Ionic Equilibria (A2)

1. The ionic product of water, K_w
2. pH
3. Acid dissociation constant, K_a and pK_a
4. Buffer solution
5. pH indicators for acid-base titrations
6. Solubility product, K_{sp}.
7. The common ion effect.

The ionic product of water, Kw (A2)

Water is able to act as either:

- an acid (by donating protons, H^+)

or

- a base (by accepting protons).

The following equilibrium exists in pure water,

H^+ donated

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons \underset{\text{acid}}{H_3O^+_{(aq)}} + \underset{\text{base}}{OH^-_{(aq)}}$$

H_3O^+ – hydroxonium ion.

or

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium expression:

$$K_c = \frac{[H^+_{(aq)}][OH^-_{(aq)}]}{[H_2O_{(l)}]}$$

The extent of ionisation of water is very low.

The concentration of hydrogen ions and hydroxide ions in pure water is extremely small.

The concentration of water is regarded as being constant.

The new equilibrium expression:

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

K_w - ionic product of water

[ ] - the equilibrium concentration in $mol\,dm^{-3}$

The value of K_w

The value of K_w varies with temperature.

At 25°C (room temperature),

$$K_w = 1.00 \times 10^{-14}\ mol^2\,dm^{-6}$$

pK_w

$$pK_w = -\log_{10} K_w$$

at 25°C, $pK_w = 14$.

The pH of pure water

In pure water at room temperature (25°C),

$$K_w = 1.00 \times 10^{-14}\ mol^2\,dm^{-6}$$

$$[H^+][OH^-] = 1.00 \times 10^{-14}$$

$[H^+] = [OH^-]$ in pure water.

$$[H^+]^2 = 1.00 \times 10^{-14}$$

$$[H^+] = 1.00 \times 10^{-7}\ mol\,dm^{-3}$$

since $pH = -\log_{10}[H^+]$

$pH = 7$ for pure water at 25°C

<u>The variation of the pH of pure water with temperature</u>

The formation of hydrogen ions and hydroxide ions from water is an <u>endothermic</u> process.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \qquad \Delta H = +ve$$

When the temperature of water is increased, according to Le Chatelier's Principle, the equilibrium will move to lower the temperature. Endothermic reaction is favoured.

The forward reaction will be favoured and more hydrogen ions and hydroxide ions will be formed.

As the temperature increases, the value of Kw increases.

T(°C)	Kw ($mol^2 dm^{-6}$)	pH
0	0.114×10^{-14}	7.47
10	0.293×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.008×10^{-14}	7.00
30	1.471×10^{-14}	6.92
40	2.916×10^{-14}	6.77
50	5.476×10^{-14}	6.63
100	51.3×10^{-14}	6.14

temperature increases → pH of pure water falls.

Note:

The pH falls as temperature increases does not mean that water becomes more acidic at higher temperature.

In the case of pure water, there are always the same number of hydrogen ions and hydroxide ions.

That means that the water remains neutral – even if its pH changes.