

Acids and Bases

- Arrhenius definition of acids and bases: An acid releases H^+ ions when dissolved in water
A base releases HO^- ions when dissolved in water
- Brønsted – Lowry definition of acids and bases: An acid is a *proton donor*
A base is a *proton acceptor*
- A conjugate acid – base pair differ by H^+ .

For example NH_4^+ is the conjugate acid of NH_3 and NH_3 is the conjugate base of NH_4^+ .

Write the formula of the conjugate bases		Write the formula of the conjugate acids	
H_3O^+		OH^-	
H_2SO_4		H_2O	
$HClO_4$		Cl^-	
CH_3COOH		NH_3	

$[H^+]$ is used as a measure of acidity and for convenience a log scale is often employed:

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

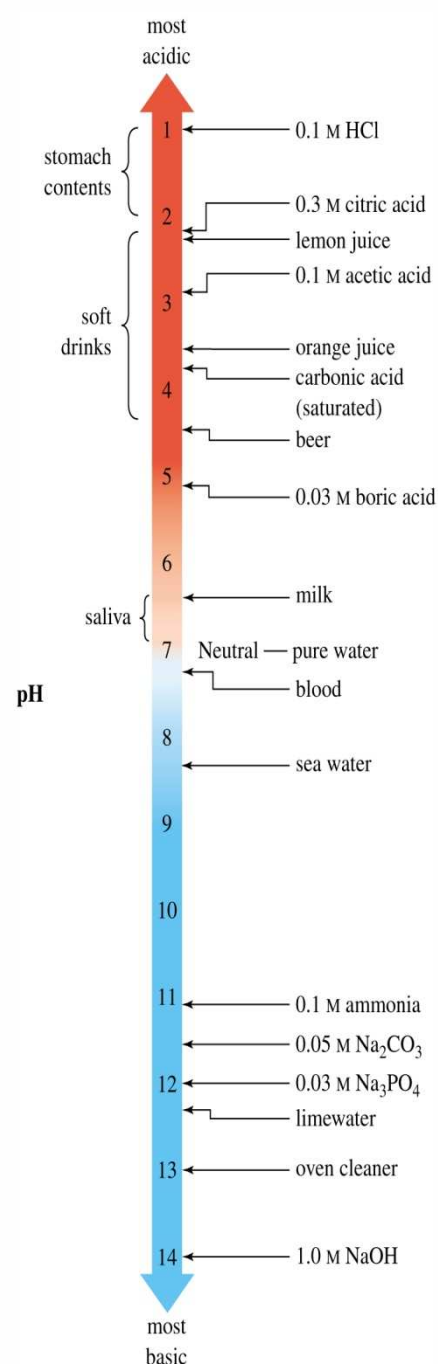
$$pOH = -\log [OH^- (aq)]$$

In neutral solution $[H^+] = [OH^-] = 1 \times 10^{-7}$ at 25 °C and $pH = 7$

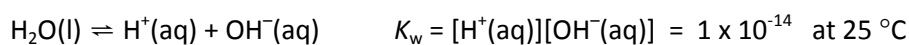
In acid solution $[H^+] > 1 \times 10^{-7}$ and $[OH^-] < 1 \times 10^{-7}$ and $pH < 7$

In basic solution $[H^+] < 1 \times 10^{-7}$ and $[OH^-] > 1 \times 10^{-7}$ and $pH > 7$

Note: $H^+(aq)$ and $H_3O^+(aq)$ are used interchangeably.



Autoionisation of Water



$$pK_w = -\log K_w = -\log (1 \times 10^{-14}) = 14$$

- pH and pOH may be interconverted using pK_w consequently it is convention to report all solutions – both acidic and basic ones in terms of pH.

$$pK_w = \text{pH} + \text{pOH} = 14$$

Example: Calculate the pH of a 0.002 M solution of sulfuric acid?

$$[\text{H}_2\text{SO}_4] = 0.002 \text{ M}$$

$\therefore [\text{H}^+] = 0.004 \text{ M}$ (one mole of H_2SO_4 dissociates to give two moles of protons)

$$\text{pH} = -\log (0.004) = 2.4$$

(NB number of significant figures is given by the mantissa of log term.)

Question: Calculate the pH of the following three solutions:

i) 0.001 M HNO_3 $[\text{H}^+] =$ $\therefore \text{pH} =$

ii) 0.001 M NaOH $[\text{OH}^-] =$ $\therefore \text{pOH} =$
and $\text{pH} = 14 - \text{pOH} =$

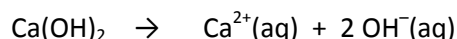
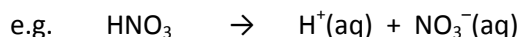
iii) The solution resulting from mixing 400 mL of 0.05 M HCl with 600 mL of 0.05 M NaOH .

iv) What is the $[\text{H}^+]$ of a solution with a pH of 4.5 ?

v) What is the $[\text{OH}^-]$ of a solution with a pH of 12.2 ?

