Week 9 Equilibria Involving Acids & Bases

Self-ionisation of water

Through reaction with itself:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

At equilibrium, $K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$.

The concentration of water in aqueous solutions is virtually constant at about 56 M, thus:

$$[H_3O^+][OH^-] = K \times [H_2O]^2 = \text{a constant}$$

This expression can also be written as:

$$K_w = [H_3O^+][OH^-]$$

K_w is called the **ionisation constant of water**.

In pure water at 25°C, the concentration of both $[H_3O^+]$ and $[OH^-]$ is 10^{-7} M. Therefore, the value of K_w at 25°C can be calculated:

$K_w = [H_3O^+]\,[OH^-] = 10^{-7} \text{ X } 10^{-7} = 1.0 \text{ X } 10^{-14}\ M^2$

Acidic and basic solutions

In acidic solutions, H_3O^+ ions are formed by reaction with the acid with water as well as self-ionisation of water.
The concentration of H_3O^+ ions will be greater than 10^{-7} M at 25°C.
Since the product $[H_3O^+]\,[OH^-]$ remains constant, the concentration of OH^- ions in an acidic solution must be less than 10^{-7} M at 25°C.
The opposite is true for basic solutions.

In summary, at 25°C:

- in pure water and neutral solutions: $[H_3O^+] = [OH^-] = 10^{-7}$ M
- in acidic solutions: $[H_3O^+] > 10^{-7}$ M and and $[OH^-] < 10^{-7}$ M
- in basic solutions: $[H_3O^+] < 10^{-7}$ M and $[OH^-] > 10^{-7}$ M

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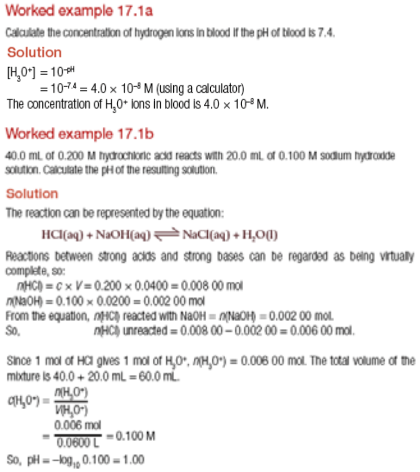
pH: a convenient way to measure acidity

$pH = -\log_{10}[H_3O^+]$

or when re-arranged, $[H_3O^+] = 10^{-pH}$

- For pure water at 25°C, $[H_3O^+] = 10^{-7}$ M, so $pH = -\log_{10}10^{-7} = 7$.
- For acidic solutions, $[H_3O^+] > 10^{-7}$ M; so pH < 7
  e.g. 0.020 M HCl at 25°C has $[H_3O^+] = 0.020$ M
  so $pH = -\log_{10}0.020 = 1.7$.
- For basic solutions, $[H_3O^+] < 10^{-7}$ M; so pH > 7
  e.g. 0.300 M NaOH at 25°C has $[OH^-] = 0.300$ M
  Since $[H_3O^+]\,[OH^-] = 1.0 \text{ X } 10^{-14}\ M^2$
  $[H_3O^+] \text{ X } 0.30\ M = 1.0 \text{ X } 10^{-14}\ M^2$
  $[H_3O^+] = (1.0 \text{ X } 10^{-14}\ M^2)/0.30\ M = 3.33 \text{ X } 10^{-14}$ M
  Therefore, $pH = -\log_{10}(3.33 \text{ X } 10^{-14}) = 13.5$



Worked example 17.1a

Calculate the concentration of hydrogen ions in blood if the pH of blood is 7.4.

Solution

$[H_3O^+] = 10^{-pH}$
$= 10^{-7.4} = 4.0 \times 10^{-8}$ M (using a calculator)
The concentration of H_3O^+ ions in blood is 4.0×10^{-8} M.

Worked example 17.1b

40.0 mL of 0.200 M hydrochloric acid reacts with 20.0 mL of 0.100 M sodium hydroxide solution. Calculate the pH of the resulting solution.

Solution

The reaction can be represented by the equation:

$$HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$$

Reactions between strong acids and strong bases can be regarded as being virtually complete, so:
$n(HCl) = c \times V = 0.200 \times 0.0400 = 0.008\,00$ mol
$n(NaOH) = 0.100 \times 0.0200 = 0.002\,00$ mol
From the equation, $n(HCl)$ reacted with NaOH $= n(NaOH) = 0.002\,00$ mol.
So, $n(HCl)$ unreacted $= 0.008\,00 - 0.002\,00 = 0.006\,00$ mol.

