pH and Ionic Equilibria pH and Ionic Equilibria

#Chemistry

Acids and Bases

Bronsted Løwry Theory:

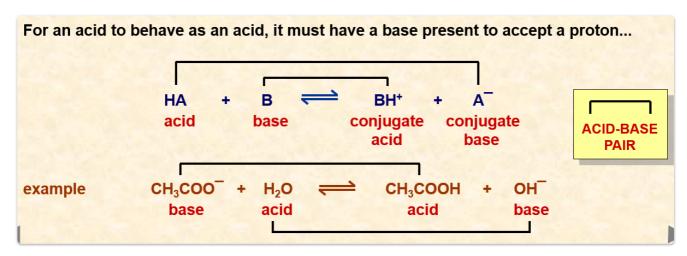
Acids: Proton Donor: $HCl o H^+{}_{(aq)} + Cl^-{}_{(aq)}$

Base: Proton Acceptor: $NH_{3(aq)} + H^+{}_{(aq)} o NH_4{}^+{}_{(aq)}$

Conjugate Systems:

Acids are related to bases: $Acids \rightleftharpoons Proton + Conjugate\ Base$

Bases are related to Acids: $Base + Proton \rightleftharpoons Conjugate \ Acid$



Strong Acids and Bases:

Strong Acids completely dissociate (split up) into ions in aqueous solution.

Monoprotic Acids

$$HCl
ightarrow H^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$$

$$HNO_3
ightarrow {H^+}_{(aq)} + NO_3^-{}_{(aq)}$$

Diprotic Acids

$$H_2SO_4
ightarrow 2H^+{}_{(aq)}+SO_4{}_{(aq)}$$

Bases:

$$NaOH_{(s)}
ightarrow NA^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$

Weak Acids partially dissociate into ions in aqueous solutions.

 $holdsymbol{?}$ E.g. Ethanoic Acid $CH_3COOH
ightharpoonup CH_3COO^-{}_{(aq)} + H^+{}_{(aq)}$ Conjugate Acid

- The weaker the acid, the less it dissociates, thus the more the equilibrium lies to the left.
- The relative strengths of acids can be expressed as K_a or pK_a values.

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

The dissociation constant for the weak acid HA is:

$$K_a = rac{[{H^+}_{(aq)}][{A^-}_{(aq)}]}{[HA_{(aq)}]} \ mol \ dm^{-3}$$

When a weak base dissolves in water an equilibrium is set up:

The weaker the base, the less it dissociates, thus the more the equilibrium lies to the left.

The relative strengths of acids can be expressed as K_b or pK_b values.

$$pOH = -\log[OH^-{}_{(aq)}]$$
 $pH + pOH = 14$

[] represents the concentration in $mol dm^{-3}$.

Ionic product of water - K_w

Despite being covalent, water conducts electricity to a very small extent.

This is due to slight ionisation:

$$H_2O_{(l)}+H_2O_{(l)}
ightleftharpoons H_3O^+{}_{(aq)}+OH^-{}_{(aq)}$$

Applying the equilibrium law to the second equation gives:

$$K_c = rac{[{H^+}_{(aq)}][O{H^-}_{(aq)}]}{[H_2O_{(l)}]}$$

As the dissociation is small, the water concentration is very large compared with the dissociated ions and any changes to its value are insignificant; its concentration can be

regarded as constant.

$$K_w = [{H^+}_{(aq)}][O{H^-}_{(aq)}]\ mol^2\ dm^{-6}$$

Because the constant is based on an equilibrium, K_w varies with temperature.

The Value of K_w

| The value of K _w varies with temperature because it is based on an equilibrium. | | | | | | | | | | |
|--|------|------|-----|------|------|--|--|--|--|--|
| Temperature / °C | 0 | 20 | 25 | 30 | 60 | | | | | |
| K _w / 1 x 10 ⁻¹⁴ mol ² dm ⁻⁶ | 0.11 | 0.68 | 1.0 | 1.47 | 5.6 | | | | | |
| H ⁺ / x 10 ⁻⁷ mol dm ⁻³ | 0.33 | 0.82 | 1.0 | 1.27 | 2.37 | | | | | |
| рН | 7.48 | 7.08 | 7 | 6.92 | 6.63 | | | | | |
| | | | | | | | | | | |

This tells us about the equation $H_2O_{(l)} \rightleftharpoons H^+{}_{(aq)} + OH^-{}_{(aq)}$ that:

- K_w gets larger as the temperature increases
- This means the concentration of H^+ and OH^- ions gets greater
- This means the equilibrium has moved to the right
- If the concentration of H^+ increases then the pH decreases
- pH decreases as the temperature increases

Because the equation moves to the right as the temperature goes up, it must be an Endothermic process

Relationship between pH and pOH

Because H^+ and OH^- ions are produced in equal amounts when water dissociates, their concentrations will be the same.

| [H*] | 10 ⁰ | 10 ⁻¹ | 10-2 | 10 -3 | 10-4 | 10 -5 | 10 -6 | 10 -7 | 10-8 | 10 -9 | 10 -10 | 10 ⁻¹¹ | 10-12 | 10 ⁻¹³ | 10-14 |
|--------------------|------------------------|-------------------|-------------------|--------------|---------------|--------------|--------------|--------------|--------------------|--------------|---------------|----------------------|-------|-------------------|-------|
| OH_ | 10-14 | 10 ⁻¹³ | 10 ⁻¹² | 10-11 | 10 -10 | 10 -9 | 10-8 | 10 -7 | 10 -6 | 10-5 | 10-4 | 10 ⁻³ | 10-2 | 10-1 | 10-0 |
| рН | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| рОН | 14 | 13 | 12 | 11 | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0 |
| STRONGLY ACIDIC | | | | | KLY | NEUTRAL | | | WEAKLY ALKALINE | | | STRONGLY ALKALINE | | | |

Palculating the \$pH\$ of 0.02M HCI:

$$HCl
ightarrow H^+ + Cl^-$$

$$[H^+] = 0.02 M = 2 imes 10^{-2}
m mol~dm^{-3}$$

The dissociation constant for a weak acid - K_a

A weak monobasic acid (HA) dissociates in water thus.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Applying the equilibrium law, we get:

$$K_c = rac{[H_3 O^+{}_{(aq)}][A^-{}_{(aq)}]}{[HA_{(aq)}][H_2 O_{(aq)}]}$$

Assumptions:

• For a weak acid, there is little dissociation.

 $[HA {= {(aq)}}]_{= {equil}} \text{ } \{\text{xtasciitilde}[HA {= {(aq)}}] {= {undis}}\}$

This assumption becomes less valid for stronger weak acids where there is more dissociation.

In dilute solution, the concentration of water is large compared with the dissociated ions and any changes to its value are insignificant; its concentration can be regarded as 'constant'.

 H_2O is constant

A weak acid dissociates as follows:

$$HA_{(aq)}
ightleftharpoons H^+{}_{(aq)} + A^-{}_{(aq)}$$

$$K_a = rac{[{H^+}_{(aq)}][{A^-}_{(aq)}]}{[HA_{(aq)}]} \; ext{mol dm}^{-3}$$