

Topic: Acid-Base Equilibria (Olympiad 2015)

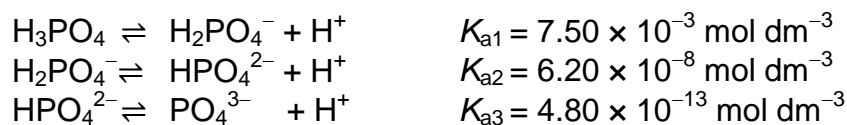
[MJC Prelim 2011/ P3/ Q2]

1 (a) A buffer solution is prepared by adding 10.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ potassium hydroxide to 25.00 cm^3 of $0.400 \text{ mol dm}^{-3}$ ethanoic acid. (pK_a of ethanoic acid is 4.75)

- (i) What is meant by the term *buffer*?
- (ii) Explain how the solution above acts as a buffer when H^+ ions are added.
- (iii) Calculate the pH of the buffer solution formed. pH=3.8

[JJC Prelim 2011/ P2/ Q3]

Phosphoric acid is a tribasic acid. The values of the three acid dissociation constants at 25°C of phosphoric acid are given below.

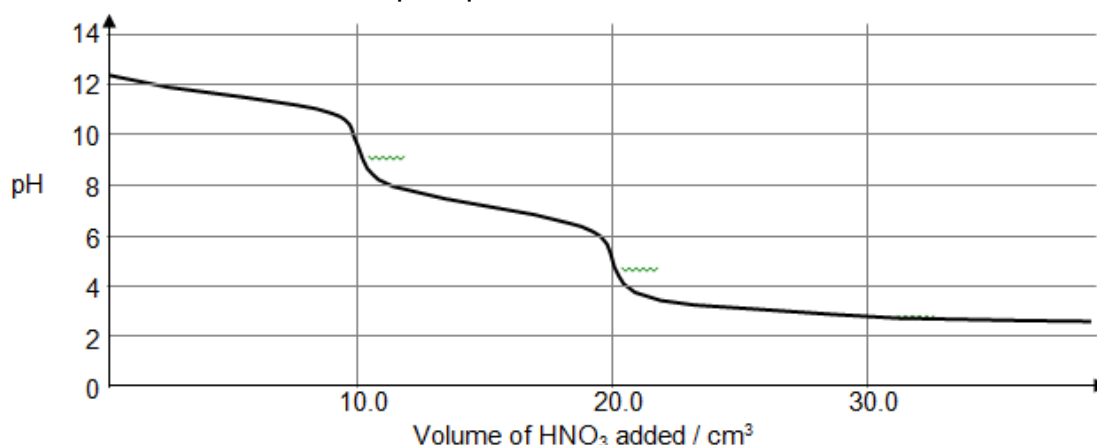


- (b) Suggest why there is a decreasing trend in the K_a values.
- (c) Identify the conjugate acid of HPO_4^{2-} and the conjugate base of HPO_4^{2-} .
- (d) Calculate the K_b of HPO_4^{2-} . $K_b = 1.61 \times 10^{-7} \text{ mol dm}^{-3}$

A phosphate buffer system (made of H_2PO_4^- and HPO_4^{2-}) serves to buffer the intracellular fluid of cells.

- (e) (i) Explain what is meant by a *buffer solution*.
- (ii) Write an equation to show how the phosphate buffer system acts as a buffer when a small amount of base is added.
- (iii) Using the data provided, calculate the pH of the phosphate buffer when the ratio of $[\text{H}_2\text{PO}_4^-] : [\text{HPO}_4^{2-}]$ is 2 : 1. pH = 6.91

The diagram below shows the pH changes when $0.0305 \text{ mol dm}^{-3} \text{ HNO}_3$ is added to a 25.0 cm^3 solution of sodium phosphate, Na_3PO_4 .



- (f) Calculate the initial concentration of the sodium phosphate solution.

$0.0122 \text{ mol dm}^{-3}$

- (g) State the volume of HNO_3 required to reach the point where the buffer (made of H_2PO_4^- and HPO_4^{2-}) is operating at its maximum buffering capacity.

