Chapter 9A: Acid-Base Equilibria

I   Theories of Acids and Bases

Learning Objectives
- show understanding of, and apply the Arrhenius theory of acids and bases
- show understanding of, and apply the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases
- show understanding of, and apply the Lewis theory of acids and bases (including non-aqueous system, e.g. reaction between BF_3 and NH_3)

1. **The Arrhenius Theory of acids and bases** (O level)
   In 1884, the Swedish chemist Svante Arrhenius proposed acids and bases as

Acid	Base
An *acid* is a hydrogen-containing substance that ionises and **releases hydrogen ions** (i.e. H^+ ions) **when dissolved in water**.	A *base* is a hydroxide-containing substance that ionises and **releases hydroxide ions** (i.e. OH^- ions) **when dissolved in water**.
Example: $HCl \text{ (aq)} \rightarrow H^+ \text{ (aq)} + Cl^- \text{ (aq)}$	*Example*: $NaOH \text{ (aq)} \rightarrow Na^+ \text{ (aq)} + OH^- \text{ (aq)}$

- **Limitations of Arrhenius theory**:
  - It <u>restricted</u> acid-base reactions to those which occur in <u>aqueous solutions</u>.
  - It <u>did not account for the basic properties of ammonia</u> and some organic substance (e.g. amines) that <u>do not contain the hydroxide group</u>.

- **Hydrated proton, H^+ (aq)**
  - The hydrogen ion (H^+) is essentially a proton with very high charge density due to small size (~ 10^{-15} m diameter), which attracts any molecule with lone pair of electrons.
  - Hence, <u>water molecule forms a dative covalent bond to the H^+ ion</u> to produce **hydronium ion** (or hydroxonium ion), H_3O^+.
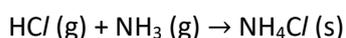
$$H_2O \text{ (}l\text{)} + H^+ \text{ (aq)} \rightarrow H_3O^+$$
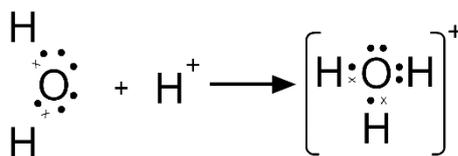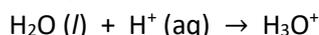
  - Note: Although hydrogen ion (H^+) do not exist alone in aqueous solution, however for simplicity, $\underline{H^+ \text{ (aq)}}$ and $\underline{H_3O^+ \text{ (aq)}}$ will be used interchangeably throughout the chapter.
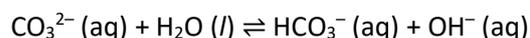
2. **The Brønsted–Lowry Theory of acids and bases**
   In 1923, J.N. Brønsted and T.M. Lowry proposed acids and bases as

Acid	Base
An *Brønsted–Lowry acid* is a **proton donor**	A *Brønsted–Lowry base* is a **proton acceptor**

Example:

$HCl \text{ (g)} + NH_3 \text{ (g)} \rightarrow NH_4Cl \text{ (s)}$ $CO_3^{2-} \text{ (aq)} + H_2O \text{ (}l\text{)} \rightleftharpoons HCO_3^- \text{ (aq)} + OH^- \text{ (aq)}$

acid   base   base   acid

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9A. Acid-Base Equilibria

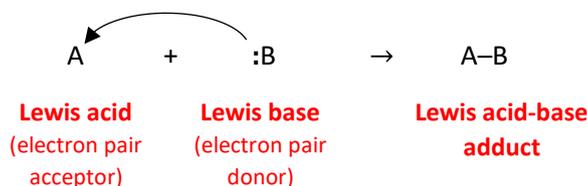- **Limitations of Brønsted–Lowry theory**:
  It cannot explain why certain compounds such as BF_3 or $AlCl_3$ behave as acids but <u>do not contain any hydrogen atoms</u>.

