1. **Calculate the pH**

   a) **in a 0.1 M hydrogen sulphide solution**

   b) **in a 0.1 M sodium sulphide solution and**

   c) **in a 0.1 M sodium hydrogen sulphide solution.**

1/a) H$_2$S solution: c = 0.10 M

   \[ K_{a1} = 9.1 \times 10^{-8} \]

   \[ K_{a2} = 1.2 \times 10^{-15} \]

   \[ [H^+] = \sqrt{K_a \cdot c} = \sqrt{(9.1 \times 10^{-8}) \times 0.1} = 9.539 \times 10^{-5} \text{ M} \]

   \[ \text{pH} = -\log([H^+]) = -\log(9.539 \times 10^{-5}) = 4.020 \]

1/b) Na$_2$S solution: c = 0.10 M

   \[ K_a \times K_b = K_w \]

   that is \[ K_b = \frac{K_w}{K_{a2}} = \frac{10^{-14}}{1.2 \times 10^{-15}} = 8.333 \]

   In this case c$_{\text{weak base}} \ll K_b$, that is the equation to use is:

   \[ [\text{OH}^-] = K_b \cdot \frac{c - [\text{OH}^-]}{[\text{OH}^-]} \]

   \[ [\text{OH}^-]^2 = K_b (c - [\text{OH}^-]) \]

   \[ [\text{OH}^-]^2 + (K_b \times [\text{OH}^-]) - (K_b \times c) = 0 \]

   By solving the equation, \[ [\text{OH}^-] = \frac{-K_b \pm \sqrt{K_b^2 + 4 \times (K_b \times c)}}{2} = 9.85 \times 10^{-2} \text{ M} \]

   \[ \text{pOH} = -\log([\text{OH}^-]) = -\log(9.85 \times 10^{-2}) = 1.066 \]

   \[ \text{pH} = 14 - 1.066 = 12.934 \]

1/c) NaHS solution: c = 0.1 M

   \[ [H^+] = \sqrt{K_{a1} \times K_{a2}} = \sqrt{9.1 \times 10^{-8} \times 1.2 \times 10^{-15}} = 1.045 \times 10^{-11} \text{ M} \]

   \[ \text{pH} = -\log([H^+]) = -\log(1.045 \times 10^{-11}) = 10.98 \]

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

   \[ [H^+] = \sqrt{K_{a1} \times K_{a2}} = \sqrt{4.3 \times 10^{-7} \times 5.6 \times 10^{-11}} = 4.907 \times 10^{-9} \text{ M} \]

   \[ \text{pH} = -\log([H^+]) = -\log(4.907 \times 10^{-9}) = 8.31 \]

3. **What is the pH of a 0.2 M carbonic acid solution?**

   H$_2$CO$_3$ solution: c = 0.20 M

   \[ K_{a1} = 4.30 \times 10^{-7} \cdot \]

   \[ K_{a2} = 5.60 \times 10^{-11} \]

   \[ [H^+] = \sqrt{K_a \cdot c} = \sqrt{(4.3 \times 10^{-7}) \times 0.2} = 2.932 \times 10^{-2} \text{ M} \]

   \[ \text{pH} = -\log([H^+]) = -\log(2.932 \times 10^{-2}) = 3.533 \]
4. What is the pH of the buffer solution that was prepared by mixing 100.00 cm\(^3\) of 0.40 mol/dm\(^3\) \(\text{NaH}_2\text{PO}_4\)-solution and 50 cm\(^3\) of 0.50 mol/dm\(^3\) \(\text{Na}_2\text{HPO}_4\) solution?

\[
c_{\text{NaH}_2\text{PO}_4} = 0.400 \text{ M} \quad V(\text{NaH}_2\text{PO}_4) = 100 \text{ cm}^3 \quad n(\text{NaH}_2\text{PO}_4) = 0.04 \text{ mol}
\]
\[
c_{\text{Na}_2\text{HPO}_4} = 0.500 \text{ M} \quad V(\text{Na}_2\text{HPO}_4) = 50 \text{ cm}^3 \quad n(\text{Na}_2\text{HPO}_4) = 0.025 \text{ mol}
\]

\[K_{a2} = 6.17 \times 10^{-8}\]

\[
[H^+] = K_{a2} \frac{c_{\text{weak acid}}}{c_{\text{weak base}}} = 6.17 \times 10^{-8} \times \frac{0.04}{0.025} = 9.872 \times 10^{-8} \text{ M}
\]

\[\text{pH} = -\log [H^+]\]
\[\text{pH} = -\log 9.872 \times 10^{-8} = 7.005\]

5. We added 0.5; 1.0; 1.5 and 2.0 equivalent of base to a 0.10 mol/dm\(^3\) \(\text{H}_2\text{CO}_3\) solution. What is the pH of the solution at the different degrees of titration if we neglect the change in the volume of the solution.

