

DP IB Chemistry: HL


Your notes

18.2 Calculations Involving Acids & Bases

Contents

- * 18.2.1 Acid & Base Dissociation Constants
- * 18.2.2 Acid & Base Problem Solving



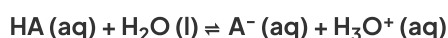
Your notes

18.2.1 Acid & Base Dissociation Constants

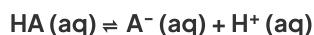
Acid & Base Dissociation Constants

Weak acids

- A **weak acid** is an acid that **partially** (or incompletely) **dissociates** in aqueous solutions
 - For example, most carboxylic acids (e.g. ethanoic acid), HCN (hydrocyanic acid), H₂S (hydrogen sulfide) and H₂CO₃ (carbonic acid)
 - In general, the following equilibrium is established:



OR



- At equilibrium, the majority of HA molecules remain unreacted
- The position of the equilibrium is more over to the **left** and an equilibrium is established
- As this is an equilibrium, we can write an equilibrium constant expression for the reaction
- This constant is called the **acid dissociation constant**, K_a , and has the units mol dm⁻³

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

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

Copyright © Save My Exams. All Rights Reserved

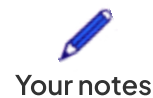
Acid dissociation constant expressions

- Carboxylic acids are weak acids
 - For example, propanoic acid, CH₃CH₂COOH (aq), dissociates according to the following equation which leads to the K_a expression for propanoic acid:



OR





$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

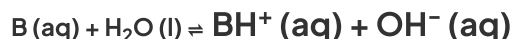
Copyright © Save My Exams. All Rights Reserved

Acid dissociation constant expressions for propanoic acid

- Values of K_a are very small
 - For example, K_a for propanoic acid = $1.34 \times 10^{-5} \text{ mol dm}^{-3}$
- When writing the equilibrium expression for weak acids, we assume that the concentration of H_3O^+ (aq) due to the ionisation of water is negligible

Weak bases

- A weak base will also ionise in water and we can represent this with the **base dissociation constant, K_b**
- In general the equilibrium established is:

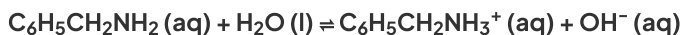


$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Copyright © Save My Exams. All Rights Reserved

Base dissociation constant expression

- Amines are weak bases
 - For example, 1-phenylmethanamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ (aq), dissociates according to the following equation which leads to the K_b expression for 1-phenylmethanamine:



$$K_b = \frac{[\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2]}$$

Copyright © Save My Exams. All Rights Reserved

Base dissociation constant expression for 1-phenylmethanamine

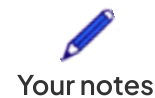
$\text{p}K_a$ and $\text{p}K_b$

- The range of values of K_a and K_b is very wide and for weak acids, the values themselves are very small numbers

Table of K_a values

Acid	$K_a / \text{mol dm}^{-3}$
Methanoic, HCOOH	1.77×10^{-4}
Ethanoic, CH_3COOH	1.74×10^{-5}
Benzoic, $\text{C}_6\text{H}_5\text{COOH}$	6.46×10^{-5}
Carbonic, H_2CO_3	4.30×10^{-7}

Copyright © Save My Exams. All Rights Reserved



- For this reason, it is easier to work with another term called $\text{p}K_a$ for acids or $\text{p}K_b$ for bases
- In order to convert the values we need to apply the following calculations:

$$\text{p}K_a = -\log K_a \quad K_a = 10^{-\text{p}K_a}$$

$$\text{p}K_b = -\log K_b \quad K_b = 10^{-\text{p}K_b}$$

 Table of $\text{p}K_a$ values

Acid	$K_a / \text{mol dm}^{-3}$	$\text{p}K_a$
Methanoic, HCOOH	1.77×10^{-4}	3.75
Ethanoic, CH_3COOH	1.74×10^{-5}	4.75
Benzoic, $\text{C}_6\text{H}_5\text{COOH}$	6.46×10^{-5}	4.18
Carbonic, H_2CO_3	4.30×10^{-7}	6.36

