Acids and Bases

Overview of Acids and Bases

Arrhenius Acids and Bases

Acids dissociate in water to form protons (H^+)

Bases dissociate in water to form ^-OH

Restrictions: 1) only in water, 2) only ^-OH is a base

What about organic molecules and non-aqueous solutions?

Brønsted Acids and Bases

Acids are proton donors. **Bases** are proton acceptors. [No restriction to being in water / No restriction to ^-OH being the base]

Curved arrow mechanism of acid-base reactions:

1) Start the arrow from the base pair/negative charge of the base and attack the most acidic hydrogen of the acid.

2) Break the bond of the hydrogen and move the electrons to the other atom.

Remember: curved arrows show movement of electrons

* Both Arrhenius and Brønsted definitions are from **Proton Perspective**. What if there is not proton involved?

Lewis Acids and Bases

Lewis acid is an **electron pair acceptor**.

Lewis base is an **electron pair donor**.

So, in the Lewis theory, acids and bases are described in terms of **electrons**.

* None of the Acid-Base theories contradict to one another.

As a general pattern: identify **acids** as [illegible] and **bases** as [illegible]

Acid Strength

What does it mean "strong acid"?

Generally speaking, the more the acid dissociates into a proton, the stronger it is.

The dissociation of the acid is a reversible reaction that is described by equilibrium constant:

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

The stronger the acid, the larger the Ka.

Notice that $Ka = Keq\,[H_2O]$

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Acid Strength and pKa

The Ka values of ethyl alcohol (1) and ethyl amine (2) are shown below:

The alcohol is a stronger acid because its Ka is higher.

To simplify the numbers, **-logKa** is used, which is the **pKa** of the given acid.

$$pKa = -logKa$$

$$pKa_1 = -logKa_1 = 16 \quad < \quad pKa_2 = -logKa_2 = 38$$

So, **the stronger the acid, the lower the pKa value** (it is the opposite for Ka.)

Below are **pKa** values of some common functional groups:

Increasing Acidity

What makes the Acid Strong ?

The **strength of the acid** is dictated by the **stability of the conjugate base** that forms when the acid dissociates. **The stronger the acid, the more stable its conjugate base.**

Stable A^- means more acid dissociation, more proton, thus stronger acid

There are a few factors to be considered when assessing the stability of the conjugate base.

1) The first and the key factor is the **atom** to which the hydrogen is connected. Mainly its **atomic Size (Polarizability)** and **Electronegativity**.

* Within the **same row**, atomic sizes don't change much, so **electronegativity** is the key.

Oxygen is more electronegative, that is why the alcohol is more acidic.

$$pKa_1 = 16 \quad < \quad pKa_2 = 38$$

* When comparing elements in **different rows**, the atomic size is the key.

Large atoms have higher **polarizability** and handle the negative charge better as the charge is spread over.

Thiols are more acidic even though oxygen is more electronegative than sulfur.

The sulfur atom is larger and stabilizes the negative charge better.

2) When comparing the same atom, check which conjugate base is **Resonance stabilized**

3) The third factor for determining the acidity is called **Induction**.

Induction or inductive effect is the transmission of charge through atoms.

Electronegative atoms pull the negative charge and help to stabilize the conjugate base.

The more electronegative, the more electron withdrawing – the stronger the acid

The closer the electronegative atom to the hydrogen, the stronger the acid

Increasing Acidity

4) The fourth factor is the **hybridization** of the atom connected to the hydrogen.

This explains the great difference of **pKa** values of alkanes, alkenes and alkynes:

sp orbital is more electronegative than sp^3, so **the more S character, the stronger the acid**

Therefore, the **acidity**: alkynes > alkenes > alkanes

The priority order: Atom, Resonance, Induction, Orbital for determining the acidity of a compound is known as **ARIO**.

Aromaticity also stabilizes the conjugate base:

The Position of Equilibrium for an Acid-Base Reaction

Is the following acid-base reaction possible?

Acid-Base reactions are reversible, so another way of asking the question is:

Is the equilibrium of the reaction shifted to the right (products) or to the left (reactants)?

To answer this question, you need to remember that the **equilibrium of an acid-base reaction is shifted towards the weaker acid** (and the base).

So, you need to compare the pKa of the acid (left side) and the conjugate acid (right side).

The **equilibrium will be shifted to the higher pKa** (weaker acid) side.

In this case the **pKa** of the conjugate acid is greatly higher the acid **pKa**, so the equilibrium is shifted to the right. Therefore the right pointing arrow is drawn bigger.

Choosing a Base to Deprotonate a Given Compound

Suppose you need to deprotonate the following compound:

(Deprotonate means remove the most acidic proton)

First, find its **pKa value**: pKa = 25

Write the chemical equation of the compound reacting with a conjugate base (B^-):

The pKa of the conjugate acid must be higher than 25, i.e. weaker acid is formed.

Pick a compound from a pKa table with **pKa > 25**. Amides are used often (pKa = 38).

Choosing an Acid to Protonate a Given Compound

Suppose you need a reagent to protonate (quench) **alkali** ($CH_3CH_2CH_2CH_2Li$) which is a very reactive base and needs to be quenched before being disposed.

To do that, write the chemical equation of alkali with an acid (HB):

The pKa of butane (the conjugate acid of alkali) is 50. Therefore, the pKa of HB acid must be smaller than 50 – stronger acid reacts, weaker acid forms.

Acetone is often used as a proton donor (acid) for protonating the alkali because its pKa is 19 so it is a lot stronger of an acid than butane:

Henderson-Hasselbalch Equation

This equation shows whether the compound with a given pKa is in the acidic or basic (deprotonated) form in an aqueous solution depending on the pH of that solution.

$$pKa = pH + \log\frac{[HA]}{[A^-]}$$

Key points and implications of the Henderson-Hasselbalch equation:

1) If the pH < pKa: $\log\frac{[HA]}{[A^-]} > 0$, $[HA] > [A^-]$, compound exists mainly in its **acidic form**

2) If the pH = pKa: $\log\frac{[HA]}{[A^-]} = 0$, $[HA] = [A^-]$ (since $\log 1 = 0$)

3) If the pH > pKa: $\log\frac{[HA]}{[A^-]} < 0$, $[A^-] > [HA]$, compound exists mainly in its **basic form**

acidic — basic

For example, **Aspirin** (acetylsalicylic acid) must be deprotonated (basic form) to be physiologically active.

The pKa of aspirin (carboxylic acid) is ~3. Therefore, it is mainly in the acidic form before reaction in stomach (pH ~ 2), while in the environment of the cell (pH 7.4), the drug will be in its active basic form.

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