Strong and weak acids and bases

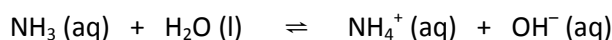
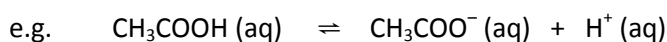
The terms *strong* and *weak* have a specific meaning in an acid – base context. *Strong* indicates complete dissociation into ions,



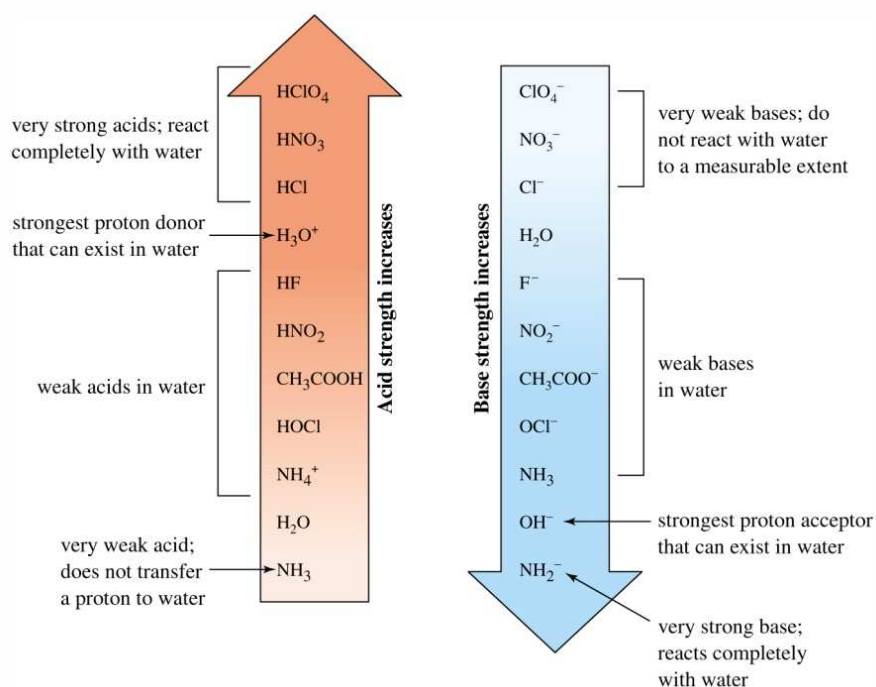
and the concentration of the ions, and hence pH, is obtained directly from the amount of starting material.

- Common strong acids are: HCl, HBr, HI, HNO₃, H₂SO₄ and HClO₄
- Common strong bases are: NaOH, KOH, Ca(OH)₂, Ba(OH)₂

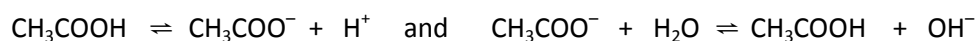
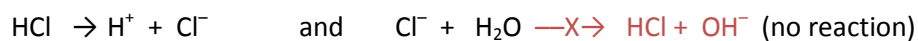
Weak indicates an equilibrium exists between the ions and the undissociated compound in solution with, very often, the undissociated compound dominating. The pH of this solution may only be calculated if the equilibrium constant, *K*, as well as the concentration of the starting material is known.



- Common weak acids include: HF, HNO₂, H₃PO₄, CH₃COOH and other carboxylic acids
- Common weak bases include: F⁻, NO₂⁻, CH₃COO⁻, NH₃ and most organic amines

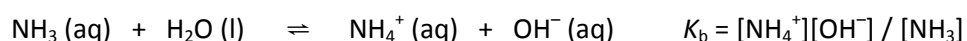
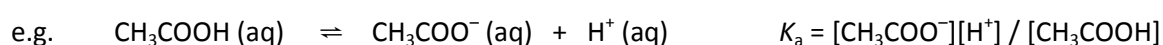


There is a direct relationship between the strength of an acid and its conjugate base. So a strong acid (e.g. HCl) is completely dissociated in water and its conjugate base (Cl^-) is a very, very weak base and shows no tendency to accept a proton. A weak acid (e.g. CH_3COOH) is in equilibrium with its ions in water and its conjugate (CH_3COO^- , a weak base) is also in equilibrium in water.



Quantification

The position of equilibrium of a *weak* acid or base is given by the value of K_a and K_b respectively.



For convenience the values are usually recorded as $\text{p}K_a$ or $\text{p}K_b$ values where $\text{p}K_a = -\log K_a$.