15 cm^3

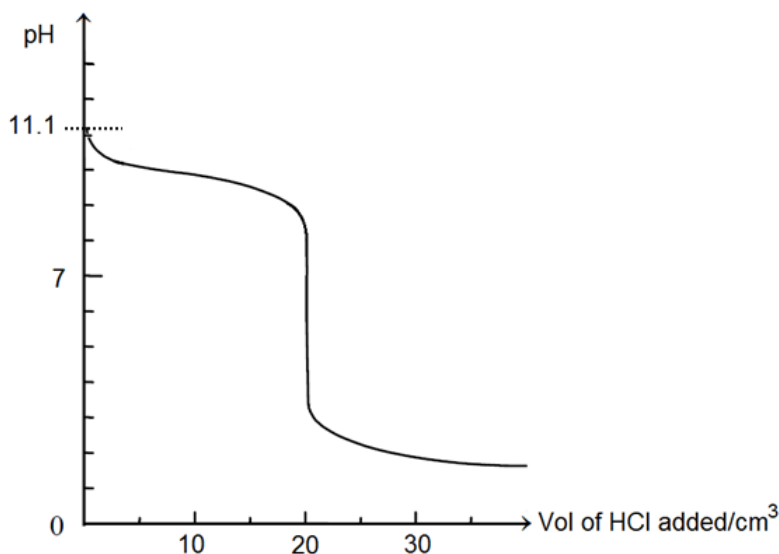
- (h) (i) From the table below, select an indicator that is most suitable for determining the **second** equivalence point in the titration shown on the graph.

Indicator	pKa	acid form	base form
methyl yellow	3.3	red	yellow
bromocresol green	4.9	yellow	blue
chlorophenol red	6.0	yellow	red
bromothymol blue	7.1	yellow	blue
phenolphthalein	9.3	colourless	purple

- (ii) Suggest the colour change observed with this indicator at the end point.

[NJC Prelim 2011/ P3/ Q4]

- 3 (a) 20.0 cm^3 of 0.10 mol dm^{-3} solution of propylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, was titrated against 0.10 mol dm^{-3} solution of hydrochloric acid. The following titration curve was obtained.



- (i) Calculate the base dissociation constant, K_b , of propylamine with the use of initial pH on the titration curve.

$K_b = 1.61 \times 10^{-5} \text{ mol dm}^{-3}$

- (ii) Explain the pH value obtained at equivalence point with the aid of an appropriate equation.

- (iii) A student used phenolphthalein to carry out the above titration.

Comment on the suitability of this indicator.

(iv) An aqueous solution of propylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3\text{Cl}$ can act as a buffer solution.

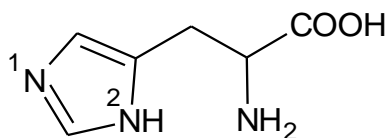
(I) State the volume of hydrochloric acid at which the buffer operates at its maximum buffer capacity.

10 cm³

(II) Write suitable equations to illustrate the buffering action of an aqueous solution of $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3\text{Cl}$ when small amounts of NaOH or HCl is added to it.

[NYJC Prelim 2013/ P3/ 5(c), (d)]

- 4 (c) Histidine is utilized by your body to develop and maintain healthy tissues. It is especially important in the myelin sheath that coat nervous cells to ensure the transmission of messages from your brain to organs throughout your body. Histidine also stimulates the secretion of the digestive enzymes gastrin and is also required to manufacture both red and white blood cells.



Structure of histidine

Histidine contains a total of 3 nitrogen atoms and each N atom exhibit different properties in aqueous solution.

(ii) There are three pK_a values associated with the histidine: 1.8, 6.0, 9.2. Assuming that the ^2N atom does not exhibit any basic properties, make use of the three pK_a values to suggest the major species present in solutions of histidine with the following pH values.

- pH 1
- pH 5
- pH 7
- pH 11

(iii) Consider the buffer solution at pH = 5, calculate what fraction of the histidine side chains will carry a positive charge at pH 5.