Since 1 mol of HCl gives 1 mol of H_3O^+, $n(H_3O^+) = 0.006\,00$ mol. The total volume of the mixture is 40.0 + 20.0 mL = 60.0 mL.

$$c(H_3O^+) = \frac{n(H_3O^+)}{V(H_3O^+)} = \frac{0.006 \text{ mol}}{0.0600 \text{ L}} = 0.100 \text{ M}$$

So, $pH = -\log_{10} 0.100 = 1.00$

How is pH affected by temperature?

The ionisation constant for water is:

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\ M^2$ at 25°C

We can use this relationship to calculate $[H_3O^+]$ or $[OH^-]$ at 25°C
But what about at other temperatures?

The self-ionisation reaction for water is endothermic

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq);\ \Delta H = +57\ kJ\ mol^{-1}$

Therefore, as T° increases, the forward reaction will be favoured.
$[H_3O^+]$ and $[OH^-]$ increase causing K_w to rise and pH to decrease.

If T° decreases, the position of the equilibrium favours the back reaction, $[H_3O^+]$, $[OH^-]$ and K_w all decrease, causing pH to increase.

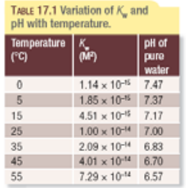
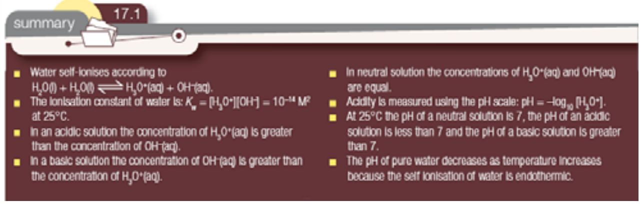


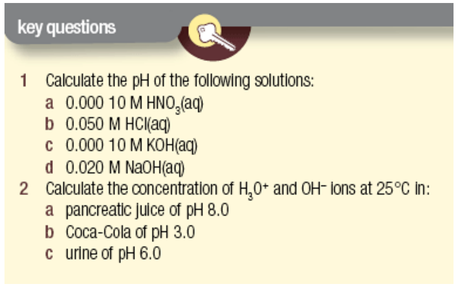
TABLE 17.1 Variation of K_w and pH with temperature.

Temperature (°C)	K_w (M^2)	pH of pure water
0	1.14×10^{-15}	7.47
5	1.85×10^{-15}	7.37
15	4.51×10^{-15}	7.17
25	1.00×10^{-14}	7.00
35	2.09×10^{-14}	6.83
45	4.01×10^{-14}	6.70
55	7.29×10^{-14}	6.57



summary 17.1

- Water self-ionises according to $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$.
- The ionisation constant of water is: $K_w = [H_3O^+][OH^-] = 10^{-14}\ M^2$ at 25°C.
- In an acidic solution the concentration of $H_3O^+(aq)$ is greater than the concentration of $OH^-(aq)$.
- In a basic solution the concentration of $OH^-(aq)$ is greater than the concentration of $H_3O^+(aq)$.
- In neutral solution the concentrations of $H_3O^+(aq)$ and $OH^-(aq)$ are equal.
- Acidity is measured using the pH scale: $pH = -\log_{10}[H_3O^+]$.
- At 25°C the pH of a neutral solution is 7, the pH of an acidic solution is less than 7 and the pH of a basic solution is greater than 7.
- The pH of pure water decreases as temperature increases because the self ionisation of water is endothermic.



key questions

1 Calculate the pH of the following solutions:
  a 0.000 10 M $HNO_3(aq)$
  b 0.050 M HCl(aq)
  c 0.000 10 M KOH(aq)
  d 0.020 M NaOH(aq)
2 Calculate the concentration of H_3O^+ and OH^- ions at 25°C in:
  a pancreatic juice of pH 8.0
  b Coca-Cola of pH 3.0
  c urine of pH 6.0

Acidity Constants

Most acid-base reactions in water can be considered as equilibrium reactions
e.g. HCl ionises in water thus:

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

The equilibrium constant can be expressed as:

$$K = \frac{[H_3O^+][Cl^-]}{[HCl][H_2O]}$$

Since the concentration of the solvent water is virtually constant, we can write thus:

$$K[H_2O] = \frac{[H_3O^+][Cl^-]}{[HCl]} = K_a$$

The quantity K_a is known as the **acidity constant**.

