Solutions for the problems about
“Calculation of pH in the case of polyprotic acids and bases”

1. 20 cm³ of phosphoric acid solution is titrated with 0.075 M sodium hydroxide using phenolphthalein indicator ($pK_{a\text{phenolphthalein}} = 9.8$). The average volume of sodium hydroxide solution needed to reach the equivalence point of the titration is 13.25 cm³. What is the molarity of the phosphoric acid solution?

The distribution curve of the indicator, together with its colors as a function of pH

The titration curve of phosphoric acid, showing also the colors of the indicator

We can see from the titration curve of phosphoric acid that phenolphthalein indicator changes its color after adding two equivalents of strong base to the titrated solution (that is $pK_{a\text{phenolphthalein}}$ is around the pH for Na₂HPO₄ which is $\frac{pK_{a3} + pK_{a2}}{2} = \frac{11.75 + 7.21}{2} = 9.48$).

So, the reaction we can monitor by this titration is:

$$H_3PO_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{HPO}_4 + 2 \text{H}_2\text{O}$$

The molar amount of NaOH is: $n_{\text{NaOH}} = c_{\text{NaOH}} \times V_{\text{NaOH}} = 0.075 \text{ M} \times 13.25 \text{ cm}^3 = 0.99375 \text{ mmol}$. From the previous chemical equation, $n_{\text{H}_3\text{PO}_4} = 0.5 \times n_{\text{NaOH}} = 0.496875 \text{ mmol}$. This amount is in 20 mL of phosphoric acid solution, so the concentration of this solution is: $c_{\text{H}_3\text{PO}_4} = \frac{n_{\text{H}_3\text{PO}_4}}{V_{\text{H}_3\text{PO}_4}} = \frac{0.496875 \text{ mmol}}{20 \text{ mL}} = 0.02484 \text{ mol/L}$.

2. Calculate the pH when mixing...

a) 10 cm³ of 0.04 M sulphuric acid and 10 cm³ of 0.115 M sodium hydroxide solutions

b) 10 cm³ of 0.12 M sodium carbonate and 20 cm³ of 0.06 M sodium hydroxide solutions

Does the pH of the solution mixtures change by 10-fold dilution?

a) The molar amounts are: $n_{\text{H}_2\text{SO}_4} = c_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4} = 0.04 \text{ M} \times 10 \text{ cm}^3 = 0.4 \text{ mmol}$ and $n_{\text{NaOH}} = c_{\text{NaOH}} \times V_{\text{NaOH}} = 0.115 \text{ M} \times 10 \text{ cm}^3 = 1.15 \text{ mmol}$

We have a more then 2-fold excess of NaOH, so the acid-base reaction is:

$$\text{H}_2\text{SO}_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{O}$$

The amount of NaOH excess (which determines the pH of the solution) is: $n_{\text{NaOH}}^{\text{excess}} = n_{\text{NaOH}} - (2 \times n_{\text{H}_2\text{SO}_4}) = 0.35 \text{ mmol}$. The total volume of the resulting solution is 20 mL, so the concentration of the NaOH excess is:

$$c_{\text{NaOH}}^{\text{excess}} = \frac{n_{\text{NaOH}}^{\text{excess}}}{V_{\text{total}}} = \frac{0.35 \text{ mmol}}{20 \text{ mL}} = 0.0175 \text{ M}.$$
In the case of a strong base (like NaOH), $[\text{OH}^-] = c_{\text{strong base}} = 0.0175 \text{ M}$

\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(0.0175) = 1.757 \]

This is a strong base solution, so the pH does change by 10-fold dilution. The pH of the solution after the dilution is:

\[ [\text{OH}^-]_{\text{10-fold dilution}} = 0.00175 \text{ M} \]

\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(0.00175) = 2.757 \]

\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 2.757 = 11.243 \]

b) The molar amounts are:

- $n_{\text{Na}_2\text{CO}_3} = c_{\text{Na}_2\text{CO}_3} \times V_{\text{Na}_2\text{CO}_3} = 0.12 \text{ M} \times 10 \text{ cm}^3 = 1.2 \text{ mmol}$ and
- $n_{\text{NaOH}} = c_{\text{NaOH}} \times V_{\text{NaOH}} = 0.06 \text{ M} \times 20 \text{ cm}^3 = 1.2 \text{ mmol}$

$\text{Na}_2\text{CO}_3$ is a weak base and NaOH is a strong base, so to calculate the pH we need to take into account only the strong base. The total volume of the resulting solution is 30 mL ($= V_{\text{Na}_2\text{CO}_3} + V_{\text{NaOH}}$), so the concentration of the NaOH is:

\[ c_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{V_{\text{total}}} = \frac{1.2 \text{ mmol}}{30 \text{ mL}} = 0.04 \text{ M}. \]

In the case of a strong base (like NaOH), $[\text{OH}^-] = c_{\text{strong base}} = 0.04 \text{ M}$

\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(0.04) = 1.398 \]

\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 1.398 = 12.602 \]

This is a strong base solution, so the pH does change by 10-fold dilution. The pH of the solution after the dilution is:

\[ [\text{OH}^-]_{\text{10-fold dilution}} = 0.004 \text{ M} \]

\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(0.00175) = 2.398 \]

\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 2.398 = 11.602 \]

3. We have 21.50 g of sodium phosphate and an optional amount of concentrated hydrochloric acid (36 % (m/m), $\rho = 1.18 \text{ g/cm}^3$) to prepare 100.00 cm$^3$ pH = 7.000 buffer. What volume of concentrated hydrochloric acid should be used if we use up the total amount of sodium phosphate?

![Distribution curve of phosphoric acid](image)

At pH = 7.000, $[\text{H}^+] = 10^{-\text{pH}} = 1.00 \times 10^{-10} \text{ M}$. From this chart, we can see that at pH 7.00 there is a $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ (or $\text{NaH}_2\text{PO}_4 / \text{Na}_2\text{HPO}_4$) buffer system. To calculate the pH of this buffer, we use the following formula:

\[ [\text{H}^+] = K_{a2} \frac{c_{\text{H}_2\text{PO}_4^-}}{c_{\text{HPO}_4^{2-}}} = K_{a2} \frac{n_{\text{H}_2\text{PO}_4^-}}{n_{\text{HPO}_4^{2-}}} \]

So, \[ \frac{n_{\text{H}_2\text{PO}_4^-}}{n_{\text{HPO}_4^{2-}}} = \frac{[\text{H}^+]}{K_{a2}} = 1.621 \text{ and } n_{\text{NaH}_2\text{PO}_4} = 1.621 \times n_{\text{Na}_2\text{HPO}_4}. \]
At the same time, we know that the molar amount of the original Na$_3$PO$_4$ ($n_{Na_3PO_4} = \frac{m_{Na_3PO_4}}{M.W._{Na_3PO_4}} = \frac{21.50 \text{ g}}{163.95 \text{ g/mol}} = 0.13114 \text{ mol}$) equals the sum of the molar amount of NaH$_2$PO$_4$ and Na$_2$HPO$_4$ in the resulting buffer solution. That is, $n_{Na_3PO_4} = 0.13114 \text{ mol} = n_{NaH_2PO_4} + n_{Na_2HPO_4} = (1.621 \times n_{NaH_2PO_4}) + n_{Na_2HPO_4} = 2.621 \times n_{Na_2HPO_4}$. From this, $n_{Na_2HPO_4} = 0.13114 \text{ mol} / 2.621 = 0.05004 \text{ mol}$ and $n_{NaH_2PO_4} = 1.621 \times n_{NaH_2PO_4} = 1.621 \times 0.05004 \text{ mol} = 0.08110 \text{ mol}$. The reactions between HCl and Na$_3$PO$_4$ are the following:

$$\text{Na}_3\text{PO}_4 + \text{HCl} \rightarrow \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O} \quad \text{to make Na}_2\text{HPO}_4$$
$$\text{Na}_3\text{PO}_4 + 2 \text{HCl} \rightarrow \text{NaH}_2\text{PO}_4 + 2 \text{H}_2\text{O} \quad \text{to make NaH}_2\text{PO}_4.\$$