3. **The Lewis Theory of acids and bases**
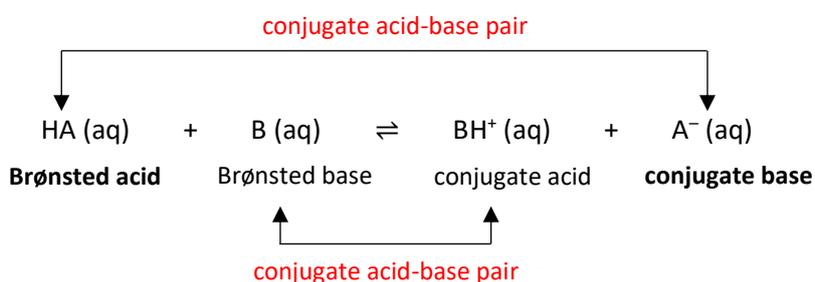   In 1938, G.N. Lewis proposed acids and bases as

Acid	Base
A *Lewis acid* is any **electron pair acceptor**	A *Lewis base* is any **electron pair donor**
⚕ To be able to accept an electron pair, a Lewis acid must be vacant orbitals.	⚕ To be able to donate an electron pair, a Lewis acid must have lone pair of electrons.
Example: ⚕ <u>All cations</u> are Lewis acids since they are able to accept electron (e.g. Cu^{2+}, Fe^{2+}, Fe^{3+}) ⚕ An atom, ion or molecule with an <u>incomplete octet of electrons</u> can act as a Lewis (e.g. BF_3, AlF_3) ⚕ Molecules where the central atom can have <u>more than 8 valence electrons</u> (i.e. expand octet) can be Lewis acids (e.g. $SiBr_4$, SiF_4)	

- ⚕ When a Lewis acid reacts with a Lewis base, a **pair of electrons** is **transferred from the base to the acid**, forming a dative covalent bond. The resulting product is called an addition product or adduct.

$$A \quad + \quad :B \quad \rightarrow \quad A–B$$

<div align="center">

Lewis acid   **Lewis base**   **Lewis acid-base**
(electron pair   (electron pair   **adduct**
acceptor)   donor)

</div>

4. **Conjugate acid-base pairs**
   Consider an acid HA and base B,

<div align="center">

conjugate acid-base pair

$$HA\ (aq) \quad + \quad B\ (aq) \quad \rightleftharpoons \quad BH^+\ (aq) \quad + \quad A^-\ (aq)$$

Brønsted acid   Brønsted base   conjugate acid   **conjugate base**

conjugate acid-base pair

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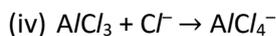|	Forward reaction	Backward reaction
(Brønsted) **acid**	**HA** is an acid as it donates a proton (H^+) to B.	**BH⁺** is an acid as it donates a proton (H^+) to A^-.
(Brønsted) **base**	**B** is a base as it accepts a proton (H^+) from HA.	**A⁻** is a base as it accepts a proton (H^+) from BH^+.

- ⚕ In each conjugate pair, the acid and base differ from each other by a proton (H^+).

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Summary:

	Acid	Base
Arrhenius theory	A substance that ionises and **releases hydrogen ions** (i.e. H⁺ ions) **when dissolved in water**.	A substance that ionises and **releases hydroxide ions** (i.e. OH⁻ ions) **when dissolved in water**.
Brønsted–Lowry theory	A *Brønsted–Lowry acid* is a **proton donor**	A *Brønsted–Lowry base* is a **proton acceptor**
Lewis theory	A *Lewis acid* is any **electron pair acceptor**	A *Lewis base* is any **electron pair donor**

Practice 1 – Theories of Acids and Bases (L1)
Identify the acid and base present in the following reactions.