a) At the beginning of the titration:

\[\text{pH} = -\log[H^+] = -\log(2.074 \times 10^{-4}) = 3.683\]

b) after the addition of 0.5 equivalent of base:

\[K_{a1} = 4.30 \times 10^{-7}\]

\[\text{pH} = -\log[H^+] = -\log(4.30 \times 10^{-7}) = 6.366\]

c) after the addition of 1.0 equivalent of base:

\[\text{pH} = -\log[H^+] = -\log(4.907 \times 10^{-9}) = 8.31\]

d) after the addition of 1.5 equivalent:

\[\text{pH} = -\log[H^+] = -\log(5.60 \times 10^{-11}) = 10.76\]
\[
\text{pH} = - \log 5.60 \times 10^{-11}
\]

**pH = 10.25**

e) after the addition of 2.0 equivalent of base:

\[
K_w \times K_a = K_W \quad \text{that is} \quad \frac{K_w}{K_a} = \frac{10^{-14}}{5.60 \times 10^{-11}} = 1.786 \times 10^{-4} \text{ M}
\]

In this case \(c_{\text{weak base}} >> K_b\), that is the equation to use is:

\[
[\text{OH}^-] = \sqrt{K_b \cdot c_{\text{weak base}}} = \sqrt{(1.786 \times 10^{-4}) \times 0.1} = 4.226 \times 10^{-6} \text{ M}
\]

\[
\text{pOH} = -\log[\text{OH}^-] = -\log(4.226 \times 10^{-6}) = 2.374
\]

\[
\text{pH} = 14.00 - \text{pH} = 14.00 - 2.374 = 11.626
\]

6. We would like to prepare a buffer solution with pH = 8.50. We have the following solutions: 0.200 mol/dm\(^3\) NaH\(_2\)PO\(_4\) solution and 0.200 mol/dm\(^3\) Na\(_2\)HPO\(_4\) solution. How should we mix the two solutions to get the buffer with pH = 8.50?

\[
\text{pH} = 8.50 \rightarrow \text{pH} = -\log[H^+] \\
[H^+] = 3.162 \times 10^{-9} \text{ M}
\]

\[
[H^+] = K_{a_2} \frac{n_{\text{acid}}}{n_{\text{salt}}} \\
3.162 \times 10^{-9} = 6.17 \times 10^{-8} \times \frac{n_{\text{acid}}}{n_{\text{salt}}}
\]

\[
\frac{n_{\text{acid}}}{n_{\text{salt}}} = 0.05125
\]

At this stage you have to choose any volume from the buffer to continue the calculation. For example I take 5.00 L of the buffer. The total concentration of the solution will be 0.200 mol/dm\(^3\). So:

\[
n = 0.200 \times 5.00 = 1 \text{ mol} \quad \text{(this is the molar amount of phosphate that is the sum of the molar amount of the two forms of phosphate in the solution)}
\]

\[
n_{\text{acid}} + n_{\text{salt}} = 1.00 \\
n_{\text{salt}} = 1.00 - n_{\text{acid}}
\]

\[
\frac{n_{\text{acid}}}{1 - n_{\text{acid}}} = 0.05125
\]

\[
0.05125 - 0.05125 \times n_{\text{acid}} = n_{\text{acid}}
\]

\[
0.05125 = 1.05125 \times n_{\text{acid}}
\]

\[
n_{\text{acid}} = 0.04875 \text{ mol}
\]
7. What is the pH of the solution that was prepared by dissolving 3.71 g Na₂CO₃ in 250.0 cm³ of 0.1 mol/dm³ H₂CO₃ solution?

V = 250.0 cm³
c = 0.100 mol/dm³
n(H₂CO₃) = c × V = 0.250 × 0.1 = 0.0250 mol

m(Na₂CO₃) = 3.71 g
M(Na₂CO₃) = 106.0 g/mol
n(Na₂CO₃) = \( \frac{3.71}{106} = 0.035 \text{mol} \)

H₂CO₃ + CO₃²⁻ = 2 HCO₃⁻
0.025 mol 0.035 mol

A reaction takes place between carbonic acid and carbonate ions; the whole amount of the carbonic acid reacts:
n(CO₃²⁻)excess = 0.035 – 0.025 = 0.010 mol
n(HCO₃⁻) = 2 × 0.025 = 0.050 mol

This will be a buffer system:

\[ [H^+] = K_a \frac{n(HCO_3^-)}{n(CO_3^{2-})} = 5.60 \times 10^{-11} \times \frac{0.01}{0.05} = 2.80 \times 10^{-10} \text{M} \]

\[ \text{pH} = -\log[H^+] \]
\[ \text{pH} = 9.553 \]

8. We titrate 10.0 cm³ of a 0.100 M phosphoric acid solution with a 0.10 M sodium hydroxide solution. What is the pH of the solution after the addition of 0.5; 1.4; 2.7 and 3.5 equivalent of base?