Copyright © Save My Exams. All Rights Reserved

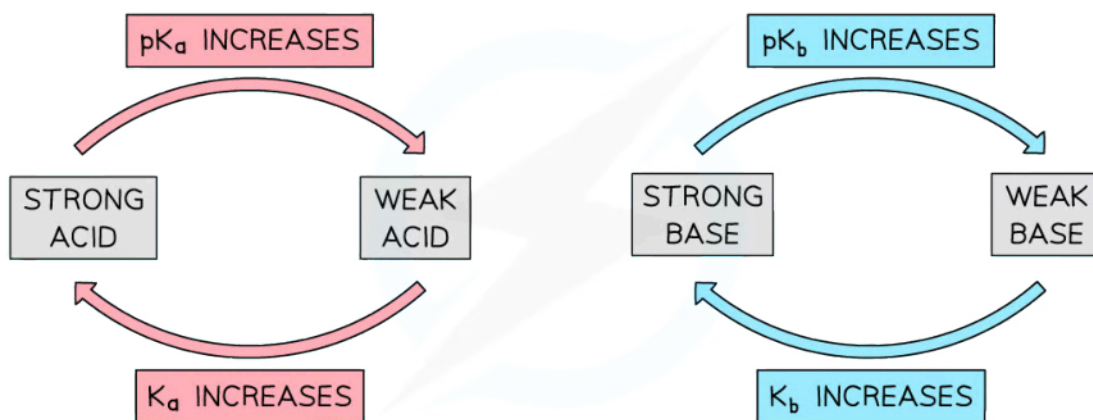
- The range of $\text{p}K_a$ values for most weak acids lies between 3 and 7

Relative Strengths of Acids and Bases

- The larger the K_a value, the stronger the acid
- The larger the $\text{p}K_a$ value, the weaker the acid
- The larger the K_b value, the stronger the base
- The larger the $\text{p}K_b$ value, the weaker the base



Your notes



Copyright © Save My Exams. All Rights Reserved

pK_a and pK_b tell us the relative strengths of acids and bases

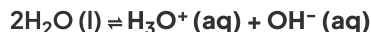


Your notes

Relating K_w to K_a

The Ionic Product of Water and Temperature

- In all aqueous solutions, an equilibrium exists in water where a few water molecules dissociate into protons and hydroxide ions
- We can derive an equilibrium constant for the reaction:



- The concentration of water is constant, so the expression for K_w is:

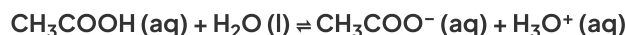
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- This is a specific equilibrium constant called the **ionic product for water**
- The product of the two ion concentrations is $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C

- For conjugate acid-base pairs, K_a and K_b are related to K_w

$$K_a K_b = K_w$$

- The conjugate base of ethanoic acid is the ethanoate ion, $\text{CH}_3\text{COO}^-(\text{aq})$



acid

conjugate base

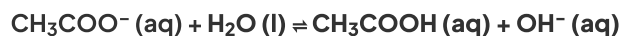
- We can then put this in to the K_a expression

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

Copyright © Save My Exams. All Rights Reserved

Acid dissociation constant for ethanoic acid

- The ethanoate ion will react with water according to the following equation



- We can then put this in to the K_b expression

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

Copyright © Save My Exams. All Rights Reserved

Base dissociation constant for the ethanoate ion

- Now, these two expressions can be combined, which corresponds to



Your notes

- $K_a K_b = K_w$
- $K_a K_b = 10^{-14}$
- Or we could say that
 - $pK_a + pK_b = pK_w$
 - $pK_a + pK_b = 14$
 - This makes the numbers much more easy to deal with as using $K_a K_b = 10^{-14}$ will give very small numbers

$$K_a K_b = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$= [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

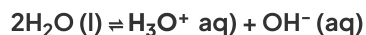
Copyright © Save My Exams. All Rights Reserved