The total molar amount of HCl needed is: $n_{\text{HCl}} = n_{\text{Na}_2\text{HPO}_4} + (2 \times n_{\text{NaH}_2\text{PO}_4}) = 0.21224 \text{ mol}$. The mass of HCl is: $m_{\text{HCl}} = n_{\text{HCl}} \times M.W._{\text{HCl}} = 0.21224 \text{ mol} \times 36.458 \text{ g/mol} = 7.7385 \text{ g HCl}$. The mass of the solution containing this mass of HCl is: $m_{\text{solution}} = \frac{36\% \times m_{\text{HCl}}}{100\%} = 21.494 \text{ g solution}$. The volume of this solution is: $V_{\text{solution}} = \frac{m_{\text{solution}}}{\rho_{\text{solution}}} = \frac{21.494 \text{ g}}{1.18 \text{ g/cm}^3} = 18.21 \text{ cm}^3$.

4. A 0.1 M glycine (amino acetic acid) solution is prepared by weighing the calculated amount of glycine and dissolving it in water. What is the pH of the solution?

Glycine is an ampholite, so its pH is: $\text{pH} = \frac{pK_{a1} + pK_{a2}}{2} = \frac{2.350 + 9.550}{2} = 5.950$

5. What is the pH of a sodium hydrogen carbonate solution?

NaHCO$_3$ is an ampholite, so its pH is: $\text{pH} = \frac{pK_{a1} + pK_{a2}}{2} = \frac{6.367 + 10.252}{2} = 8.309$

6. What is the pH of a 0.05 M sulphuric acid solution?

Sulphuric acid has a strong first and a weak second deprotonation step. So, its reactions in water are:

$$\text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}^+$$
$$\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+ \quad K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

The concentration of H$^+$ ion formed in the first deprotonation reaction is 0.05 M, and the concentration of H$^+$ ion formed in the second deprotonation step is X M. So:

$$[\text{H}^+]_{\text{total}} = (0.05 + X) \text{ M}$$
$$[\text{HSO}_4^-]_{\text{total}} = (0.05 - X) \text{ M}$$
$$[\text{SO}_4^{2-}]_{\text{total}} = X \text{ M}$$

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$, so $1.2 \times 10^{-2} = \frac{(0.05 + X) \cdot X}{(0.05 - X)}$. Solving this equation will give $X = 0.0085095 \text{ M}$, so $[\text{H}^+]_{\text{total}} = (0.05 + X) \text{ M} = 0.0585095 \text{ M}$. From this, pH = 1.233.
7. Specify the following acid/base systems and calculate their pH!
   a) 15 cm$^3$ of 0.05 M phosphoric acid solution + 37.5 cm$^3$ of 0.04 M sodium hydroxide solution
   b) 10 cm$^3$ of 0.05 M sodium carbonate solution + 5 cm$^3$ of 0.05 M of sodium chloride solution

a) The molar amounts are: $n_{\text{H}_3\text{PO}_4} = c_{\text{H}_3\text{PO}_4} \times V_{\text{H}_3\text{PO}_4} = 0.05 \, \text{M} \times 15 \, \text{cm}^3 = 0.75 \, \text{mmol}$ and $n_{\text{NaOH}} = c_{\text{NaOH}} \times V_{\text{NaOH}} = 0.04 \, \text{M} \times 37.5 \, \text{cm}^3 = 1.5 \, \text{mmol}$
We have a 2-fold excess of NaOH, so the acid-base reaction is:
$$\text{H}_3\text{PO}_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{HPO}_4 + 2 \text{H}_2\text{O}$$
$\text{Na}_2\text{HPO}_4$ is an ampholite, so its pH is: $\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_3}}{2} = \frac{7.210 + 11.750}{2} = 9.480$

