

Acid Base Equilibria

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ACID-BASE : Arrhenius

The most basic of the acid-base concepts is the

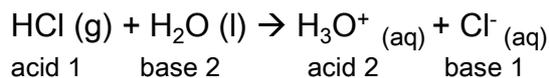
Arrhenius theory

Acids are substances that dissociate in water to produce hydronium ions, H_3O^+ and **bases** are substances that dissociate in water to produce hydroxide ions, OH^-

Acid Base: Bronsted-Lowry

A Bronsted-Lowry acid is defined as a substance that can donate a proton.

A Bronsted-Lowry base is defined as a substance that can accept a proton.



Each acid is linked to a conjugate base on the other side of the equation.

Calculating pH

Indicates the acidity of the solution

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

Where $[\text{H}^+]$ is the concentration of hydrogen ions in the solution

From the French *pouvoir hydrogene*
 ("hydrogen power" or power of hydrogen)

Calculating pH

$$\text{pH} = -\log[\text{H}^+(\text{aq})]$$

If $[\text{H}^+(\text{aq})] = 0.01\text{M}$
then $\text{pH} = -\log(0.01) = 2.00$

If $[\text{H}^+(\text{aq})] = 0.000001\text{M}$
then $\text{pH} = -\log(0.000001) = 6.00$

Always give pH to 2d.p.

Calculating pH of strong acids

Strong acids completely dissociate.

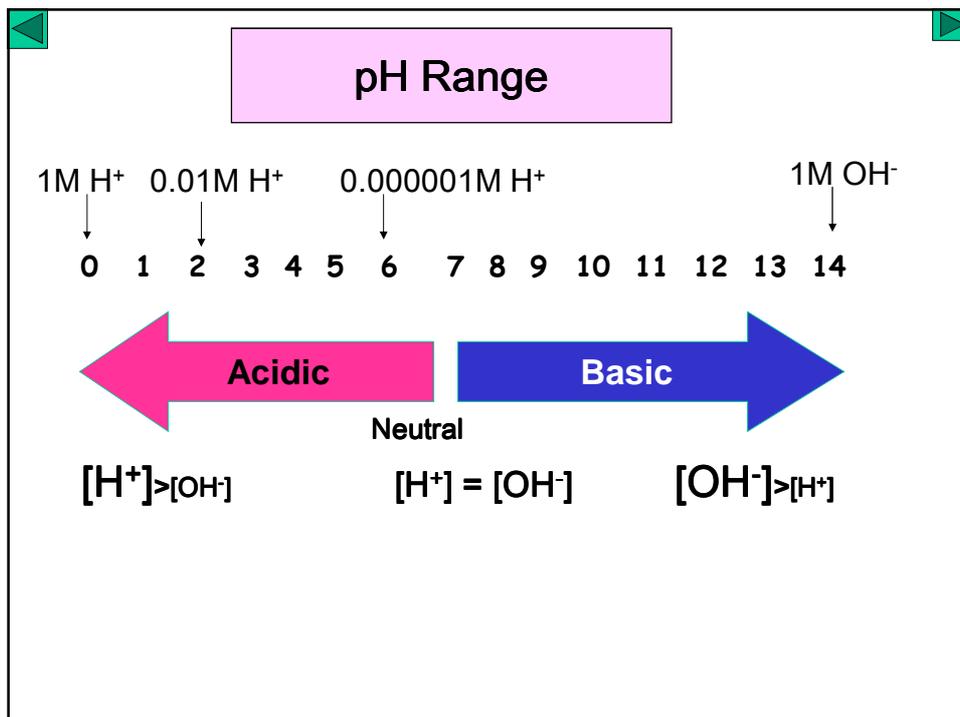
For HCl and HNO_3 the $[\text{H}^+(\text{aq})]$ will be the same as the original concentration of the acid.

For 0.1M HCl the pH will be $-\log[0.1] = 1.00$

For strong acids with a concentration $>1\text{M}$ the pH will be negative.

