{-10}) = 9.879$$

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

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



New concentration of  $NH_3 = 0.1 - 0.001 = 0.099$  moles

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

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

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

$$\text{pH} = -\log(1.459 \times 10^{-10})$$

$$= 9.83$$

### Example six

Calculate the pH of a solution obtained when 25cm<sup>3</sup> of 0.02 M HCl are added to 25cm<sup>3</sup> of 0.04M NH<sub>3</sub>. (pK<sub>b</sub> of ammonia is 4.76 at 25°C).

### Solution

1000cm<sup>3</sup> of hydrochloric acid contains 0.02 moles

25cm<sup>3</sup> of hydrochloric acid contains  $\frac{0.02 \times 25}{1000} = 5 \times 10^{-4}$  moles

1000cm<sup>3</sup> of ammonia solution contains 0.04 moles

25cm<sup>3</sup> of ammonia solution contains  $\frac{0.04 \times 25}{1000} = 10 \times 10^{-3}$  moles



One mole of HCl reacts with one mole of NH<sub>3</sub>

Therefore moles of ammonia reacting =  $5 \times 10^{-4}$

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

The buffer formed is composed of excess NH<sub>3</sub> and the salt formed NH<sub>4</sub>Cl

Total volume of the mixture = (25 + 25) = 50cm<sup>3</sup>

Concentration of ammonium ions in the mixture =  $\frac{5 \times 10^{-4} \times 1000}{50} = 0.01 \text{ mol dm}^{-3}$

Concentration of ammonia in the mixture =  $\frac{5 \times 10^{-4} \times 1000}{50} = 0.01 \text{ mol dm}^{-3}$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$K_b = 10^{-4.76} = 1.738 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{OH}^-] = \frac{K_b[\text{NH}_3]}{[\text{NH}_4^+]} = \frac{1.738 \times 10^{-5} \times 0.01}{0.01} = 1.738 \times 10^{-5} \text{ moles}$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$1 \times 10^{-14} = [\text{H}^+] \times 1.738 \times 10^{-5}$$

$$[\text{H}^+] = 5.754 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(5.754 \times 10^{-10}) = 9.24$$

### 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

$$pH=10$$

$$[H^+] = 1.00 \times 10^{-10} \text{ moldm}^{-3}$$

$$pK_b = 4.76$$

$$K_b = 1.74 \times 10^{-5} \text{ moldm}^{-3}$$

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

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

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

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

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

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

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