

# DP IB Chemistry: HL

  
Your notes

## 18.2 Calculations Involving Acids & Bases

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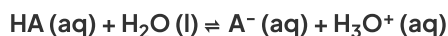
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## 18.2.1 Acid & Base Dissociation Constants

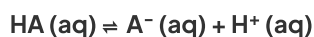
### Acid & Base Dissociation Constants

#### 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), H<sub>2</sub>S (hydrogen sulfide) and H<sub>2</sub>CO<sub>3</sub> (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<sup>-3</sup>

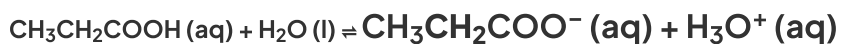
$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

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

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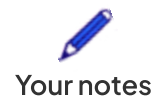
#### Acid dissociation constant expressions

- Carboxylic acids are weak acids
  - For example, propanoic acid, CH<sub>3</sub>CH<sub>2</sub>COOH (aq), dissociates according to the following equation which leads to the  $K_a$  expression for propanoic acid:



OR





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

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

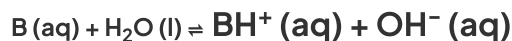
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### Acid dissociation constant expressions for propanoic acid

- 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  $\text{H}_3\text{O}^+$  (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:

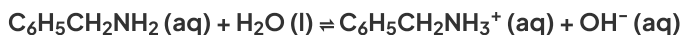


$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

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### 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:



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

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### Base dissociation constant expression for 1-phenylmethanamine

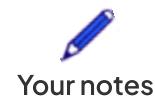
### $\text{p}K_a$ and $\text{p}K_b$

- 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, $\text{HCOOH}$	$1.77 \times 10^{-4}$
Ethanoic, $\text{CH}_3\text{COOH}$	$1.74 \times 10^{-5}$
Benzoic, $\text{C}_6\text{H}_5\text{COOH}$	$6.46 \times 10^{-5}$
Carbonic, $\text{H}_2\text{CO}_3$	$4.30 \times 10^{-7}$

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- 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, $\text{HCOOH}$	$1.77 \times 10^{-4}$	3.75
Ethanoic, $\text{CH}_3\text{COOH}$	$1.74 \times 10^{-5}$	4.75
Benzoic, $\text{C}_6\text{H}_5\text{COOH}$	$6.46 \times 10^{-5}$	4.18
Carbonic, $\text{H}_2\text{CO}_3$	$4.30 \times 10^{-7}$	6.36

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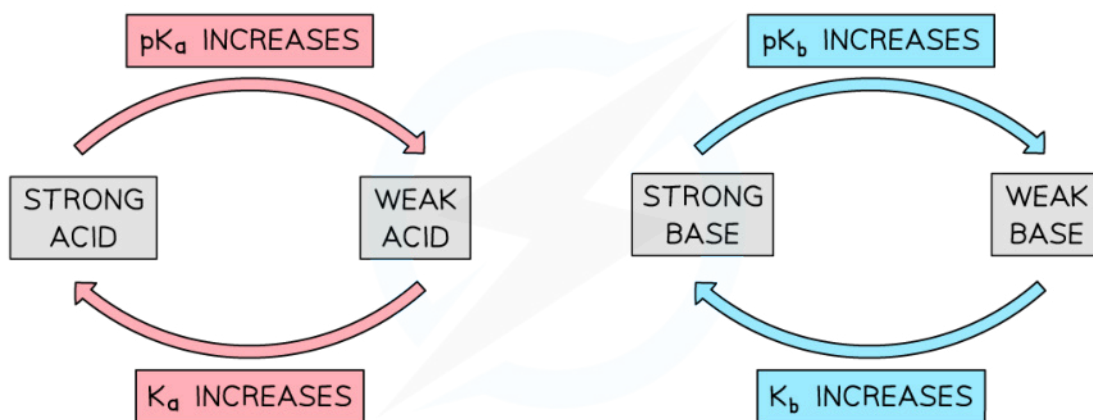
- The range of  $\text{p}K_a$  values for most weak acids lies between 3 and 7

### 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



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*pK<sub>a</sub> and pK<sub>b</sub> tell us the relative strengths of acids and bases*

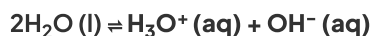


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## Relating Kw to Ka

### 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:

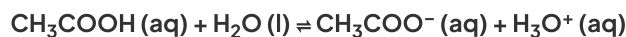
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- 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  $25^\circ\text{C}$

- 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

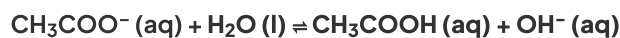
- We can then put this in to the  $K_a$  expression

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

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#### **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

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

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#### **Base dissociation constant for the ethanoate ion**



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- Now, these two expressions can be combined, which corresponds to
  - $K_a K_b = K_w$
  - $K_a K_b = 10^{-14}$
- 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

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

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

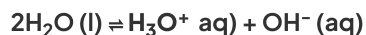
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#### Combining $K_a K_b$ expressions