What is the pH of a solution of

- a) 0.02M HCl
- b) 0.05M HNO_3
- c) 0.001M HBr



Finding [H⁺] from pH

[H₃O⁺] = 1 × 10^{-pH}

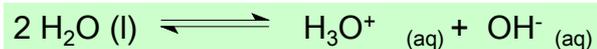
On most calculators this is done by pressing
Inv (or 2nd function) → log → - number(pH)

What is the concentration of the following acids

- HCl with a pH of 1.50
- HNO₃ with a pH of 2.10

Ionic Product for water

In all aqueous solutions and pure water the following equilibrium occurs



This can be simplified to



This equilibrium has the following equilibrium expression

$$K_c = \frac{[\text{H}^+ (\text{aq})][\text{OH}^- (\text{aq})]}{[\text{H}_2\text{O} (\text{l})]}$$

Rearrange to

$$K_c \times [\text{H}_2\text{O} (\text{l})] = [\text{H}^+ (\text{aq})][\text{OH}^- (\text{aq})]$$

$$K_w = [\text{H}^+ (\text{aq})][\text{OH}^- (\text{aq})]$$

Because $[\text{H}_2\text{O} (\text{l})]$ is much bigger than the concentrations of the ions, we assume its value is constant

$$K_w = [\text{H}^+ (\text{aq})][\text{OH}^- (\text{aq})]$$

At 25°C the value of K_w for all aqueous solutions is $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

This expression can be used to calculate $[\text{H}^+ (\text{aq})]$ ions if we know the $[\text{OH}^- (\text{aq})]$ ions

$$\text{In pure water } [\text{H}^+ (\text{aq})] = [\text{OH}^- (\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

In a solution of 0.1M NaOH what is the concentration of the H^+ and OH^- ions ?

In a strong base there is complete dissociation which means that $[\text{OH}^- (\text{aq})] = 0.1\text{M}$

Calculating pH of strong base

For bases we generally know the concentration of hydroxide ion.

To work out the pH we need to work out $[H^+(aq)]$ using the K_w expression.

Example: What is the pH of the strong base 0.1M NaOH

Assume complete dissociation.

$$K_w = [H^+(aq)][OH^-(aq)] = 1 \times 10^{-14}$$

$$[H^+(aq)] = K_w / [OH^-(aq)] = 1 \times 10^{-14} / 0.1 = 1 \times 10^{-13} \text{ M}$$

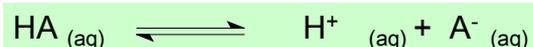
$$pH = -\log[1 \times 10^{-13}] = 13.00$$

Weak acids

Weak acids slightly dissociate when dissolved in water, giving an equilibrium mixture.



We can simplify this to



$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

For weak acids such as ethanoic acid the K_a is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$.

The larger K_a the stronger the acid

Calculating pH of a weak acid

What is the pH of a solution of 0.01M ethanoic acid (K_a is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$)

Write the expression for K_a



$$K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{CH}_3\text{CO}_2^-_{(\text{aq})}]}{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]}$$

To make the calculation easier two assumptions are made:

1) $[\text{H}^+_{(\text{aq})}]_{\text{eqm}} = [\text{CH}_3\text{CO}_2^-_{(\text{aq})}]_{\text{eqm}}$ because they have dissociated according to a 1:1 ratio

2) As the amount of dissociation is small we assume that the initial concentration of the ethanoic acid has remained constant.

$$\text{So } [\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]_{\text{eqm}} = [\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]_{\text{initial}}$$

Rewrite expression using assumptions

$$K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{H}^+_{(\text{aq})}]}{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]} = \frac{[\text{H}^+_{(\text{aq})}]^2}{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}$$

Replace $[\text{CH}_3\text{CO}_2^-_{(\text{aq})}]$ with $[\text{H}^+_{(\text{aq})}]$ using assumption 1