The K_a of HCl is 10^7 M at 25°C
This means that in HCl solutions, most of the acid is converted to H_3O^+ and Cl^-
This is why HCl is classed as a strong acid.

By contrast, the K_a of ethanoic acid is 1.75 X 10^{-5} M at 25°C

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

In ethanoic solutions, the position of the equilibrium favours the reactants and there is relatively small amount of products.

Ethanoic acid is classed as a weak acid because at equilibrium only a small proportion of the acid has been ionised.

The K_a can be used as a measure of an acid's strength.

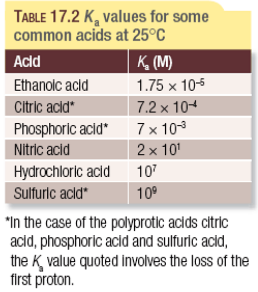
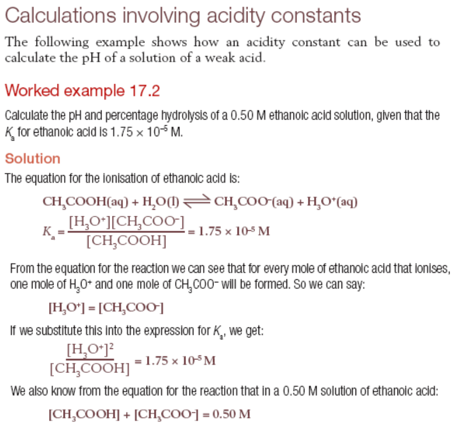


TABLE 17.2 K_a values for some common acids at 25°C

Acid	K_a (M)
Ethanoic acid	1.75×10^{-5}
Citric acid*	7.2×10^{-4}
Phosphoric acid*	7×10^{-3}
Nitric acid	2×10^{1}
Hydrochloric acid	10^{7}
Sulfuric acid*	10^{9}

*In the case of the polyprotic acids citric acid, phosphoric acid and sulfuric acid, the K_a value quoted involves the loss of the first proton.



Calculations involving acidity constants

The following example shows how an acidity constant can be used to calculate the pH of a solution of a weak acid.

Worked example 17.2

Calculate the pH and percentage hydrolysis of a 0.50 M ethanoic acid solution, given that the K_a for ethanoic acid is 1.75×10^{-5} M.

Solution

The equation for the ionisation of ethanoic acid is:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.75 \times 10^{-5}\ M$$

From the equation for the reaction we can see that for every mole of ethanoic acid that ionises, one mole of H_3O^+ and one mole of CH_3COO^- will be formed. So we can say:

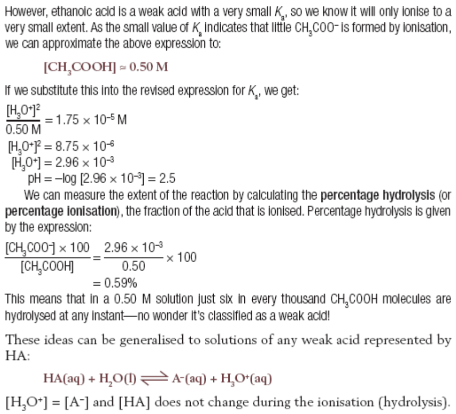
$$[H_3O^+] = [CH_3COO^-]$$

If we substitute this into the expression for K_a, we get:

$$\frac{[H_3O^+]^2}{[CH_3COOH]} = 1.75 \times 10^{-5}\ M$$

We also know from the equation for the reaction that in a 0.50 M solution of ethanoic acid:

$$[CH_3COOH] + [CH_3COO^-] = 0.50\ M$$



However, ethanoic acid is a weak acid with a very small K_a, so we know it will only ionise to a very small extent. As the small value of K_a indicates that little CH_3COO^- is formed by ionisation, we can approximate the above expression to:

$$[CH_3COOH] \simeq 0.50\ M$$

If we substitute this into the revised expression for K_a, we get:

$$\frac{[H_3O^+]^2}{0.50\ M} = 1.75 \times 10^{-5}\ M$$

$$[H_3O^+]^2 = 8.75 \times 10^{-6}$$

$$[H_3O^+] = 2.96 \times 10^{-3}$$

$$pH = -\log [2.96 \times 10^{-3}] = 2.5$$

We can measure the extent of the reaction by calculating the **percentage hydrolysis** (or **percentage ionisation**), the fraction of the acid that is ionised. Percentage hydrolysis is given by the expression:

$$\frac{[CH_3COO^-] \times 100}{[CH_3COOH]} = \frac{2.96 \times 10^{-3}}{0.50} \times 100$$

$$= 0.59\%$$

This means that in a 0.50 M solution just six in every thousand CH_3COOH molecules are hydrolysed at any instant—no wonder it's classified as a weak acid!

