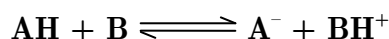


Acidity, Basicity and pK_a

Introduction

- Many reactions are **catalysed** by **acids** or **bases**. For example, a **protonated carbonyl group** is a **better electrophile** than a **normal carbonyl group**.
- **pK_a** tells us how **acidic** (or not) a given **hydrogen atom** in a **molecule** is. pH tells us how **acidic** a **solution** is.
- The **basic Bronnsted definition** of acids and bases are:
 - An **acid** is a **species** having a tendency to **lose a proton**.
 - A **base** is a **species** having a tendency to **accept a proton**.
- **Free hydrogen ions** are **extremely unstable** (so much so that they can even protonate things like **methane!**) Therefore, for any acid and any base, the equilibrium established is:



Where **AH** is an acid and **A⁻** is its **conjugate base** and **B** is a base and **BH⁺** is its conjugate acid. In other words, **every acid has a conjugate base associated with it, and vice versa**.

- In many such reactions, when **acids** or **bases** are **dissolved** into **water**, **water** acts as the **acid** or **base**. This ability of water to acts as **both an acid and a base** makes it an **amphoteric compound**.

To a certain extent, **all** compounds are **amphoteric**, because they can always be **(de)protonated** by a **stronger acid/base**.

- When water behaves as a **base**, it **accepts H⁺** and forms a **hydronium ion**; **H₃O⁺**. When it behaves as an **acid**, it **loses a proton**, and forms a **hydroxide ion**; **OH⁻**.
- **HCl** is a **very strong acid**. It is **completely dissociated** in solution. **Acetic acid**, on the other hand, is fairly **weak**, and it is **not fully dissociated**.

pH and pK_a

- The pH of a solution is a measure of the **acidity of the solution**. It is defined as:

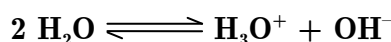
$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+])$$

Where $[\text{H}_3\text{O}^+]$ is the **concentration of hydronium ions** in the **solution**.

- Consequently, the pH of a solution depends on two things:
 - *The concentration of the solution* – if we have two solutions of the **same acid**, the **more concentrated** solution will have **more free H_3O^+** ions and therefore a **lower pH**.
 - *The acid in question* – if we have two **equally concentrated solutions** of acids, the solution of a **strong acid** will have a **lower pH** than that of a **weak acid**, because it is **more fully dissociated** and therefore **produces more H_3O^+** ions. **HCl**, for example, is **completely dissociated**.

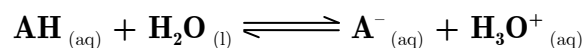
Therefore, we see that **pH** does not measure the **strength of an acid**, but the **acidity of a given solution**.

- The **pH** of water is **7**. This means that a solution of **pure water** has a $10^{-7} \text{ mol dm}^{-3}$ of **hydronium ions**. This can only happen through the **autoprotolysis of water**:



This means that in water, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$.

- To be clearer about what a **strong** and **weak** acid is, we look at the reaction:



The **position of the equilibrium** is measured by the **equilibrium constant**, K_{eq} :

$$K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{AH}][\text{H}_2\text{O}]}$$

Now, in **dilute solutions of acid**, $[\text{H}_2\text{O}]$ stays **roughly constant** at about 56 mol dm^{-3} . We therefore define a new equilibrium constant – the **acidity constant K_a** :

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

This is also expressed in **logarithmic form** as follows:

$$\text{p}K_a = -\log_{10} K_a$$

Because of the **minus sign**, the **lower the $\text{p}K_a$** , the **higher the K_a** and the **stronger the acid**.

- It turns out that the $\text{p}K_a$ of an acid is the pH at which it is **exactly half-dissociated**. This can be shown by re-arranging the expression for K_a :

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

$$\text{pH} = \text{p}K_a - \log\left(\frac{[\text{AH}]}{[\text{A}^-]}\right)$$

Clearly, when $[\text{AH}] = [\text{A}^-]$, $\text{pH} = \text{p}K_a$.

- This information is rather useful:
 - At a pH **above** the $\text{p}K_a$, the acid exists as A^- in water, and will therefore be **fairly soluble**.
 - At a pH **below** the $\text{p}K_a$, the acid exists mostly as **HA** in water, and will probably be **less soluble**.