b) The molar amounts are: $n_{\text{Na}_2\text{CO}_3} = c_{\text{Na}_2\text{CO}_3} \times V_{\text{Na}_2\text{CO}_3} = 0.05 \, \text{M} \times 10 \, \text{cm}^3 = 0.5 \, \text{mmol}$
NaCl has no effect on the pH. So, the resulting solution is a weak base ($\text{Na}_2\text{CO}_3$), and its concentration after mixing the two solutions is: $c_{\text{Na}_2\text{CO}_3} = \frac{n_{\text{Na}_2\text{CO}_3}}{V_{\text{total}}} = \frac{0.5 \, \text{mmol}}{10 \, \text{cm}^3 + 5 \, \text{cm}^3} = 0.03 \, \text{M}$. For $\text{Na}_2\text{CO}_3$, $K_{b_1} = \frac{K_w}{K_{b_2}} = \frac{10^{-14}}{5.60 \times 10^{-11}} = 1.786 \times 10^{-4}$. In this case, there is no 3 log unit difference between $c_{\text{weak acid}}$ and $K_{b_1}$, so $[\text{OH}^-] = K_{b_1} \cdot \frac{c_{\text{weak base}} - [\text{OH}^-]}{[\text{OH}^-]}$
From this, $[\text{OH}^-] = 0.002352 \, \text{M}$.
$p\text{OH} = -\log([\text{OH}^-]) = -\log(0.002352) = 2.629$
$p\text{H} = 14.00 - p\text{OH} = 14.00 - 2.629 = 11.371$

8. Nicotine (C$\text{}_{10}$H$\text{}_{14}$N$\text{}_{2}$) is a diprotic weak base.
   a) What is the pH of a 0.05 M nicotine solution?
   b) What is the pH after adding one equivalent of hydrochloric acid?
   c) Is it possible to determine the concentration of a nicotine solution by acid-base titration? If yes, how can it be done?

a) Nicotine is a weak base, and $c_{\text{weak base}} >> K_{b_1}$, so $[\text{OH}^-] = \sqrt{K_{b_1} \cdot c_{\text{weak base}}} = \sqrt{(7.0 \times 10^{-7}) \times 0.05} = 1.87 \times 10^{-4} \, \text{M}$.
$p\text{OH} = -\log([\text{OH}^-]) = -\log(1.87 \times 10^{-4}) = 3.728$
$p\text{H} = 14.00 - p\text{OH} = 14.00 - 3.728 = 10.272$

b) After adding one equivalent of strong acid to a diprotic weak base, we have an ampholite and its pH is: $p\text{OH} = \frac{pK_{b_1} + pK_{b_2}}{2} = \frac{6.155 + 10.854}{2} = 8.504$
$p\text{H} = 14.00 - p\text{OH} = 14.00 - 8.505 = 5.496$

c) It is possible to determine the concentration of a nicotine by acid-base titration, using a strong acid (e.g. HCl solution) to titrate the nicotine solution with an indicator changing its color around pH 5.496. Using this indicator, the acid-base reaction is:
nicotine + HCl → nicotine·HCl

So, one molecule of nicotine reacts with one equivalent of strong acid.

Distribution curve of nicotine as a function of pH

Titration of nicotine with HCl titrant

9. 50 cm$^3$ of 0.200 M maleic acid solution is titrated by 0.500 M sodium hydroxide solution. Calculate the volume of titrant and the pH...

a) after adding one equivalent of base.

b) after adding two equivalents of base.

a) Maleic acid is a biprotic weak acid (H$_2$mal), so, after adding one equivalent of base, we have got an ampholite (Hmal$^-$ or NaHmal), and its pH is: $\text{pH} = \frac{pK_{a1} + pK_{a2}}{2} = \frac{2.000 + 6.260}{2} = 4.130$.
The acid-base reaction is:

$$\text{H}_2\text{mal} + \text{NaOH} \rightarrow \text{NaHmal} + \text{H}_2\text{O}$$