- The stronger the acid the smaller the $\text{p}K_a$ value (and the larger K_a value);
- The stronger the base the smaller the $\text{p}K_b$ value (and the larger K_b value)

Examples:

Acid:	NH_4^+	CH_3COOH	HF	H_3PO_4
$\text{p}K_a$	9.24	4.76	3.17	2.15
Acid strength increases	→	→	→	→

Acid:	HPO_4^{2-}	H_2PO_4^-	H_3PO_4
$\text{p}K_a$	12.38	7.20	2.15
Acid strength increases	→	→	→

Base:	H_2PO_4^-	F^-	CH_3COO^-	NH_3
$\text{p}K_b$	11.85	10.83	9.24	4.76
Base strength increases	→	→	→	→

(Recap: $\text{pH} + \text{pOH} = \text{p}K_w = 14$; but also $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14$)

Question: Rank the following substances in order of increasing acidity.

HCl, H_2CO_3 ($\text{p}K_a = 6.35$), HClO_2 ($\text{p}K_a = 1.95$), HF ($\text{p}K_a = 3.17$), HCN ($\text{p}K_a = 9.21$),

How do you know if an acid-base reaction will occur?

A comparison of $\text{p}K_a$ values enables us to determine whether a reaction between a weak acid and a weak base will occur.

Example: Will hydroxide react with acetic acid to form water and the acetate ion?



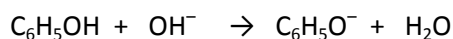
Compare the values of $\text{p}K_a$ for the two conjugate acid-base pairs; the more acidic one will be dissociated. Therefore acetic acid will react with OH^- . In fact all acids with a $\text{p}K_a < 15.7$ will react with OH^- .

Example: Will hydrogencarbonate (HCO_3^-) react with phenol ($\text{C}_6\text{H}_5\text{OH}$)? Data: H_2CO_3 ($\text{p}K_a = 6.35$), $\text{C}_6\text{H}_5\text{OH}$ ($\text{p}K_a = 10.0$).

The answer is 'no'. The reaction of hydrogencarbonate with phenol will not be favoured



But phenol will react with hydroxide ions. Data: H_2O ($\text{p}K_a = 15.7$), $\text{C}_6\text{H}_5\text{OH}$ ($\text{p}K_a = 10.0$).



Question: Indicate with a \surd or X which of the following acid – base reactions will occur.

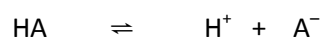
		Base		
		NH_2^- ($\text{p}K_a = 25$)	OH^- ($\text{p}K_a = 15.7$)	HCO_3^- ($\text{p}K_a = 6.35$)
Acid	Carboxylic acid ($\text{p}K_a \sim 5$)			
	Phenol ($\text{p}K_a \sim 10$)			
	Alcohol ($\text{p}K_a \sim 17$)			

Buffer

A buffer is a solution composed of moderate quantities of both members of a conjugate acid-base pair (e.g. CH_3COOH and CH_3COO^-). It maintains a solution at approximately constant pH even when small quantities of H^+ or OH^- are added.

Relationship between pK_a and pH

The equilibrium between a conjugate acid – base pair is affected by pH.



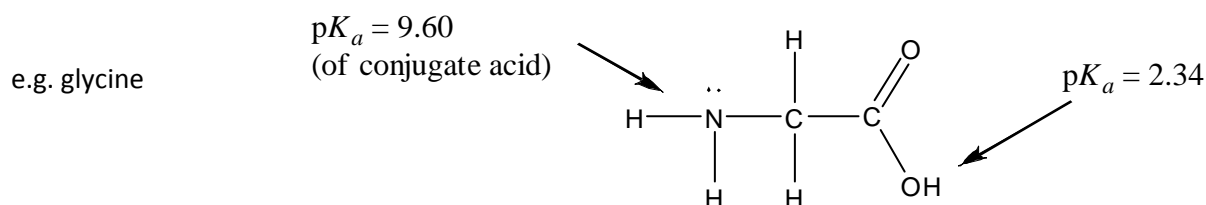
At high $[\text{H}^+]$, (low pH), the equilibrium is towards the left and visa versa. Comparison of pH with pK_a of the weak acid/base system indicates in which direction the equilibrium lies.

- If the pH is on the 'acid side' of the pK_a , the conjugate acid will predominate.
- If the pH is on the 'base side' of the pK_a , the conjugate base will predominate.

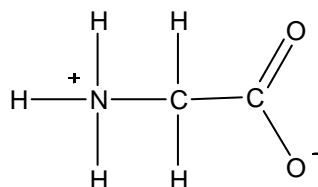
Example: Which of CH_3COOH / CH_3COO^- will dominate at a physiological pH = 7.4 given CH_3COOH $\text{pK}_a = 4.76$?

Ans: $\text{pH} > \text{pK}_a$ ie pH is on the 'base side' of the pK_a so the conjugate base will dominate: CH_3COO^-

- An amino acid contains (at least) two groups that are acid base active – a carboxylic acid and an amine. Each group has a pK_a associated with it.



At physiological pH, this will exist in an ionic form:



Question: Benzoic acid (structure below, $\text{pK}_a = 4.19$) is found in mouth wash preparations. What will its structure be at pH = 7 and at pH = 2?