Combining $K_a K_b$ expressions

- Or rearranging these:
 - $K_a = K_w / K_b$
 - $K_b = K_w / K_a$

The ionic product of water, K_w

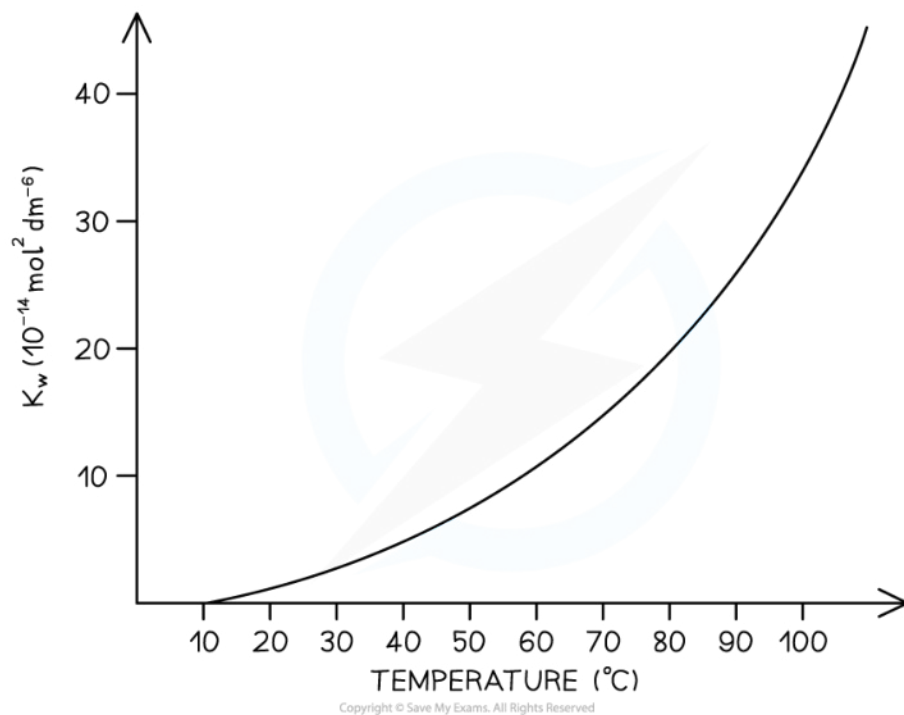
- The ionisation of water is an **endothermic** process



- In accordance with Le Châtelier's principle, an increase in temperature will result in the forward reaction being favoured
 - This causes an increase in the concentration of the hydrogen and hydroxide ions
 - This leads to the **magnitude of K_w increasing**
 - Therefore, the **pH will decrease**
- Increasing the temperature, decreases the pH of water (becomes more acidic)
- Decreasing the temperature, increases the pH of water (becomes more basic)



Your notes



Relationship between K_w and temperature



Your notes

18.2.2 Acid & Base Problem Solving

Acid & Base Calculations

pH

- The acidity of an aqueous solution depends on the number of H_3O^+ ions in solution
- pH is defined as:

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

- Where $[\text{H}_3\text{O}^+]$ is the concentration of H_3O^+ ions in mol dm^{-3}
- Similarly, the **concentration of H^+** of a solution can be calculated if the pH is known by rearranging the above equation to:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

- The pH scale is a logarithmic scale with base 10
- This means that each value is 10 times the value below it
 - For example, pH 5 is 10 times more acidic than pH 6
- pH values are usually given to 2 decimal places

pOH

- The basicity of an aqueous solution depends on the number of hydroxide ions, OH^- , in solution
- pOH is defined as:

$$\text{pOH} = -\log [\text{OH}^-]$$

- Where $[\text{OH}^-]$ is the concentration of hydroxide ions in mol dm^{-3}
- Similarly, the **concentration of OH^-** of a solution can be calculated if the pOH is known by rearranging the above equation to:

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

- If you are given the concentration of a basic solution and need to find the pH, this can be done by:

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-]$$

- Alternatively, if you are given the $[\text{OH}^-]$ and calculate the pOH, the pH can be found by:

$$\text{pH} = 14 - \text{pOH}$$



Your notes

Worked example

pH and H_3O^+ calculations

1. Find the pH when the hydrogen ion concentration is $1.60 \times 10^{-4} \text{ mol dm}^{-3}$
2. Find the hydrogen ion concentration when the pH is 3.10

Answers

Answer 1:

The pH of the solution is:

- $\text{pH} = -\log [\text{H}_3\text{O}^+]$
 - $\text{pH} = -\log 1.6 \times 10^{-4}$
 - $\text{pH} = \mathbf{3.80}$

Answer 2:

The hydrogen concentration can be calculated by rearranging the equation for pH

- $\text{pH} = -\log [\text{H}_3\text{O}^+]$
- $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
 - $[\text{H}_3\text{O}^+] = 10^{-3.10}$
 - $[\text{H}_3\text{O}^+] = \mathbf{7.94 \times 10^{-4} \text{ mol dm}^{-3}}$

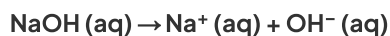
Worked example

pH calculations of a strong alkali

1. Calculate the pH of 0.15 mol dm^{-3} sodium hydroxide, NaOH
2. Calculate the hydroxide concentration of a solution of sodium hydroxide when the pH is 10.50

Answers

Sodium hydroxide is a strong base which ionises as follows:



Answer 1:

The pH of the solution is:

- $[\text{H}^+] = K_w \div [\text{OH}^-]$
 - $[\text{H}^+] = (1 \times 10^{-14}) \div 0.15 = 6.66 \times 10^{-14}$
- $\text{pH} = -\log[\text{H}^+]$