The amount of maleic acid in the 50 cm$^3$ sample is: $n_{\text{H}_2\text{mal}} = c_{\text{H}_2\text{mal}} \times V_{\text{H}_2\text{mal}} = 0.2 \text{ M} \times 50 \text{ cm}^3 = 10 \text{ mmol}$. From the acid-base equation, $n_{\text{NaOH}} = n_{\text{H}_2\text{mal}} = 10 \text{ mmol}$. So, the volume of base added is: $V_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{c_{\text{NaOH}}} = \frac{10 \text{ mmol}}{0.500 \text{ M}} = 20 \text{ cm}^3$.

b) After adding two equivalents of base, the resulting solution is a weak base (Na$_2$mal), so to calculate the pH, we need its concentration and its $pK_b$. The acid-base reaction is:

$$\text{H}_2\text{mal} + 2 \text{NaOH} \rightarrow \text{Na}_2\text{mal} + 2 \text{H}_2\text{O}$$

The amount of maleic acid in the 50 cm$^3$ sample is: $n_{\text{H}_2\text{mal}} = c_{\text{H}_2\text{mal}} \times V_{\text{H}_2\text{mal}} = 0.2 \text{ M} \times 50 \text{ cm}^3 = 10 \text{ mmol}$. From the acid-base equation, $n_{\text{NaOH}} = 2 \times n_{\text{H}_2\text{mal}} = 20 \text{ mmol}$. So, the volume of base added is: $V_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{c_{\text{NaOH}}} = \frac{20 \text{ mmol}}{0.500 \text{ M}} = 40 \text{ cm}^3$.

The concentration of the formed weak base (Na$_2$mal) after mixing the two solutions is:

$$c_{\text{Na}_2\text{mal}} = \frac{n_{\text{Na}_2\text{mal}}}{V_{\text{total}}} = \frac{10 \text{ mmol}}{50 \text{ cm}^3 + 40 \text{ cm}^3} = 0.1 \text{ M}.$$
At the same time, \( K_{b1} = \frac{K_w}{K_{a2}} = \frac{10^{-14}}{5.50 \cdot 10^{-7}} = 1.81 \cdot 10^{-8} \). In this case, there is more than 3 log unit difference between \( c_{\text{weak acid}} \) and \( K_{b1} \), so \( [\text{OH}^-] = \sqrt{K_{b1} \cdot c_{\text{weak base}}} = \sqrt{1.81 \cdot 10^{-8} \cdot 0.1} = 4.495 \cdot 10^{-5} \text{ M} \).

\( \text{pOH} = -\log[\text{OH}^-] = -\log(4.495 \cdot 10^{-5}) = 4.347 \)

\( \text{pH} = 14.00 - \text{pOH} = 14.00 - 2.629 = 9.653 \)

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10. Calculate the % distribution of the species formed in a solution of phthalic acid at \( \text{pH} = 4.50 \).

\( \text{pH} = 4.50 \), so \( [\text{H}^+] = 10^{-\text{pH}} = 3.1627 \cdot 10^{-5} \text{ mol/dm}^3 \). We also know the \( K_{a1} \) and \( K_{a2} \) values for phthalic acid, so:

\[
X_{A^-} = \frac{1}{1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}}} = 0.10705, \text{ that is } 10.705 \% \text{ of } A^2^- (\text{pht}^2-) .
\]

\[
X_{HA^-} = \frac{\frac{[\text{H}^+]}{K_{a2}}}{1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}}} = 0.02495, \text{ that is } 2.495 \% \text{ of } HA^- (\text{Hpht}^-).
\]

\[
X_{H_2A} = \frac{\frac{[\text{H}^+]^2}{K_{a1}K_{a2}}}{1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}}} = 0.86800, \text{ that is } 86.800 \% \text{ of } H_2A (\text{H}_2\text{pht}).
\]