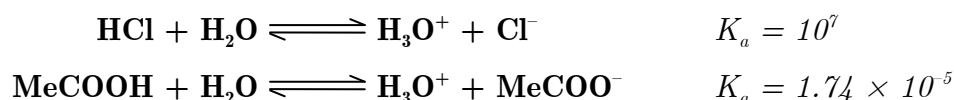
[All vice-versa for a base, of course].

For example, **phenol** has a $\text{p}K_a$ of **10**:

- At a pH of, say, **5**, it exists in its **acidic form** and is a **poor nucleophile**, because the **HOMO** is an **oxygen lone pair**.
- At a pH of, say, **14**, however, it exists in its **conjugate base** form, and is a **very good nucleophile**, because the **HOMO** is not an **oxygen lone pair** in an anion.
- These properties can be used to **separate compounds** – for example, a mixture of **benzoic acid** and **toluene** can first be **washed** with **NaOH** (the benzoic acid goes into the **aqueous layer**), and the resulting **aqueous layer** treated with **HCl**, which causes the benzoic acid to **precipitate**.

What makes a strong acid?

HCl is a **much stronger acid** than **acetic acid**:



This is to do with the **strength (stability)** of the **conjugate base**; Cl^- is *not strong enough* to **deprotonate** H_3O^+ , but **acetate** is. In other words, the *chloride ion is inherently more stable than the acetate ion*.

- An acid's $\text{p}K_a$ depends on the **stability of its conjugate base**.

- The **stronger** the **acid HA**, the **weaker** its **conjugate base A⁻**.
- The **stronger** the **base A⁻**, the **weaker** the **conjugate acid HA**.
- For example:
 - **HI**, with a pK_a of **-10**, is a **strong** enough **acid** to protonate most functional groups. It's **conjugate base**, **I⁻**, is **not really basic at all**.
 - **Methyl lithium (MeLi)** is a **very powerful base**, which behaves as **CH₃⁻**. The “**conjugate acid**” is **methane**, which **isn't really acidic** with $pK_a = 48!$
- There are several factors that determine the **stability** of the **conjugate base**. These **include**:
 - **Which element** the **negative charge** is on. The **more electronegative** the element is, the **more stable** the conjugate base.
 - How **delocalised** the **negative charge** is on the **conjugate base**. The **more delocalised**, the **more stable** the conjugate base.
- Other factors, apart from the stability of the conjugate base, that affect pK_a are:
 - The **strength** of the **H–A bond**.
 - The **solvent** (how **good** it is at **stabilising** the **ions** formed).

The location of the negative charge

The **more electronegative** the **element** on which the **negative charge** is located, the **more stable** the **conjugate base**, and the **stronger** the **acid**.

For example:

pK_a of second row			
Hydrides			
CH ₄	NH ₃	H ₂ O	HF
48	33	16	3

Clearly, **F⁻** is **more stable** than **CH₃⁻** because **fluorine** is much more **electronegative** than **carbon**.

The strength of the H–A bond

Clearly, the **stronger** the **H–A bond**, the **harder** it is for the acid to **donate** a proton, and the **weaker** the acid becomes. For example:

pK_a of group VII

Hydrides

HF	HCl	HBr	HI
-3	-7	-9	-10

Even though the **conjugate bases** become **less electronegative**, the **acid strength increases**. This is because the **H–Hal** bond gets **weaker**. [And also because the **negative charge** can be **stabilised** on a **larger anion**].

The delocalisation of the negative charge

Consider the following:

pK_a of group VII

Hydrides

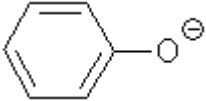

HClO	HClO ₂	HCl ₃	HClO ₄
7.5	2	-1	-10

In each case, we are **removing a proton** from the **same environment** (an O–H). However:

- The **conjugate base** of **HClO** is **ClO⁻** – the **negative charge** is **localised** on a **single oxygen**.
- The **conjugate base** of **HClO₄** is **ClO₄⁻** – the **negative charge** is **delocalised** over **all 4 oxygens**.