What is the pH of a solution of 0.01M ethanoic acid
(K_a is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$)

$$K_a = \frac{[\text{H}^+_{(\text{aq})}]^2}{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}$$

$$1.7 \times 10^{-5} = \frac{[\text{H}^+_{(\text{aq})}]^2}{0.01}$$

$$[\text{H}^+_{(\text{aq})}]^2 = 1.7 \times 10^{-5} \times 0.01$$

$$[\text{H}^+_{(\text{aq})}] = \sqrt{(1.7 \times 10^{-7})} = 4.12 \times 10^{-4}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (4.12 \times 10^{-4})$$

$$= 3.38$$

pKa

Sometimes K_a is quoted as pKa

$$\text{pKa} = -\log (K_a)$$

What is the pKa of ethanoic acid (K_a $1.7 \times 10^{-5} \text{ mol dm}^{-3}$)

$$\begin{aligned} \text{pKa} &= -\log (1.7 \times 10^{-5}) \\ &= 4.75 \end{aligned}$$

The larger the value of K_a the smaller the value of pKa
The stronger the acid the smaller the value of pKa

Name	Equation with conjugate base	Ka mol dm ⁻³ .	Pka
Hydrofluoric	$\text{HF}_{(\text{aq})} \rightleftharpoons \text{F}^{-}_{(\text{aq})} + \text{H}^{+}_{(\text{aq})}$	5.60×10^{-4}	3.25
Ethanoic acid	$\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})} \rightleftharpoons \text{CH}_3\text{CO}_2^{-}_{(\text{aq})} + \text{H}^{+}_{(\text{aq})}$	1.7×10^{-5}	4.75
Hydrocyanic acid	$\text{HCN}_{(\text{aq})} \rightleftharpoons \text{CN}^{-}_{(\text{aq})} + \text{H}^{+}_{(\text{aq})}$	4.9×10^{-10}	9.31

The larger the value of Ka the smaller the value of pKa
 The stronger the acid the smaller the value of pKa

Why do some acids react with sodium carbonate to give CO₂ ?

Ethanoic acid will react with sodium carbonate



The H⁺ ions produced in this reaction force the following equilibria involving carbonate ions to the left (by le Chatelier), producing CO₂



However if the acid is a weaker acid than carbonic i.e. has a ka < 4.5 x 10⁻⁷ mol dm⁻³ then it will not be able to donate protons to the carbonic acid and no CO₂ will be produced.

Eg Boric acid has a ka of 5.8 x 10⁻¹⁰ mol dm⁻³ and does not react with sodium carbonate. $\text{H}_3\text{BO}_3 \rightleftharpoons \text{H}^{+} + \text{HBO}_3^{-}$

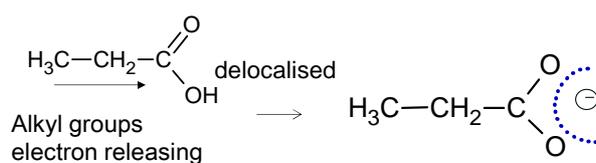
Strength of Acids

• Trichloroethanoic acid	2.3×10^{-1}
• Dichloroethanoic acid	5.0×10^{-2}
• Chloroethanoic acid	1.3×10^{-3}
• Benzoic acid	6.3×10^{-5}
• Ethanoic acid	1.7×10^{-5}
• Carbonic acid	4.5×10^{-7}
• Boric acid	5.8×10^{-10}
• Phenol	1.28×10^{-10}

Decreasing
acid
strength

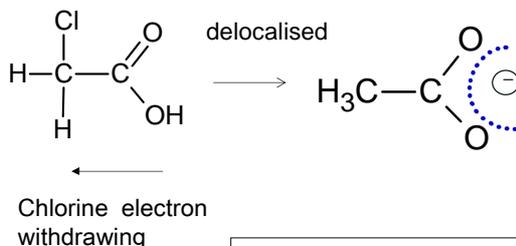
Acids
below
carbonic
acid will
not give off
CO₂ with
sodium
carbonate

Strength of Carboxylic acids



Increasing chain length pushes electron density on to the COO⁻ ion, making it more negative and less stable. This makes the acid less strong.

Propanoic acid less acidic than ethanoic acid



Electronegative chlorine atoms withdraw electron density from the COO⁻ ion, making it less negative and more stable. This makes the acid more strong.

chloroethanoic acid more acidic than ethanoic acid