- (d) 25.0 cm³ of 0.150 mol dm⁻³ of diethylamine solution, $(\text{CH}_3\text{CH}_2)_2\text{NH}$, was placed in a conical flask and titrated against a solution of 0.200 mol dm⁻³ hydrochloric acid from a burette.

Given that the K_b of $(\text{CH}_3\text{CH}_2)_2\text{NH}$ is 8.60×10^{-4} mol dm⁻³,

(i) explain what is meant by the term base dissociation constant, K_b of diethylamine.

(ii) Calculate the pH at equivalence point. pH= 6.00

- 5 Stalagmites and stalactites are natural formations in limestone caves. Stalagmites are formed by the deposition of minerals by water on the ground. The formation of a stalagmite starts when water dissolves minerals, predominantly calcium carbonate, as it seeps into cracks in the ground. This mineral rich solution will continue the downward travel until the crack reaches an opening into a cave. Over time, the deposited build up and form a column growing up from the ground. The corresponding formation on the ceiling of the cave is known as a stalactite.

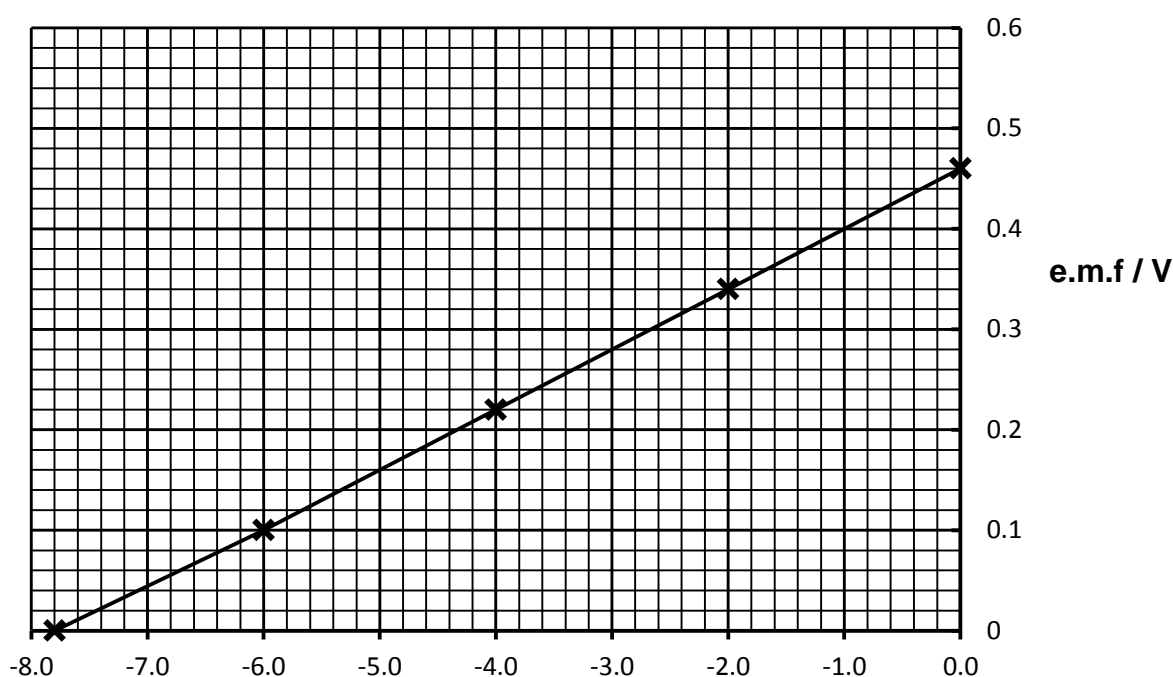
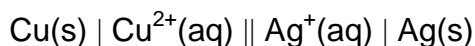
- (a) Write an equation to describe the formation of stalagmite.
- (b) Given that the solubility of calcium carbonate is $6.94 \times 10^{-3} \text{ g dm}^{-3}$, calculate the solubility product of calcium carbonate.
- (c) The formation of a stalagmite can take thousands of years. Given that the mass of water that flows through a crack in the ceiling of a limestone cave is 50 tons per year (1 ton = 1000 kg), determine the number of years it would take for a stalagmite, weighing 500 kg, to form.