V(H₃PO₄) = 10.0 cm³
c(H₃PO₄) = 0.100 mol/dm³
n(H₃PO₄) = 0.001 mol

c(NaOH) = 0.100 mol/dm³

a) after the addition of 0.5 equivalent of base:
\[ H_3PO_4 + OH^- \iff H_2PO_4^- + H_2O \]

\[ n(H_3PO_4) = 0.001 \text{ mol} \]

Half-equivalent of base: its molar amount will be half of the molar amount of phosphoric acid.
\[ n(\text{NaOH}) = 0.0005 \text{ mol} \]

As a result of the reaction: \( n(H_3PO_4) = 0.0005 \text{ mol} \)
\[ n(\text{NaH}_2\text{PO}_4) = 0.0005 \text{ mol} \]

The concentration of the acid and the salt:
\[ c(H_3PO_4) = \frac{0.0005}{0.015} = 0.0333 \text{ mol/dm}^3 \]
\[ c(\text{NaH}_2\text{PO}_4) = \frac{0.0005}{0.015} = 0.0333 \text{ mol/dm}^3 \]

\[ [H^+] = K_{a1} \frac{c_{H_3PO_4}}{c_{\text{NaH}_2\text{PO}_4}} = 7.59 \times 10^{-3} \times \frac{0.0333}{0.0333} = 7.59 \times 10^{-3} \text{ M} \]

**pH = 2.12**

b) 1.4 equivalent of base: its molar amount will be 1.4 times the molar amount of phosphoric acid.
\[ n(\text{NaOH}) = 0.0014 \text{ mol} \]

As a result of the reaction: \( n(\text{Na}_2\text{HPO}_4) = 0.0004 \text{ mol} \)
\[ n(\text{NaH}_2\text{PO}_4) = 0.0006 \text{ mol} \]

The concentration of the acid and the salt:
\[ c(\text{Na}_2\text{HPO}_4) = \frac{0.0004}{0.024} = 0.1667 \text{ mol/dm}^3 \]
\[ c(\text{NaH}_2\text{PO}_4) = \frac{0.0006}{0.024} = 0.025 \text{ mol/dm}^3 \]

\[ [H^+] = K_{a2} \frac{c_{\text{NaH}_2\text{PO}_4}}{c_{\text{Na}_2\text{HPO}_4}} = 6.17 \times 10^{-8} \times \frac{0.025}{0.01667} = 9.253 \times 10^{-8} \text{ M} \]

**pH = 7.034**

c) 2.7 equivalent of base: its molar amount is 2.7 times the molar amount of phosphoric acid.
\[ n(\text{NaOH}) = 0.0027 \text{ mol} \]

As a result of the reaction: \( n(PO_4^{3-}) = 0.0007 \text{ mol} \)
\[ n(\text{Na}_2\text{HPO}_4) = 0.0003 \text{ mol} \]
\[ V(\text{solution}) = 10 + \frac{0.0027}{0.1} = 37 \text{cm}^3 \]

The concentration of the acid and the salt:
\[ c(\text{Na}_2\text{PO}_4) = \frac{0.0007}{0.037} = 0.01892 \text{ mol/dm}^3 \]
\[ c(\text{Na}_2\text{HPO}_4) = \frac{0.0003}{0.037} = 0.08108 \text{ mol/dm}^3 \]

This will be a basic buffer:

\[ K_{a3} \times K_{b1} = K_W \quad \text{that is} \quad K_{b1} = \frac{K_W}{K_{a3}} = \frac{10^{-14}}{1.78 \times 10^{-12}} = 5.618 \times 10^{-3} \text{ M} \]

\[ [\text{OH}^-] = K_{b1} \frac{c_{\text{Na}_2\text{HPO}_4}}{c_{\text{Na}_2\text{PO}_4}} = 5.618 \times 10^{-3} \times \frac{0.01892}{0.08108} = 1.311 \times 10^{-3} \text{ M} \]

\[ \text{pOH} = 2.882 \]
\[ \text{pH} = 14 - \text{pOH} = 14 - 2.882 = 11.118 \]

e) 3.5 equivalent of base: its molar amount is 3.5 times the molar amount of phosphoric acid.
\[ n(\text{NaOH}) = 0.0035 \text{ mol} \]
\[ n(\text{NaOH})_{\text{excess}} = 0.0035 - 0.001 \times 3 = 0.0005 \text{ mol} \]

Besides the excess of NaOH (which is a strong base) we will have a weak base, Na\textsubscript{3}PO\textsubscript{4}. So the amount of NaOH will determine the pH of the solution.

\[ V(\text{solution}) = 10 + \frac{0.0035}{0.1} = 45 \text{ cm}^3 = 0.045 \text{ dm}^3 \]

\[ c(\text{NaOH}) = \frac{0.0005}{0.045} = 0.0111 \text{ mol/dm}^3 \]

\[ \text{pOH} = -\log[\text{OH}^-] \]
\[ \text{pOH} = -\log 0.0111 \]
\[ \text{pOH} = 1.954 \]
\[ \text{pH} = 14 - \text{pOH} = 12.046 \]