(i) $NaOH (aq) + HNO_3 (aq) \rightarrow NaNO_3 (aq) + H_2O (l)$

(ii) $HCO_3^- (aq) + H_2O (l) \rightarrow H_2CO_3 (aq) + OH^- (aq)$

(iii) $CH_3NH_2 (aq) + H_2O (l) \rightleftharpoons CH_3NH_3^+ (aq) + OH^- (aq)$

(iv) $AlCl_3 + Cl^- \rightarrow AlCl_4^-$

(v) $NaH (s) + H_2O (l) \rightarrow NaOH (aq) + H_2 (g)$

(vi)

(vii) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$
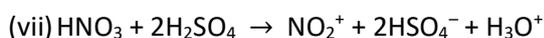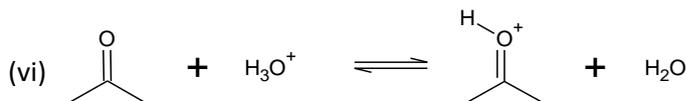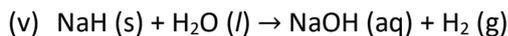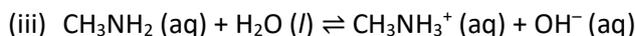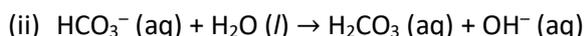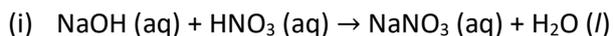
Practice 2 – Theories of Acids and Bases (L1)
Which of the following might act as a Lewis base: NH₃, CH₄, F⁻, OH⁻?
Explain your answer.

9A. Acid-Base Equilibria

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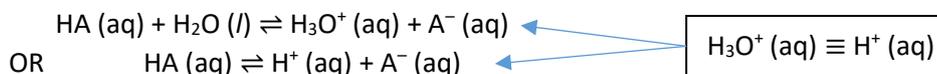
II   Strength of Acids and Base

Learning Objectives
- explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

1. **Degree of dissociation (α)**

   Consider the acid-base equilibrium of an acid, HA, in water is shown below:

   $$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$$

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

   $$\boxed{H_3O^+\ (aq) \equiv H^+\ (aq)}$$

   - **Degree of dissociation (α)**:

     It is the **fraction** (or percentage) **of molecules that dissociate into ions at equilibrium**.

     $$\boxed{\alpha = \frac{[\mathbf{H^+}]_{\text{dissociated}}}{[\mathbf{HA}]_{\text{initial}}} \quad \text{or} \quad \alpha = \frac{[\mathbf{H^+}]_{\text{dissociated}}}{[\mathbf{HA}]_{\text{initial}}} \times 100\%}$$

   ➢ The **degree** (or extent) of **dissociation** determines the **strength of acid** (or base).

2. **Strength of acids**

   An acid can be classified as strong or weak acid/base on its **degree of dissociation** in **aqueous solution**.

	Strong acid	Weak acid
Definition	A *strong acid* is one which undergoes complete dissociation in aqueous solution.	A *weak acid* is one which undergoes partial dissociation in aqueous solution.
Example	HCl (aq), HNO$_3$, H$_2$SO$_4$	CH$_3$COOH, H$_2$CO$_3$
Equation	HCl (aq) + H$_2$O (l) $\rightarrow$ H$_3$O$^+$ (aq) + Cl$^-$ (aq) or HCl (aq) $\rightarrow$ H$^+$ (aq) + Cl$^-$ (aq)	CH$_3$COOH (aq) + H$_2$O (l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + CH$_3$COO$^-$ (aq) or CH$_3$COOH (aq) $\rightleftharpoons$ H$^+$ (aq) + CH$_3$COO$^-$ (aq)
[H$^+$]	[H$^+$] = [HCl]$_{\text{initial}}$	At equilibrium: [H$^+$] < [CH$_3$COOH]$_{\text{initial}}$

3. **Concentration**

   The *concentration* of an acid in aqueous solution is the <u>amount of the acid per unit volume of the solution</u>.

   $$\boxed{\text{concentration (mol dm}^{-3}) = \frac{n\ (\text{mol})}{V\ (\text{dm}^3)}}$$

   - Strength of acid ≠ concentration of acid
     ➢ **Strength** of acid/base is determined by its degree/extent of dissociation in aqueous solution.
     ➢ **Concentration** of acid/base = no. of moles of acid/base dissolved in 1 dm^3 of solution.

