

Acid Base Equilibrium

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Acid base theories

Arrhenius Theory

Brønsted – Lowry Theory

Lewis acid – base Theory

Acid Base behaviour

In this unit when ever we discuss acids and bases we study the behaviour of compounds when dissolved in water

The solvent is all the time Water

Arrhenius Theory

Acid - any substance that increases the hydronium (H_3O^+) ion concentration in neutral water. (or H^+ ions for simplicity)

Base - any substance that increases the hydroxide (OH^-) ion concentration in neutral water.

The following pages shows some examples of acids and bases

Strong Acids = K_a is very large

Perchloric acid HClO_4

Hydroiodic acid HI

Hydrobromic acid HBr

Sulfuric acid H_2SO_4

Hydrochloric acid HCl

Nitric acid HNO_3

Memorise these examples

Weak Acid = K_a is very small at 25°C

Sulfurous acid H_2SO_3 $K_a = 1.2 \times 10^{-2}$

Hydrogen sulphate ion HSO_4^- $K_a = 1.0 \times 10^{-2}$

Phosphoric acid H_3PO_4 $K_a = 7.1 \times 10^{-4}$

Citric acid $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ $K_a = 7.1 \times 10^{-4}$

Nitrous acid HNO_2 $K_a = 7.1 \times 10^{-4}$

Hydrofluoric acid HF $K_a = 6.8 \times 10^{-4}$

Formic Acid HCO_2H $K_a = 1.8 \times 10^{-4}$

Weak Acids continued at 25oC

Acetic acid $\text{HC}_2\text{H}_3\text{O}_3$ $K_a = 1.8 \times 10^{-5}$

Carbonic acid H_2CO_3 $K_a = 4.5 \times 10^{-7}$

Hydrogen cyanide HCN $K_a = 6.2 \times 10^{-10}$

Ammonium ion NH_4^+ $K_a = 5.7 \times 10^{-10}$

Bicarbonate ion HCO_3^- $K_a = 4.7 \times 10^{-11}$

Water H_2O $K_a = 1.8 \times 10^{-16}$

Arrhenius Bases

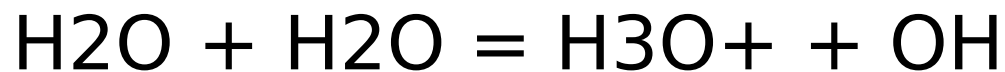
Sodium hydroxide NaOH

Ammonium hydroxide NH_4OH

Calcium hydroxide $\text{Ca}(\text{OH})_2$ (Lime water)

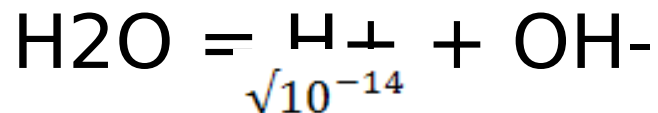
K_w and pH

Water is weakly dissociated and the equilibrium can be shown like this



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

$K_w = 10^{-14}$ at 25°C for water



pH

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

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\begin{aligned}\text{For water } \text{pH} &= -\log[10^{-7}] \\ &= -[-7\log 10] \\ &= 7\end{aligned}$$

$$\text{Similarly } \text{pOH} = 7$$

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

$$\text{pOH} = 14 - \text{pH}$$

Brønsted Lowry Theory

An acid is a proton donor

A base is a proton acceptor

An amphoteric substance is one that can act both as an acid and a base.

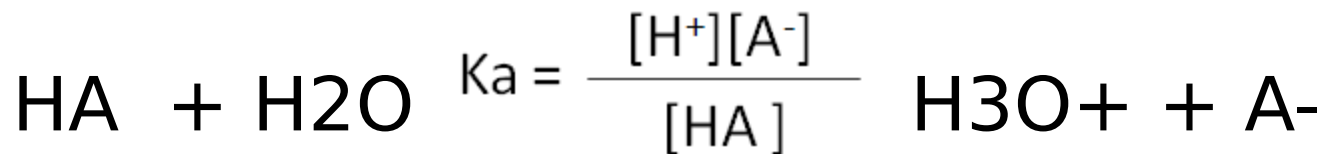
Amphoteric substances are proton acceptors or donors eg. H_2O , HCO_3^- , etc.