You may assume that there is no loss of calcium carbonate during the formation of the stalagmite.

- (d) Using the **concept of solubility product**, give a detailed explanation of the process, starting from the flow of water into the crack to the formation of the stalagmite.

[NYJC Prelim 2012/ P3/ Q2(b),(c)]

- 6 (a) The graph below shows the variation in electromotive force (e.m.f.) of the following electrochemical cell with $\lg [\text{Ag}^+(\text{aq})]$ at 298 K.



- (i) Using the information from the **$\lg [\text{Ag}^+(\text{aq})]$** to the standard electrode potential

of the half-cell, $\text{Ag}^+(\text{aq}) \mid \text{Ag}(\text{s})$, at 298 K.

- (ii) If the $\text{Ag}^+(\text{aq})$ solution of the electrochemical cell is replaced by a saturated solution of silver bromate(V), AgBrO_3 , in 0.1 mol dm^{-3} potassium bromate(V) and the e.m.f. of the cell measured at 298 K is +0.27 V, determine

(I) the concentration of $\text{Ag}^+(\text{aq})$ ions in the saturated solution, and

(II) the solubility product of silver bromate(V) at 298 K.

- (b) Solid silver nitrate was slowly dissolved in a solution **Q** containing ethanedioate, $\text{C}_2\text{O}_4^{2-}$, and chromate(VI), CrO_4^{2-} , ions of concentrations $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ and $1.44 \times 10^{-5} \text{ mol dm}^{-3}$ respectively.

- (i) When a permanent precipitate of silver ethanedioate first appeared, the concentration of silver ions in the solution was $2.10 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the solubility product of silver ethanedioate.

- (ii) **The dissolving of solid silver nitrate in Q was continued** until a permanent red precipitate of silver chromate(VI) first appeared. Calculate the concentrations of silver ions and ethanedioate ions at that instant.

(K_{sp} of silver chromate(VI) is $1.2 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$.)

- (iii) What is the amount of silver ethanedioate precipitated from 1.00 dm^3 of the solution?

Topic: Acid-Base Equilibria (Suggested Answers)

[MJC Prelim 2011/ P3/ Q2]

1 (i) A buffer solution is one which is capable of maintaining a fairly constant pH (by resisting pH change) when small amounts of acid or base are added to it.

(ii) When a small amount of H^+ is added $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$

The H^+ is removed as CH_3COOH by CH_3COO^- .

$[\text{H}^+]$ is slightly changed and pH of buffer solution remains fairly constant.

(iii) No. of mole of KOH = 0.00100

In the buffer solution,

No. of mol of CH_3COOK = 0.00100

No. of mol of CH_3COOH = $\left(0.400 \times \frac{25}{1000}\right) - 0.00100 = 0.00900$

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

$$\begin{aligned}\text{pH} &= 4.75 + \lg \left(\frac{\frac{0.001}{V}}{\frac{0.00900}{V}} \right) \text{ where } V \text{ is volume of buffer} \\ &= 3.80\end{aligned}$$

[JJC Prelim 2011/ P2/ Q3]

2(b) There is a decreasing trend as it is more difficult to remove H^+ from increasingly negatively charged species / anions.

(c) Congugate acid: H_2PO_4^- conjugate base: PO_4^{3-}

$$(d) K_b = \frac{1.00 \times 10^{-14}}{6.20 \times 10^{-8}} = 1.61 \times 10^{-7} \text{ mol dm}^{-3}$$

(e) (i) A buffer solution is one that resists changes in pH due to the addition of small amount of acid/ H^+ or base/ OH^- .