     Example:
0.001 mol dm^{-3} HCl (aq)	$\rightarrow$	dilute but strong acid
4.0 mol dm^{-3} CH$_3$CO$_2$H (aq)	$\rightarrow$	concentrated but weak acid
0.001 mol dm^{-3} CH$_3$CO$_2$H (aq)	$\rightarrow$	dilute and weak acid

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4. **Basicity of an acid**

Basicity of an acid refers to the **number of ionisable hydrogen (H⁺)** in one molecule of the acid.

	Number of H atoms ionisable per molecule	Example
monobasic (or monoprotic) **acid**	1	HCl, HNO_3, CH_3COOH
dibasic (or diprotic) **acid**	2	H_2SO_4, $HOOC-COOH$
tribasic (or triprotic) **acid**	3	H_3PO_4

Similarly, for base:

	Number of proton (H⁺) *accept* per molecule	Example
monoacidic (monoprotic) **base**	1	$NaOH$, KOH, NH_3
diacidic (diprotic) **base**	2	$Ba(OH)_2$, SO_4^{2-}
triacidic (triprotic) **base**	3	PO_4^{3-}

II   pH scale and Ionic Product of Water (K_w)

Learning Objectives
- explain the terms pH; K_w and apply them in calculations, including the relationship $K_w = K_a K_b$
- calculate [H⁺ (aq)] and pH values for strong acids, strong bases

1. **pH**

> The **pH** of a solution is defined as **the negative logarithm to base ten of the <u>hydrogen ion concentration in mol dm⁻³</u>**.

pH definition: $$pH = -lg[H^+]$$

- Conversely, [H⁺] can be calculated from pH: $$[H^+] = 10^{-pH}$$

- The <u>lower the pH</u>, the <u>higher the [H⁺]</u> in the aqueous solution.

2. **pOH**

The **pOH** of a solution is defined as **the negative logarithm to base ten of the <u>hydroxide ion concentration in mol dm⁻³</u>**.

pOH definition: $$pOH = -lg[OH^-]$$

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pH is <u>NOT</u> a good indicator of <u>STRENGTH</u> of an acid/base

- **pH** is an indication of the <u>concentration of hydrogen ions</u>.
- **Strength of acid** depends on <u>degree of dissociation</u>.

Example	CH_3COOH	HCl
concentration (mol dm⁻³)	0.2	1×10^{-5}
degree of dissociation, α	0.933 %	100 %
pH	2.73	5

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3. <u>pH scale</u>

A *pH scale* is a set of number (0 – 14) used to measure the acidity or alkalinity of the solution.

More acidic (increasing H⁺ concentration)

neutral (at 25°C)

More alkaline (increasing OH⁻ concentration)