These ideas can be generalised to solutions of any weak acid represented by HA:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

$[H_3O^+] = [A^-]$ and [HA] does not change during the ionisation (hydrolysis).

Buffers: Using equilibrium to resist change

Buffers are solutions that can absorb the addition of acids or bases with little change of pH. They are most easily made by mixing a weak acid and a salt of its conjugate base *e.g.* ethanoic acid and sodium ethanoate:

$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$

The important feature of this solution is that it contains significant amounts of both the weak acid and its conjugate base.
If a strong acid such as HCl is added to the equilibrium mixture of ethanoic acid/ethanoate ion, the pH will decrease, but much less than expected.
Le Chatelier's Principle is followed and the system will oppose the change and restore equilibrium.
The addition of H_3O^+ causes a net back reaction.
The addition of a strong base consumes H_3O^+, causing a net forward reaction.
In both cases the overall effect on $[H_3O^+]$ is small so the change in pH is minimal.

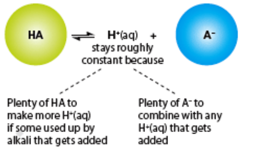


Figure 17.5
How the equilibrium between a weak acid, HA, and its conjugate base, A⁻, keeps the pH constant.

Buffers are very important in biological systems where they help maintain delicate chemical processes essential to life

pH in the body

Blood is maintained within a narrow ph band of 7.35 – 7.45.
Illnesses such as pneumonia and emphysema can lower this value to potentially lethal levels.
Hyperventilation can raise pH.

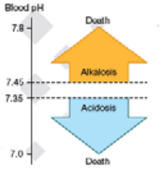
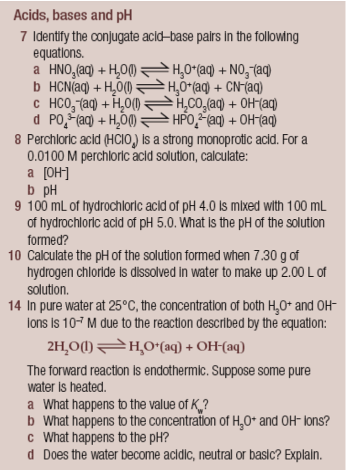


Figure 17.8
Effects of changes in blood pH.

Buffers maintain pH within limits in the body.
One of the important buffers is made up from carbonic acid and the hydrogen carbonate ion.

$H_2CO_3\ (aq) + H_2O\ (l) \rightleftharpoons HCO_3^-\ (aq) + H_3O^+\ (aq)$

- If H_3O^+ ions are added, a net back reaction occurs, removing these ions.
- If OH^- ions are added they react with H_3O^+ ions and a net forward reaction occurs.



Acids, bases and pH

7 Identify the conjugate acid–base pairs in the following equations.
  a $HNO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_3^-(aq)$
  b $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$
  c $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$
  d $PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$

8 Perchloric acid ($HClO_4$) is a strong monoprotic acid. For a 0.0100 M perchloric acid solution, calculate:
  a $[OH^-]$
  b pH

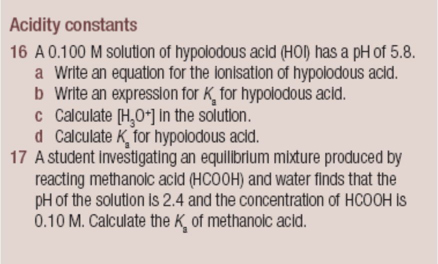
9 100 mL of hydrochloric acid of pH 4.0 is mixed with 100 mL of hydrochloric acid of pH 5.0. What is the pH of the solution formed?

10 Calculate the pH of the solution formed when 7.30 g of hydrogen chloride is dissolved in water to make up 2.00 L of solution.

14 In pure water at 25°C, the concentration of both H_3O^+ and OH^- ions is 10^{-7} M due to the reaction described by the equation:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The forward reaction is endothermic. Suppose some pure water is heated.
  a What happens to the value of K_w?
  b What happens to the concentration of H_3O^+ and OH^- ions?
  c What happens to the pH?
  d Does the water become acidic, neutral or basic? Explain.