(iii) System: Acidic buffer

$$\begin{aligned}\text{pH} &= -\lg(6.20 \times 10^{-8}) + \lg \left(\frac{1}{2}\right) \\ &= 6.91\end{aligned}$$

$$(f) [\text{PO}_4^{3-}] = (10/0 \times 0.0305) / 25.0 = 0.0122 \text{ mol dm}^{-3}$$

$$(g) 15 \text{ cm}^3$$

(h) (i) Bromocresol green

(ii) blue to green

[NJC Prelim 2011/ P3/ Q4]

3(a) (i) $\text{pOH} = 14 - 11.1 = 2.9$
 $[\text{OH}^-] = 10^{-2.9} = 0.00126 \text{ mol dm}^{-3}$
 $K_b = (0.00126)^2 / (0.10 - 0.00126)$
 $= 1.61 \times 10^{-5} \text{ mol dm}^{-3}$



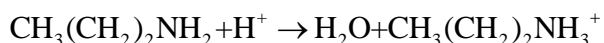
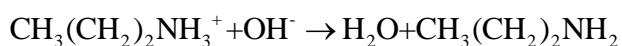
The salt produced at equivalence point is the strong conjugate acid of a weak base, or

The hydrolysis of the salt produces protons,
Hence the equivalence pH is below 7.

(iii) Not suitable. The indicator would change color before the equivalence point/the equivalence point pH is out of the working range of phenolphthalein.

(iv) (I) 10 cm^3 .

(II) On the addition of a small amt. of alkali and acid respectively,

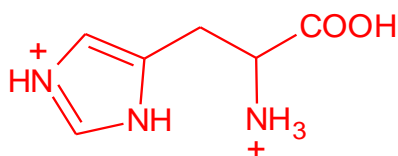


Therefore the pH of the solution remains relatively constant.

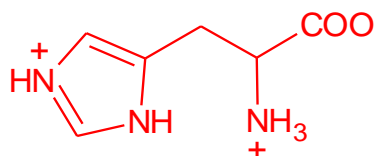
[NYJC Prelim 2013/ P3/ 5(c), (d)]

4 (c) (ii)

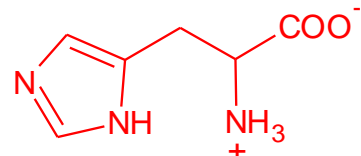
pH 1:



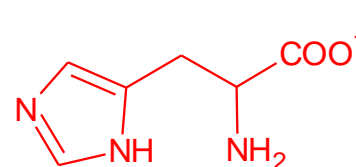
pH 5:



pH 7:



pH 11:



$$(iii) \quad pH = pK_a + \log \frac{[salt]}{[acid]} \quad 5 = 6 + \log \frac{[salt]}{[acid]}$$

$$\frac{[salt]}{[acid]} = 10^{-1} = \frac{1}{10}$$

Since $10[salt] = [acid]$

Therefore at pH 5, 10/11 of the histidine will be in the protonated form.

(d) (i) The base dissociation constant is defined as $K_b = \frac{[OH^-][(CH_3CH_2)_2NH_2^+]}{[(CH_3CH_2)_2NH]}$

(ii) $V(HCl) \text{ at neutralisation point} = \frac{(25.0)(0.150)}{(0.200)} = 18.75 \text{ cm}^3$

At equivalence point, $[salt] =$

$$\frac{n_{salt}}{V_T} = \frac{(25.0)(0.150)}{(25.0 + 18.75)} = 0.08571 \text{ mol dm}^{-3}$$

Since salt is an acidic in nature,

$$[H^+] = \sqrt{\frac{1 \times 10^{-14}}{8.6 \times 10^{-4}}} \times 0.08571 = 9.983 \times 10^{-7}$$

$$pH = -\log(9.983 \times 10^{-7}) = 6.00$$



(b) $Mr \text{ of } CaCO_3 = 40.1 + 12.0 + 3(16.0)$
 $= 100.1$

$$\text{Solubility in mol dm}^{-3} = (6.94 \times 10^{-3}) / 100.1$$

$$= 6.93 \times 10^{-5} \text{ mol dm}^{-3}$$

$$K_{sp} = [Ca^{2+}(aq)]_{eqm}[CO_3^{2-}(aq)]_{eqm}$$

$$= (6.93 \times 10^{-5})^2$$

$$= \underline{4.81 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}}$$

(c) $\text{Mass of water flowing per year} = 50 \times 1000$
 $= 50000 \text{ kg}$

$$\text{Volume of water flowing per year} = 50000 / 1 = 50000 \text{ dm}^3$$

$$\text{Mass of } CaCO_3 \text{ dissolved in 1 year} = (6.94 \times 10^{-3}) \times 50000$$

$$= 347 \text{ g} = 0.347 \text{ kg}$$

$$\text{Number of years required} = 500 / 0.347$$

$$= \underline{1440 \text{ years}}$$

(d) When water flows into the crack, it is assumed to be pure.

