

Class 6.3
Acids and Bases

CHEM 102H
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*Hydrolysis of Salts made from
Weak Acids or Weak Bases*

- When salts like NaCl or KNO₃ are dissolved in water, the pH is not much affected. But when NaCN or NH₄Cl are dissolved, the pH is changed. Why?
- CN⁻ is a base and NH₄⁺ is an acid:
$$\text{CN}^-(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HCN}(\text{aq}) + \text{OH}^-(\text{aq})$$
$$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

Hydrolysis of Salts - Example

- For NH₃, pK_b = 4.74. What is the pH of a 10⁻² M solution of NH₄Cl?

Polyprotic Acids

As we have seen, several common acids can potentially donate more than one proton.

Sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids are particularly prominent examples:

H_2SO_4 : $\text{p}K_{a1} < 0$; $\text{p}K_{a2} = 1.92$

H_3PO_4 : $\text{p}K_{a1} = 2.12$; $\text{p}K_{a2} = 7.21$; $\text{p}K_{a3} = 12.68$

What are the concentrations of all species in a 0.1 M phosphoric acid solution?

Features of Polyprotic Acids

H_3PO_4 is a representative example:

$\text{p}K_{a1} = 2.12$; $\text{p}K_{a2} = 7.21$; $\text{p}K_{a3} = 12.68$

At what pH are the concentrations of H_3PO_4 and H_2PO_4^- equal?

At that pH, what the concentrations of HPO_4^{2-} and PO_4^{3-} ?

Tough type to answer directly: What is the pH of a H_2PO_4^- or HPO_4^{2-} salt solution? (e.g., K_2HPO_4 or KH_2PO_4 solution)

Easier: what's the pH when $[\text{H}_2\text{PO}_4^-] = [\text{PO}_4^{3-}]$?

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}; \quad K_{a3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

when $[\text{H}_2\text{PO}_4^-] = [\text{PO}_4^{3-}]$,

$$\frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{K_{a2}} = K_{a3} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_3\text{O}^+]} \Rightarrow \text{pH} = \frac{1}{2}(\text{p}K_{a2} + \text{p}K_{a3})$$

But at this pH, $[\text{HPO}_4^{2-}] \gg [\text{H}_2\text{PO}_4^-] = [\text{PO}_4^{3-}]$