LOWER pH MORE ACIDIC | NEUTRAL | HIGHER pH MORE ALKALINE
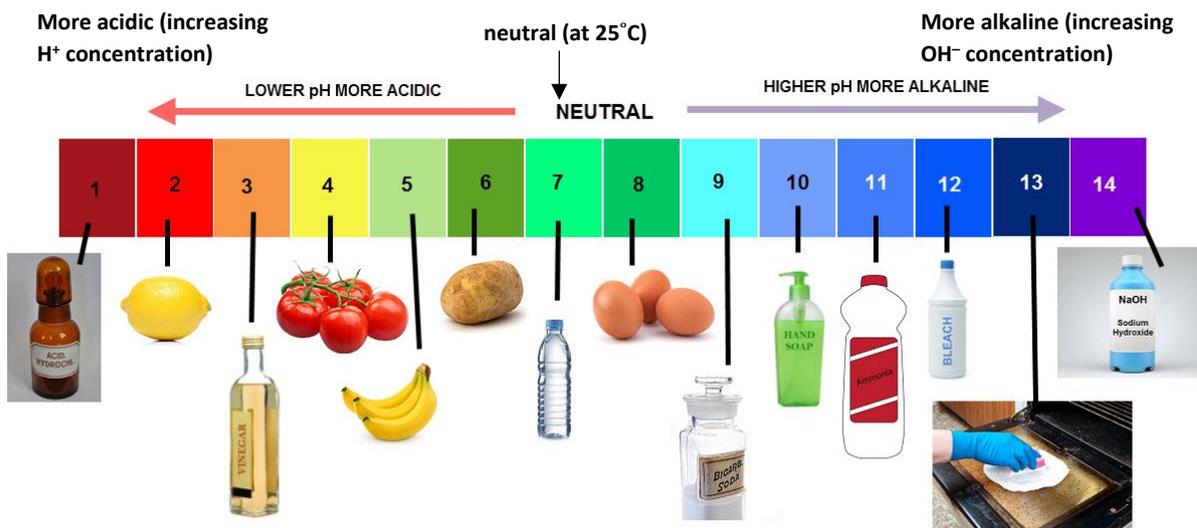
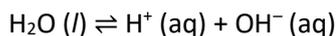- The pH of a solution can be determined accurately using the <u>pH meter</u>.

4. <u>Ionic product of water, K_w</u>

The electrical conductivity of pure water is not zero, due to the **self-ionisation of water**.

$$H_2O \ (l) + H_2O \ (l) \rightleftharpoons H_3O^+ \ (aq) + OH^- \ (aq)$$
acid   base

or simply: $$H_2O \ (l) \rightleftharpoons H^+ \ (aq) + OH^- \ (aq)$$
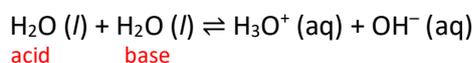
- At equilibrium: $$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

Since the extent of ionisation of very small, [H_2O] is almost constant (55.6 mol dm⁻³). Hence $K_c[H_2O]$ is another constant. Let $K_w = K_c[H_2O]$:

The *ionic product of water*, K_w: $$\boxed{K_w = [H^+][OH^-]}$$

- The value of K_w <u>depends on **temperature** only</u>:

$$\boxed{\text{At 25 °C, } K_w = [H^+][OH^-] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}$$

5. <u>pK_w</u>

pK_w is the. **negative logarithm to base ten of K_w**. $$\boxed{pK_w = -\lg K_w}$$

- pK_w can be expressed in terms of pH and pOH:
$$K_w = [H^+][OH^-]$$
$$-\lg K_w = -\lg[H^+] - \lg[OH^-]$$
$$pK_w = pH + pOH$$

$$\boxed{pK_w = pH + pOH}$$

- At 25 °C, pK_w = 14: $$\boxed{\text{At 25 °C, } pK_w = pH + pOH = 14}$$

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6. **Type of solution**

Type of solution	concentration	pH at 25 °C
Neutral solution	$[H^+] = [OH^-]$	= 7
Acidic solution	$[H^+] > [OH^-]$	< 7
Basic solution	$[H^+] < [OH^-]$	> 7

7. **The effect of temperature on K_w**

Self-ionisation of water is an **endothermic** process:

$$H_2O \ (l) \rightleftharpoons H^+ \ (aq) + OH^- \ (aq) \qquad \Delta H > 0$$

❧ **Effect of temperature on K_w:**

Temperature/ °C	10	20	**25**	40	100
K_w/ mol² dm⁻⁶	0.29×10^{-14}	0.68×10^{-14}	$\mathbf{1.00 \times 10^{-14}}$	2.92×10^{-14}	51.3×10^{-14}
pH of water	7.27	7.08	**7.00**	6.77	6.14

By Le Chatelier's principle, as <u>temperature **increases**</u>, the system will favour the endothermic reaction to absorb the heat added, hence the <u>equilibrium position shifts to the **right**</u>.

