HL

Calculations with weak acids and bases

WEAK ACIDS

The dissociation of a weak acid HA in water can be written:

$$HA(aq) \rightleftharpoons H^{+}(aq) + A^{-}(aq)$$

The equilibrium expression for this reaction is:

For example, to calculate the pH of 0.10 mol dm⁻³ CH₃COOH given that $K_a = 1.8 \times 10^{-5}$ mol dm⁻³ at 298 K:

Equilibrium concentration / mol dm $^{-3}$ (0.10 – x)

$$\begin{split} & K_{\rm a} = \frac{[{\rm CH_3COO^-}] \times [{\rm H^+}]}{[{\rm CH_3COOH}]} = \frac{x^2}{(0.10 - x)} \\ & = 1.8 \times 10^{-5} \ {\rm mol} \ {\rm dm^{-3}} \\ & \Rightarrow x^2 + (1.8 \times 10^{-5} x) - 1.8 \times 10^{-6} = 0 \\ & {\rm by \ solving \ the \ quadratic \ equation} \\ & x = 1.33 \times 10^{-3} \ {\rm mol} \ {\rm dm^{-3}} \end{split}$$

 $pH = -log_{10} 1.33 \times 10^{-3} = 2.88$

If the acids are quite weak the equilibrium concentration of the acid can be assumed to be the same as its initial concentration. Provided the assumption is stated it is usual to simplify the expression in calculations to avoid a quadratic equation. In the above example:

$$K_{a} = \frac{[\text{CH}_{3}\text{COO}^{-}] \times [\text{H}^{+}]}{[\text{CH}_{3}\text{COOH}]} \approx \frac{[\text{H}^{+}]^{2}}{0.10}$$

 $= 1.8 \times 10^{-5} \text{ mol dm}^{-3}$

$$\Rightarrow$$
 [H+] = $\sqrt{1.8 \times 10^{-6}}$ = 1.34 × 10⁻³ mol dm⁻³ pH = 2.87

Examples of other weak acid calculations

1. The pH of a 0.020 mol dm⁻³ solution of a weak acid is 3.9. Find the K₃ of the acid.

$$K_{a} = \frac{[H^{+}]^{2}}{(0.020 - [H^{+}])} \approx \frac{10^{-3.9} \times 10^{-3.9}}{0.020}$$

 $= 7.92 \times 10^{-7} \text{ mol dm}^{-3}$

2. An acid whose K_a is 4.1×10^{-6} mol dm⁻³ has a pH of 4.5. Find the concentration of the acid.

[HA] =
$$\frac{[H^+]^2}{K_a}$$
 = $\frac{10^{-4.5} \times 10^{-4.5}}{4.1 \times 10^{-6}}$
= 2.44 × 10⁻⁴ mol dm⁻³

WEAK BASES

The reaction of a weak base can be written:

$$B(aq) + H_2O(I) \longrightarrow BH^+(aq) + OH^-(aq)$$

Since the concentration of water is constant:

$$K_{b} = \frac{[\mathsf{BH}^{+}] \times [\mathsf{OH}^{-}]}{[\mathsf{B}]}$$

where $K_{\rm b}$ is the base dissociation constant

If one considers the reverse reaction of BH+ acting as an acid to give B and H+ then:

$$K_{a} = \frac{[B] \times [H^{+}]}{[BH^{+}]}$$

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$$\begin{split} K_{a} \times K_{b} &= \frac{[B] \times [H^{+}]}{[BH^{+}]} \times \frac{[BH^{+}] \times [OH^{-}]}{[B]} \\ &= [H^{+}] \times [OH^{-}] = K_{w} \end{split}$$

since p K_a = $-\log_{10} K_a$; p K_b = $-\log_{10} K_b$ and p K_w = $-\log_{10} K_w$ = 14 this can also be expressed as:

$$pK_a + pK_b = 14$$

Examples of calculations

1. The $K_{\rm b}$ value for ammonia is 1.8×10^{-5} mol dm⁻³. Find the pH of a 1.00×10^{-2} mol dm⁻³ solution.

Since
$$[NH_4^+] = [OH^-]$$
 then

$$K_{b} = \frac{[OH^{-}]^{2}}{[NH_{3}]} \approx \frac{[OH^{-}]^{2}}{1.00 \times 10^{-2}} = 1.8 \times 10^{-5}$$

$$[OH^-] = \sqrt{1.8 \times 10^{-7}} = 4.24 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\Rightarrow$$
 pOH = $-\log_{10} 4.24 \times 10^{-4} = 3.37$

$$\Rightarrow$$
 pH = 14 - 3.37 = 10.6

2. The pH of a 3.00×10^{-2} mol dm⁻³ solution of weak base is 10.0. Calculate the p $K_{\rm h}$ value of the base.

$$pH = 10.0 \text{ so } pOH = 4.0$$

$$K_{\rm b} = \frac{10^{-4} \times 10^{-4}}{3.00 \times 10^{-2}} = 3.33 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\Rightarrow$$
 p $K_{\rm b} = 6.48$

3. The IB Data Booklet value for the pK_a of methylamine (aminomethane) is 10.64. Calculate the concentration of a solution of methylamine with a pH of 10.8.

$$pK_b = 14 - 10.64 = 3.36$$
; $pOH = 3.2$

$$[\text{CH}_3\text{NH}_2] = \frac{[\text{OH}^-]^2}{\mathcal{K}_b} = \, \frac{10^{-3.2} \times 10^{-3.2}}{10^{-3.36}}$$

$$= 9.13 \times 10^{-4} \text{ mol dm}^{-3}$$