Comparing the strengths of weak acids (A2)

The position of equilibrium of the reaction between the acid and water varies from one weak acid to another.

The further to the left it lies, the weaker the acid is

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

The acid dissociation constant, Ka

The position of equilibrium is measured by an equilibrium constant of the reaction.

The lower the value for the constant, the more the equilibrium lies to the left.

For a weak acid dissociates in water,

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Applying equilibrium law,

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

For a weak acid (little dissociation) in dilute solution, the concentration of water is large compared with the dissociated ions and any changes to its value are insignificant so its concentration can be regarded as constant.

$$K_a = K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} \ mol\,dm^{-3}$$

A simpler way,

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

The dissociation constant, $\boxed{K_a = \frac{[H^+][A^-]}{[HA]}}$ mol dm^{-3}

Note: Ka is a constant at a given temperature

The weaker the acid:

- the less it dissociates
- the fewer ions it forms
- the smaller Ka

The stronger the acid:

- the more the equilibrium lies to the right
- the larger Ka.

pKa

Another way of expressing the acid dissociation constant is pKa.

$$\boxed{pKa = -\log_{10} Ka}$$

To calculate Ka from pKa

$$Ka = \text{antilog}_{10}(-pKa)$$

Example of Ka and pKa values:

Acid	$Ka/mol\,dm^{-3}$	pKa
CH_2ClCO_2H	1.4×10^{-3}	2.9
HNO_2	4.6×10^{-4}	3.3
HCO_2H	1.8×10^{-4}	3.8
CH_3CO_2H	1.8×10^{-5}	4.8
HCN	4.9×10^{-10}	9.3

Note:

The strongest acids have the highest Ka or lowest pKa values.

Thus, CH_2ClCO_2H is the strongest acid in this example.

Example

Write acid dissociation constant, Ka for the following acids in equilibrium:

i) $C_6H_5COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + C_6H_5COO^-_{(aq)}$

ii) $HCO_3^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

iii) $NH_4^+{}_{(aq)} \rightleftharpoons H^+_{(aq)} + NH_{3(aq)}$

Workings

i) $$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$$

ii) $$K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

iii) $$K_a = \frac{[H^+][NH_3]}{[NH_4^+]}$$

Example:

For the following acids or ions in the table, work out which species in the equilibrium are Bronsted-Lowry acids and which are their conjugate bases.

No	Acid or ion	Equilibrium in aqueous solution
i.	hydrate Fe^{3+} ion	$[Fe(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Fe(H_2O)_5(OH)]^{2+}$
ii.	nitric(III) acid	$HNO_2 \rightleftharpoons H^+ + NO_2^-$
iii.	carbonic acid	$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$
iv.	hydrogensilicate ion	$HSiO_3^- \rightleftharpoons H^+ + SiO_3^{2-}$

Workings

i. acid : $[Fe(H_2O)_6]^{3+}$ base : $[Fe(H_2O)_5(OH)]^{2+}$

ii. acid : HNO_2 base : NO_2^-

iii. acid : $CO_2 + H_2O$ base : HCO_3^-
(H_2CO_3)

iv. acid : $HSiO_3^-$ base : SiO_3^{2-}

Calculating Ka for a weak acid

The value of Ka for a weak acid can be calculated if given,

- the concentration of the acid
- the pH of the solution.

Weak acid in equilibrium,

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

each moleeule of HA that ionises, one H^+ ion and one A^- ion are produced.

$$[H^+] = [A^-]$$

The acid dissociation constant becomes,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{[H^+]^2}{[HA]}$$

2 assumptions,

1. The concentration of hydrogen ions produced by the ionisation of water molecules present in the solution is ignored, because the ionic product of water (1.00×10^{-14} $mol^2 dm^{-6}$) is negligible compared with the values for most weak acids
2. The ionisation of the weak acid is so small that the concentration of undissociated HA molecules present at equilibrium is approximately the same as that of the original acid.

Example.

Calculate the value of Ka for methanoic acid. A solution of 0.010 $mol dm^{-3}$ methanoic acid, HCOOH has a pH of 2.90.

Workings

Step 1 : Convert pH to $[H^+]$,

$$[H^+] = \text{antilog}_{10}(-2.90)$$
$$= 1.26 \times 10^{-3} \text{ mol dm}^{-3}$$

Step 2 : Write the acid dissociation constant expression,

$$K_a = \frac{[H^+]^2}{[HCOOH]}$$

Step 3 : Enter the values into the expression,

$$K_a = \frac{(1.26 \times 10^{-3})^2}{(0.010)}$$
$$= 1.59 \times 10^{-4} \text{ mol dm}^{-3}$$

Exercise

a. Calculate the value of Ka for the following acids:

(i) 0.0200 $mol\,dm^{-3}$ 2-aminobenzoic acid, which has a pH of 4.30

(ii) 0.0500 $mol\,dm^{-3}$ propanoic acid, which has a pH of 3.10

(iii) 0.100 $mol\,dm^{-3}$ 2-nitrophenol, which has pH of 4.10

b. Calculate pKa values for each of the acids in part a.