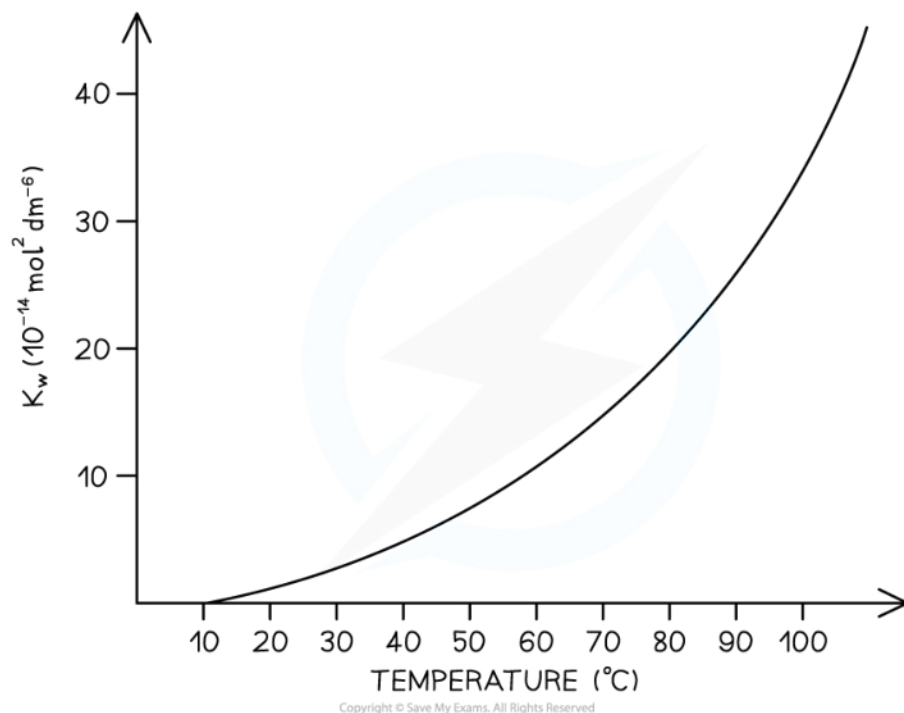
- Or rearranging these:
  - $K_a = K_w / K_b$
  - $K_b = K_w / K_a$

### 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)



**Relationship between  $K_w$  and temperature**



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## 18.2.2 Acid & Base Problem Solving

### Acid & Base Calculations

#### pH

- The acidity of an aqueous solution depends on the number of  $\text{H}_3\text{O}^+$  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  $\text{H}_3\text{O}^+$  ions in  $\text{mol dm}^{-3}$
- Similarly, the **concentration of  $\text{H}^+$**  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,  $\text{OH}^-$ , in solution
- pOH is defined as:

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

- Where  $[\text{OH}^-]$  is the concentration of hydroxide ions in  $\text{mol dm}^{-3}$
- Similarly, the **concentration of  $\text{OH}^-$**  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:

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



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### Worked example

#### pH and $\text{H}_3\text{O}^+$ 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

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

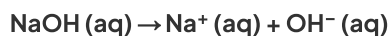
### Worked example

#### pH calculations of a strong alkali

1. Calculate the pH of  $0.15 \text{ mol dm}^{-3}$  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:

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



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- $[H^+] = (1 \times 10^{-14}) \div 0.15 = 6.66 \times 10^{-14}$
- $pH = -\log[H^+]$ 
  - $pH = -\log 6.66 \times 10^{-14} = 13.17$

## Answer 2

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

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

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

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

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

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

## $K_a$ , $pK_a$ , $K_b$ and $pK_b$

- 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:

$$pK_w = pK_a + pK_b$$

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

$$pK_a = -\log K_a \quad K_a = 10^{-pK_a}$$

$$pK_b = -\log K_b \quad K_b = 10^{-pK_b}$$

- The assumptions we must make when calculating values for  $K_a$ ,  $pK_a$ ,  $K_b$  and  $pK_b$  are:
  - The initial concentration of acid  $\approx$  the equilibrium concentration of acid
  - $[A^-] = [H_3O^+]$
  - There is negligible ionisation of the water, so  $[H_3O^+]$  is not affected
  - The temperature is  $25^\circ\text{C}$



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### Worked example

Calculate the acid dissociation constant,  $K_a$ , at 298 K for a  $0.20 \text{ mol dm}^{-3}$  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

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

### Worked example

A  $0.035 \text{ mol dm}^{-3}$  sample of methylamine ( $\text{CH}_3\text{NH}_2$ ) 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  $[\text{OH}^-]$

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

**Step 3:** Calculate the pH

- $[H^+] = K_w \div [OH^-]$ 
  - $[H^+] = (1 \times 10^{-14}) \div 3.9539 \times 10^{-3}$
  - $[H^+] = 2.5290 \times 10^{-12}$
- $pH = -\log [H^+]$ 
  - $pH = 2.5290 \times 10^{-12}$
  - $pH = 11.60$  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



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