This also rationalises the **pK_as** of various **oxygen acids**:

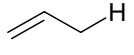
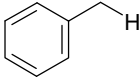
	Approximate pK _a	pK _a when R = Me	Conjugate base
RSO ₂ OH Sulfonic acids	0	-1.9	<p><i>Methane Sulfonate</i></p> <p>Charge delocalised over 3 oxygens</p>
RCO ₂ H Carboxylic acids	5	4.8	<p><i>Acetate</i></p> <p>Charge delocalised over 2 oxygens</p>

ArOH Phenol	10	10	<i>Phenoxide</i>  Charge can delocalise into the ring
ROH Alcohols	15	15.9	<i>Ethoxide</i>  Charge localised on a single oxygen.

Note:

- Conjugation can **only occur** if the **orbitals overlap**. Therefore, the two *other* lone pairs in **oxygen** in **phenoxide cannot** conjugate into the π system, because they do not overlap with it.
- This explains why even though **toluene** (CH_3Ar) is **significantly more acidic** than **methane** (CH_4), successive drops in $\text{p}K_a$ as **more phenyl rings are added** (to make CH_2Ar_2 and CH_3Ar) are **much less impressive**. Indeed, the **ortho hydrogens** in the phenyl rings **clash**, and the molecule adopts a **propeller shape**, in which each phenyl ring is **staggered** relative to the next.

Carbon acids are acids where the proton is removed from **carbon** rather than **oxygen**; there are, in general, **weaker** than **oxygen** acids, because **carbon** is **less electronegative**. If the **negative charge** can be **delocalised** on to **more electronegative atoms**, the conjugate base will be **stabilised** and the acid **stronger**. For example:

	Approximate $\text{p}K_a$	Comment
CH_3 Methane	48	The charge is localised on a single carbon
 Propene	42	The charge is delocalised over the π system
 Toluene	38	The charge is delocalised over 7 atoms , but all of them are carbon
Ketone	20	The charge is delocalised over the π system, but mostly on the oxygen, which is much better
Nitromethane	10	The charge is delocalised , mainly on oxygens of the nitro group – good!

Electron-donating or withdrawing groups

- In **both** kinds of acids, it is **not necessary** for a group to be **conjugated** in order to **spread the negative charge**. Any group that **withdraws electrons** will help.
- This is the result of **σ polarisation**, with the **electron density** towards the **more electronegative atom**.
- This effect is **passed on more and more weakly** through the **carbon skeleton**.
- In a similar way, **electron donating groups** will also **decrease acidity**.

Examples include:

- **Alkyl groups**, which are **weakly electron-releasing**.
- **Ethoxide groups**, in **esters**, are weakly electron-releasing.

Hybridisation

- **Hybridisation** also has an effect on pK_a . **s orbitals** are **closer to the nucleus** than **p orbitals**, and therefore **lower in energy**.
- This means that **the more s character an orbital has**, the **more tightly held are the electrons in it**.
- Thus, electrons in an **sp orbital** are **lower in energy** than those in an **sp³ orbital**. This explains the following observations:

pK_a values			
$\text{CH}_3\text{-CH}_3$	$\text{CH}_3\text{=CH}_3$	$\text{CH}\equiv\text{CH}$	HCN
~50	~44	25	~10

In the first case, the **lone pair** on the **conjugate base** is in an **sp³ orbital**. In the last case, the **lone pair** is in an **sp orbital**, and so the **conjugate base** is **much more stable**. In CN^- , not only is an **sp orbital** involved, but a **very electronegative element** is present.

- More **remote hybridisation** is **also important**. An **sp carbon** is **less electron donating** than an **sp³ carbon**. Therefore:

pK_a values		
$\text{CH}_3\text{CH}_2\text{COOH}$	ArCOOH	$\text{CH}\equiv\text{CHCOOH}$
4.9	4.2	1.9

Nitrogen Acids

Nitrogen acids are usually **weaker** than **oxygen acids**, because **nitrogen** is **less electronegative**. **Carbonyl groups**, however, **do help**, and inasmuch as **amines** are not acidic at all, **amides** are *slightly acidic* and **imides** (two carbonyl groups) are definitely weakly acidic.