➤ $[H^+]$ and $[OH^-]$ increases
➤ K_w increases
➤ **pH decreases** (<7) (Note: it is still **neutral** as $[H^+] = [OH^-]$)

Practice 3 – pH (L1)
At 25°C, calculate the pH and pOH of

(a) 0.001 mol dm⁻³ of NaOH

(b) 0.100 mol dm⁻³ of H_2SO_4

Practice 4 – pH (L1)
The pH of normal human blood is 7.4. Strenuous exercise can cause the condition called acidosis in which the pH falls. If the pH drops to 6.8, death may occur.

How many times greater is the hydrogen ion concentration in blood at pH 6.8 compared to that at pH 7.4?

4.0

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9A. Acid-Base Equilibria

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Practice 5 – pH (L2)

How much water must be added to 2.0 dm^3 of a solution of a strong monobasic acid of pH 2.0 in order to increase the pH to 3.0?

18 dm^3

Practice 6 – pH [TJC/2011/Prelim/P1/6] (L1)

The table below shows the values of the ionic produce of water, K_w at two different temperatures.

Temperature/ °C	K_w/ mol^2 dm^{-6}
25	1.0×10^{-14}
62	1.0×10^{-13}

Which of the following statements is correct for pure water?

A   The ionic dissociation of water is an exothermic process.

B   At 62°C, pH = 14 − pOH

C   At 62°C, pH < pOH

D   At 62°C, pH < 7

Practice 7 – pH (L2)

Find the pH of 1.0×10^{-8} mol dm^{-3} nitric acid (HNO_3).

6.96

Self-ionisation of water on pH

Self-ionisation of water will contribute to the concentration of H$^+$ and OH$^-$ in aqueous solution.

🕯   For water at 25°C,   [H$^+$] = [OH$^-$] = 1.0×10^{-7} mol dm^{-3}

🕯   For **very diluted** strong acids or base (i.e. [acid] or [base] $\leq$ **10^{-7} mol dm^{-3}**), [H$^+$] and [OH$^-$] contributed by self-ionisation of water is considered **significant**:

$$[H^+] = [H^+]_{acid} + [H^+]_{water}$$

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III   Acid dissociation constant (K_a)

Learning Objectives
- explain the terms K_a; pK_a and apply them in calculations
- calculate [H$^+$ (aq)] and pH values for weak monobasic (monoprotic) acids
  [Calculations involving weak acids/bases will **not** require solving of quadratic equations]

1. Acid dissociation constant (K_a)

Consider a weak monobasic acid, HA, which dissociates partially in water:

$$HA \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons H_3O^+ \text{ (aq)} + A^- \text{ (aq)}$$
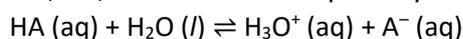
- At equilibrium:
$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Since water is present in large excess, [H$_2$O] is taken as constant.

- The *acid dissociation constant*, K_a:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

- K_a is a **measure of the strength** of the acid HA.
- K_a provides a quantitative indication of the extent to which the acid is dissociated.
- Unit of K_a: **mol dm^{-3}**
- The value of K_a is **dependent on temperature only**.

- **pK_a**

The pK_a of an acid is the **negative logarithm to base ten of the K_a** of the acid.

$$pK_a = -\lg K_a$$

2. K_a and strength of acid

The K_a values of some acids at 25 °C are shown in the table below.