When it flows through the area of the rock/soil containing calcium carbonate, the initial ionic product is 0. Since ionic product < K_{sp} , calcium carbonate starts to dissolve into the water.

As more and more calcium carbonate is dissolved, the ionic product increases until it equals the K_{sp} . At this point, there is no further dissolution as the solution is saturated.

The saturated solution flows down into the cave and drips onto the ground. When exposed to air, water evaporates. This causes the volume to decrease and hence increasing the concentration of ions in the water.

As a result, ionic product $\geq K_{sp}$. Precipitation occurs and the stalagmite starts forming.

[NYJC Prelim 2012/ P3/ Q2(b),(c)]

6 (a) (i) Let the standard electrode potential of $\text{Ag}^+(\text{aq}) | \text{Ag}(\text{s})$ half-cell be x .

When $[\text{Ag}^+(\text{aq})] = 1.00 \text{ mol dm}^{-3}$, $\lg [\text{Ag}^+(\text{aq})] = 0$

$$E_{\text{cell}}^{\circ} = +0.46 = x - (+0.34)$$

$$x = +0.46 + (+0.34) = \underline{+0.80 \text{ V}}$$

(ii) (I) From the graph, when e.m.f. of cell is +0.27 V,

$$\lg [\text{Ag}^+(\text{aq})] = -3.2.$$

$$[\text{Ag}^+(\text{aq})] = \underline{6.309 \times 10^{-4} \text{ mol dm}^{-3}}$$

$$(II) \quad K_{sp} = 6.309 \times 10^{-4} \times (0.1 + 6.309 \times 10^{-4}) = \underline{6.35 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}}$$

$$\begin{aligned} (b) \quad (i) \quad K_{sp}(\text{Ag}_2\text{C}_2\text{O}_4) &= (2.10 \times 10^{-5})^2 \times 2.50 \times 10^{-2} \\ &= \underline{1.10 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}} \end{aligned}$$

(ii) *Guide to students: Because $\text{Ag}_2\text{C}_2\text{O}_4$ and Ag_2CrO_4 both have the same formulae, thus the lower the K_{sp} , the lower solubility - silver chromate has lower K_{sp} thus it is less soluble and should ppt first if the two anions are of the same concentration.*

Note: If formulae of 2 salts are different cannot use K_{sp} to compare solubility

But different concentrations of $\text{C}_2\text{O}_4^{2-}$ and CrO_4^{2-} , so $\text{Ag}_2\text{C}_2\text{O}_4$ ppt first, then Ag_2CrO_4 .

$$K_{sp} = 1.2 \times 10^{-12} = [\text{Ag}^+]^2 \times 1.44 \times 10^{-5}$$

$$[\text{Ag}^+]^2 = 8.333 \times 10^{-8}$$

$$[\text{Ag}^+] = \underline{2.89 \times 10^{-4} \text{ mol dm}^{-3}}$$

$$1.102 \times 10^{-11} = (2.886 \times 10^{-4})^2 \times [\text{C}_2\text{O}_4^{2-}]$$

$$[\text{C}_2\text{O}_4^{2-}] = \underline{1.32 \times 10^{-4} \text{ mol dm}^{-3}}$$

(iii) $n(\text{C}_2\text{O}_4^{2-}) \text{ removed} = 2.50 \times 10^{-2} - 1.322 \times 10^{-4} = 0.02486 \text{ mol}$
 \therefore amount of silver ethanedioate ppted = 0.0249 mol