Ka – Dissociation constant of an acid

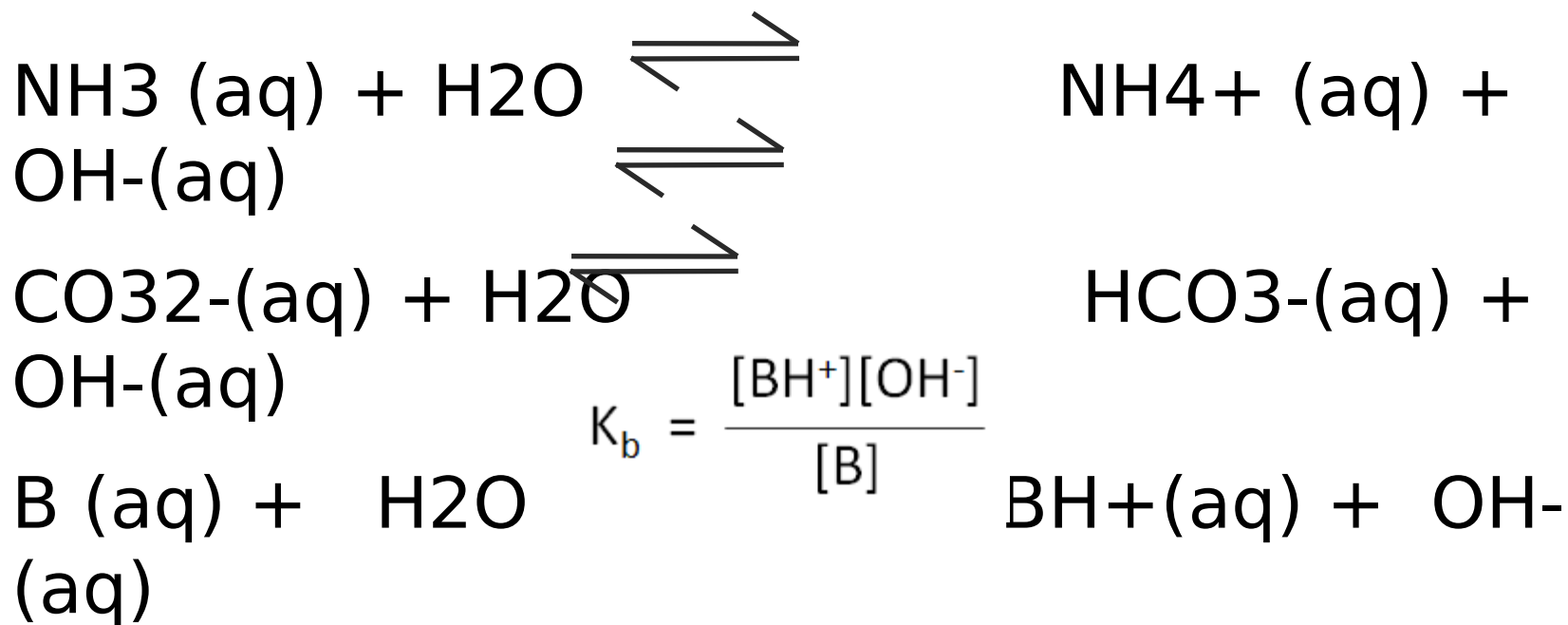
The equilibrium constant for the dissociation for a weak acid that is an equilibrium mixture



Eg.



K_b = Dissociation constant of a base



pKa and pKb

These expressions are analogous to the expression for pH. We derived it to express the concentrations in a more convenient way using whole numbers.

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

$$\text{pKb} = -\log K_b$$

Smaller value of pKa , stronger the acid

Smaller value of pKb , stronger the base.