Workings

a. (i) $[H^+] = \text{antilog}_{10}(-4.30) = 5.01 \times 10^{-5}\,mol\,dm^{-3}$

$$Ka = \frac{(5.01 \times 10^{-5})^2}{(0.0200)} = 1.26 \times 10^{-7}\,mol\,dm^{-3}$$

(ii) $[H^+] = \text{antilog}_{10}(-3.10) = 7.94 \times 10^{-4}\,mol\,dm^{-3}$

$$Ka = \frac{(7.94 \times 10^{-4})^2}{(0.0500)} = 1.26 \times 10^{-5}\,mol\,dm^{-3}$$

(iii) $[H^+] = \text{antilog}_{10}(-4.10) = 7.94 \times 10^{-5}\,mol\,dm^{-3}$

$$Ka = \frac{(7.94 \times 10^{-5})^2}{(0.100)} = 6.31 \times 10^{-8}\,mol\,dm^{-3}$$

b. (i) $pKa = -\log_{10}(1.26 \times 10^{-7}) = 6.90$

(ii) $pKa = -\log_{10}(1.26 \times 10^{-5}) = 4.90$

(iii) $pKa = -\log_{10}(6.31 \times 10^{-8}) = 7.20$

Calculating the pH of a weak acid

The pH (or $[H^+]$) value of a weak acid can be calculated if provided with:

- the concentration of the acid.
- the value of Ka for the acid.

Two assumptions,

1. The concentration of hydrogen ions produced by the ionisation of water is negligible.
2. The equilibrium concentration of the weak acid is equal to the original concentration of the weak acid.

Example.

Calculate the pH of $0.100 \text{ mol dm}^{-3}$ ethanoic acid, CH_3COOH. ($Ka = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$)

Workings

Step 1 : Write the equilibrium expression for the reaction

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

$$Ka = \frac{[H^+]^2}{[HA]}$$

Step 2 : Enter the values into the expression.

$$1.74 \times 10^{-5} = \frac{[H^+]^2}{(0.100)}$$

Step 3 : Rearrange the equation.

$$[H^+]^2 = 1.74 \times 10^{-5} \times 0.100 = 1.74 \times 10^{-6}$$

Step 4 : Take the square root.

$$[H^+] = \sqrt{1.74 \times 10^{-6}} = 1.32 \times 10^{-3}\ mol\ dm^{-3}$$

Step 5 : Calculate pH.

$$pH = -\log_{10}[H^+]$$

$$= -\log_{10}(1.32 \times 10^{-3})$$

$$= 2.88$$

Exercise

Work out the pH values of the following solutions:

a. 0.0200 mol dm^{-3} aqueous benzoic acid ($K_a = 6.3 \times 10^{-5}$ mol dm^{-3})

b. 0.0100 mol dm^{-3} hydrated $\overset{Al(H_2O)_6^{3+}}{\text{aluminium}}$ ions ($K_a = 1.0 \times 10^{-5}$ mol dm^{-3})

c. 0.100 mol dm^{-3} aqueous methanoic acid ($K_a = 1.6 \times 10^{-4}$ mol dm^{-3})

Workings

a. $$K_a = \frac{[H^+]^2}{[\text{benzoic acid}]}$$

$$[H^+]^2 = 6.3 \times 10^{-5} \times 0.0200$$

$$[H^+] = \sqrt{6.3 \times 10^{-5} \times 0.0200} = 1.12 \times 10^{-3}\ mol\ dm^{-3}$$

$$pH = -\log_{10}(1.12 \times 10^{-3}) = 2.95$$

b. $$K_a = \frac{[H^+]^2}{[Al(H_2O)_6^{3+}]}$$

$$[H^+]^2 = 1.0 \times 10^{-5} \times 0.0100$$

$$[H^+] = \sqrt{1.0 \times 10^{-5} \times 0.0100} = 3.16 \times 10^{-4}\ mol\ dm^{-3}$$

$$pH = -\log_{10}(3.16 \times 10^{-4}) = 3.5$$

c. $$K_a = \frac{[H^+]^2}{[\text{methanoic acid}]}$$

$$[H^+] = \sqrt{1.6 \times 10^{-4} \times 0.100} = 4.0 \times 10^{-3}\ mol\ dm^{-3}$$

$$pH = -\log_{10}(4.0 \times 10^{-3}) = 2.4$$

The base dissociation constant, K_b

For a weak base dissociates in water,

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

Equilibrium constant expression,

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

For weak base, the water molecules remain largely undissociated and its concentration can be regarded as constant.

$$K_b = K_c[H_2O] = \text{constant}$$

$$\boxed{K_b = \frac{[BH^+][OH^-]}{[B]}} \quad \underline{\text{mol dm}^{-3}}$$

K_b – the <u>base dissociation constant</u>.

Note: K_b is a constant at a given temperature.

pK_b

Another way of expressing the base dissociation constant is pK_b

$$\boxed{pK_b = -\log_{10} K_b}$$

To calculate K_b from pK_b

$$K_b = \text{antilog}_{10}(-pK_b)$$

Example of K_b and pK_b values:

Base	K_b/mol dm^{-3}	pK_b
$C_2H_5NH_2$	6.5×10^{-4}	3.2
CH_3NH_2	4.0×10^{-4}	3.4
NH_3	1.8×10^{-5}	4.8
$C_6H_5NH_2$	4.3×10^{-10}	9.4

Note:

The strongest bases have the highest K_b or lowest pK_b values.

Thus, $C_2H_5NH_2$ is the strongest base in this example.