Acid	formula	K_a / mol dm^{-3}	pK_a	
hydrochloric acid	HC*l*	1.3×10^6	−6.11	stronger acid
hydrofluoric acid	HF	6.6×10^{-4}	3.18	
benzoic acid	C$_6$H$_5$COOH	6.3×10^{-5}	4.20	
ethanoic acid	CH$_3$COOH	1.8×10^{-5}	4.74	
ammonium ion	NH$_4^+$	5.8×10^{-10}	9.24	
hydrocyanic acid	HCN	4.9×10^{-10}	9.31	
phenol	C$_6$H$_5$OH	1.3×10^{-10}	9.89	weaker acid

- The **stronger the acid**:
  - The **equilibrium position** lies more <u>towards the **right**</u> to dissociate more H$^+$
  - the **larger** the K_a value
  - the **smaller** the pK_a value

- <u>K_a as the indicator of strength of acids</u>:
  - K_a is the best indicator of strength of acids as it is a <u>**constant temperature**</u> and <u>**does not vary with concentration**</u>.
  - At the same temperature, K_a of a stronger acid is always higher than the K_a of a weaker acid, regardless of their concentrations.

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3. **Acid dissociation constants (K_a) of weak polyprotic acids**
   Polyprotic acids (e.g. H_2CO_3, H_3PO_4) have more than one K_a value.

   Example (H_3PO_4)

First dissociation:	H_3PO_4 (aq) $\rightleftharpoons$ H^+ (aq) + $H_2PO_4^-$	$K_{a1} = 7.5 \times 10^{-3}$ mol dm^{-3}
Second dissociation:	$H_2PO_4^-$ (aq) $\rightleftharpoons$ H^+ (aq) + HPO_4^{2-}	$K_{a2} = 6.2 \times 10^{-8}$ mol dm^{-3}
Third dissociation:	HPO_4^{2-} (aq) $\rightleftharpoons$ H^+ (aq) + PO_4^{3-}	$K_{a3} = 4.2 \times 10^{-13}$ mol dm^{-3}
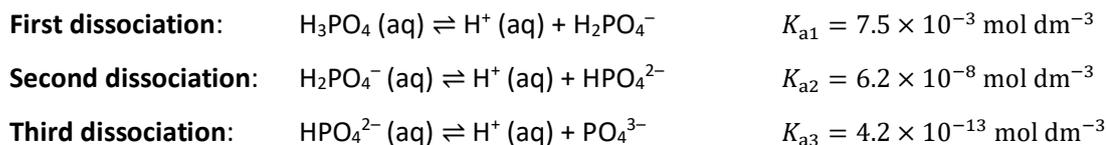
   ➤ **$K_{a1} > K_{a2} > K_{a3}$:**

   Successive K_a values become **smaller** because successive dissociations involve acidic species that are increasing more negatively charge, making the donation of positively charged H$^+$ ion increasingly more difficult.

4. **pH of weak acid**
   Since weak acid dissociate **partially** in water, [H$^+$] in the solution will be **lower** than the initial concentration of the weak acid.

   ❦ **Calculating pH of a weak acid**
   Let the initial concentration of weak acid be c mol dm^{-3} and [H$^+$] = x mol dm^{-3} at equilibrium:

Equation	HA (aq) $\rightleftharpoons$	H$^+$ (aq) +	A$^-$ (aq)
Initial (mol dm^{-3})	c	0	0
Change (mol dm^{-3})	$-x$	$+x$	$+x$
Equilibrium (mol dm^{-3})	$c - x$	x	x

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{(c-x)} = \frac{x^2}{(c-x)}$$

Since HA is a weak acid (i.e. very small K_a value), assume $x \ll c$.
Then $(c - x) \approx c$

$$\therefore \; K_a = \frac{x^2}{c} \; \rightarrow \; x = \sqrt{c \times K_a}$$

$$\boxed{[\mathbf{H^+}] = \sqrt{c \times K_a}}$$

   ➤ **Assumption for $[\mathbf{H^+}] = \sqrt{c \times K_a}$:**

   1) The [H$^+$] from the self-ionisation of water is negligible and ignored.

   2) The degree of dissociation is negligible (i.e. $x \ll c$)

Degree of dissociation, $\alpha = \dfrac{x}{c} \times 100\%$	Validity of assumption
$\alpha < 5\%$	The assumption is valid and approximation can be used.
$\alpha > 5\%$	The assumption is not valid and x has to be found by solving the quadratic equation (**not** required in syllabus).

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