Ka and Kb for Conjugate acid - base pair

For a conjugate acid base pair this is applicable.

$$K_a \times K_b = K_w$$

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



$$K_b = \frac{[HA][OH^-]}{[A^-]}$$



Conjugate acid base pairs

$$K_a \times K_b \quad K_a = \frac{[H^+][A^-]}{[HA]} \quad K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$K_a \times K_b = \frac{\cancel{[H^+][A^-]}}{\cancel{[HA]}} \times \frac{\cancel{[HA][OH^-]}}{\cancel{[A^-]}}$$

$$= [H^+][OH^-]$$

$$K_a \times K_b = K_w$$

Relationships between K_a , K_b , K_w

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$$K_w = K_a \times K_b$$

$$K_a = \frac{K_w}{K_b}$$

$$K_b = \frac{K_w}{K_a}$$

$$pK_a + pK_b = 14$$

$$pK_a + pK_b = pK_w$$

Calculations involving K_a

Calculate the value of K_a for a specific acid from the $[H^+]$ or pH of a solution for which we also know the initial concentration of the acid

Calculate the equilibrium concentrations of H^+ and A^- from the initial concentration of a specific weak acid and its K_a value

Calculations involving K_b

Calculate the value of K_a for a specific acid from the $[OH^-]$ or pOH of a solution for which we also know the initial concentration of the base or from pH as $pOH = 14 - pH$

Calculate the equilibrium concentrations of $[H^+]$ or $[OH^-]$ from the initial concentration of a specific weak base and its K_b value (Or what is almost the same is calculating the pH or pOH from the values of K_b and initial concentration of base)

Hydrolysis of Ions

There are many ionic salt's that make the aqueous solution acidic or basic.

The reaction of ionic salts with water is called "Hydrolysis of salts"

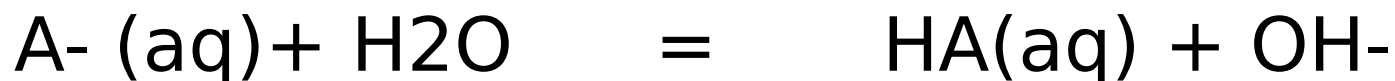
Hydrolysis can be explained using Brönsted Lowry theory.

If the conjugate acid or base is strong then there will be hydrolysis.

Weak acids and bases produce strong

Illustration of Hydrolysis

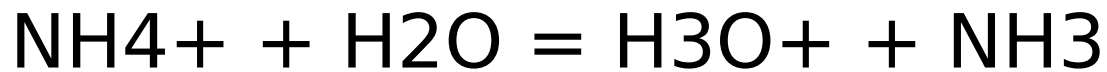
A⁻ is a strong conjugate base



The dissociation constant for the hydrolysis in this case is K_b as one of the products is a base.

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

Hydrolysis of strong conjugate acid



NH_4^+ is a strong conjugate acid therefore undergoes hydrolysis and the solution becomes more acidic or pH is lowered.

Other positive metal ions that can undergo hydrolysis is Fe^{3+} , Al^{3+} etc.

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Titration of weak acid Vs base

Acetic acid Vs NaOH

Polyprotic acids examples

H_2SO_4

H_2CO_3

H_3PO_4

Polyprotic acid

For any diprotic acid the value of $K_{a1} > K_{a2}$

It is easier to pull a H^+ from a neutral molecule than an ion

K_{a1} is usually 10^4 to 10^5 times larger than K_{a2} .

Therefore the contribution of acidity due to the second or third proton is negligible and can be ignored.

Calculating K_a from pH #1

Formic acid HCHO_2 is a monoprotic acid. In a 0.100 M solution of formic acid, the pH is 2.38 at 25°C. Calculate K_a for formic acid at this temperature.

Ans: $K_a = 1.8 \times 10^{-4}$

#1

Determine the $[H^+]$ ion concentration from pH

Make Ice table and substitute the concentration of H^+ in the table and complete it to get the equilibrium concentration of HA, H^+ and A^-

Use the values to determine the K_a for the acid.

Calculating $[H^+]$, pH from K_a for weak acid #2

The concentration of vinegar $HC_2H_3O_2$ was found to be 0.75 M acetic acid, Calculate the value for the $[H^+]$ ion concentration and pH for this acid solution if K_a for acetic acid is 1.8×10^{-5}

#2

Create an ice table initial concentration is 0.75 M for acetic acid. Change in concentration is $-x$, x and x respectively for HA, H^+ and A^-

Since K_a is very small 0.75 $-x$ can be taken as 0.75 and solve for x .

X is the concentration of H^+ use this value to calculate pH