- $\text{pH} = -\log 6.66 \times 10^{-14} = 13.17$

Answer 2

Step 1: Calculate hydrogen concentration by rearranging the equation for pH

- $\text{pH} = -\log[\text{H}^+]$
- $[\text{H}^+] = 10^{-\text{pH}}$
 - $[\text{H}^+] = 10^{-10.50}$
 - $[\text{H}^+] = 3.16 \times 10^{-11} \text{ mol dm}^{-3}$

Step 2: Rearrange the **ionic product of water** to find the concentration of hydroxide ions

- $K_w = [\text{H}^+][\text{OH}^-]$
- $[\text{OH}^-] = K_w \div [\text{H}^+]$

Step 3: Substitute the values into the expression to find the concentration of hydroxide ions

- Since K_w is $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
 - $[\text{OH}^-] = (1 \times 10^{-14}) \div (3.16 \times 10^{-11})$
 - $[\text{OH}^-] = 3.16 \times 10^{-4} \text{ mol dm}^{-3}$

K_a , $\text{p}K_a$, K_b and $\text{p}K_b$

- In reactions of weak acids and bases, we cannot make the same assumptions as for the ionisation of strong acids and bases
- For a weak acid and its conjugate base, we can use the equation:

$$K_w = K_a K_b$$

- By finding the $-\log$ of these, we can use:

$$\text{p}K_w = \text{p}K_a + \text{p}K_b$$

- Remember, to convert these terms you need to use:

$$\text{p}K_a = -\log K_a \quad K_a = 10^{-\text{p}K_a}$$

$$\text{p}K_b = -\log K_b \quad K_b = 10^{-\text{p}K_b}$$

- The assumptions we must make when calculating values for K_a , $\text{p}K_a$, K_b and $\text{p}K_b$ are:
 - The initial concentration of acid \approx the equilibrium concentration of acid
 - $[\text{A}^-] = [\text{H}_3\text{O}^+]$
 - There is negligible ionisation of the water, so $[\text{H}_3\text{O}^+]$ is not affected
 - The temperature is 25°C



Your notes



Worked example

Calculate the acid dissociation constant, K_a , at 298 K for a 0.20 mol dm^{-3} solution of propanoic acid with a pH of 4.88.

Answer

Step 1: Calculate $[\text{H}_3\text{O}^+]$ using

- $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
 - $[\text{H}_3\text{O}^+] = 10^{-4.88}$
 - $[\text{H}_3\text{O}^+] = 1.3182 \times 10^{-5}$

Step 2: Substitute values into K_a expression

- $K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{CH}_3\text{CH}_2\text{COOH}]}$
 - $K_a = \frac{(1.3182 \times 10^{-5})^2}{0.2}$
 - $K_a = 8.70 \times 10^{-10} \text{ mol dm}^{-3}$

Worked example

A $0.035 \text{ mol dm}^{-3}$ sample of methylamine (CH_3NH_2) has $\text{p}K_b$ value of 3.35 at 298 K. Calculate the pH of methylamine.

Answer

Step 1: Calculate the value for K_b using

- $K_b = 10^{-\text{p}K_b}$
 - $K_b = 10^{-3.35}$
 - $K_b = 4.4668 \times 10^{-4}$

Step 2: Substitute values into K_b expression to calculate $[\text{OH}^-]$

- $K_b = \frac{[\text{OH}^-]^2}{[\text{CH}_3\text{NH}_2]}$
- $4.4668 \times 10^{-4} = \frac{[\text{OH}^-]^2}{0.035}$
- $[\text{OH}^-] = \sqrt{4.4668 \times 10^{-4} \times 0.035}$
- $[\text{OH}^-] = 3.9539 \times 10^{-3}$

Step 3: Calculate the pH

- $[\text{H}^+] = K_w \div [\text{OH}^-]$
 - $[\text{H}^+] = (1 \times 10^{-14}) \div 3.9539 \times 10^{-3}$

- $[H^+] = 2.5290 \times 10^{-12}$
- $pH = -\log[H^+]$
 - $pH = 2.5290 \times 10^{-12}$
 - $pH = 11.60$ to 2 decimal places

OR

Step 3: Calculate pOH and therefore pH

- $pOH = -\log[OH^-]$
 - $pOH = -\log 3.9539 \times 10^{-3}$
 - $pOH = 2.4029$
- $pH = 14 - pOH$
 - $pH = 14 - 2.4029$
 - $pH = 11.60$ to 2 decimal places



Your notes