Acidity constants

16 A 0.100 M solution of hypoiodous acid (HOI) has a pH of 5.8.
  a Write an equation for the ionisation of hypoiodous acid.
  b Write an expression for K_a for hypoiodous acid.
  c Calculate $[H_3O^+]$ in the solution.
  d Calculate K_a for hypoiodous acid.

17 A student investigating an equilibrium mixture produced by reacting methanoic acid (HCOOH) and water finds that the pH of the solution is 2.4 and the concentration of HCOOH is 0.10 M. Calculate the K_a of methanoic acid.

The Contact Process for Sulfuric Acid

SO_2 (from various sources) → SO_3 → H_2SO_4

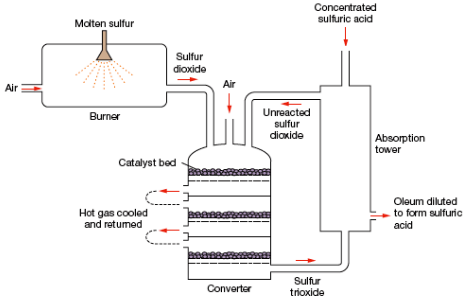


Figure 21.5
The contact process for manufacturing sulfuric acid.

Step 1: Burning sulfur

Molten sulfur is sprayed under pressure into a furnace where it burns in air to produce SO_2 gas.

$S(l) + O_2 \rightarrow SO_2(g)$; $\Delta H = -297\ kJ\ mol^{-1}$

Temperatures may reach 1000°C. The gas is cooled for the next step.

Step 2: Catalytic oxidation of sulfur dioxide

Using vanadium (V) as a catalyst:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H = -197\ kJ\ mol^{-1}$

- Performed in a reaction vessel called a converter.
- Gas stream is passed through a series of trays containing loosely packed porous pellets of catalyst.
- The reaction is exothermic and cooling is necessary (reaction maintained at 400 – 500°C and 101 kPa.
- Nearly 100% conversion is achieved.

Le Chatelier's Principle complied with

Equilibrium yield of SO_3 will increase:

- Since the reaction is exothermic, as T° decreases, the system will compensate for the reduction by favouring the forward reaction which releases energy.
- The system reacts to high pressure by favouring the forward direction because this will reduce pressure.

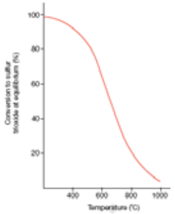


Figure 21.6
The effect of temperature on the equilibrium yield of sulfur trioxide for a typical mixture of sulfur dioxide and oxygen.

Catalyst

A conflict exists because a high equilibrium yield is favoured by low T° whereas as fast rate of production is favoured by high T°.

By using a catalyst it is possible to use lower T° and still achieve acceptable reaction rates.

Step 3: Absorption of SO_3

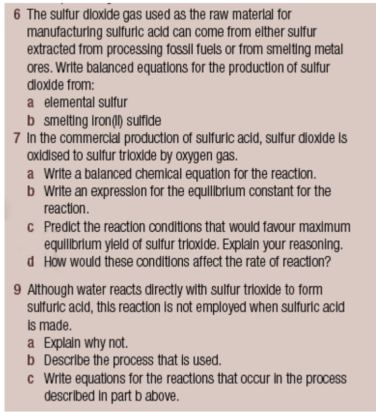
SO3 (g) + H_2O (l) (aq) $\rightarrow$ H_2SO_4 (aq); ΔH = -130 kJ mol^{-1}

Direct absorption in water is not used because of the heat evolved.

Instead, SO_3 is passed into concentrated H2SO4 in an absorption tower.
A two step reaction occurs:

SO_3 (g) + H_2SO_4 (l) $\rightarrow$ $H_2S_2O_7$ (l) (this is oleum)

$H_2S_2O_7$ (l) + H_2O (l) $\rightarrow$ $2H_2SO_4$ (l)



6 The sulfur dioxide gas used as the raw material for manufacturing sulfuric acid can come from either sulfur extracted from processing fossil fuels or from smelting metal ores. Write balanced equations for the production of sulfur dioxide from:
  a elemental sulfur
  b smelting iron(II) sulfide

7 In the commercial production of sulfuric acid, sulfur dioxide is oxidised to sulfur trioxide by oxygen gas.
  a Write a balanced chemical equation for the reaction.
  b Write an expression for the equilibrium constant for the reaction.
  c Predict the reaction conditions that would favour maximum equilibrium yield of sulfur trioxide. Explain your reasoning.
  d How would these conditions affect the rate of reaction?

9 Although water reacts directly with sulfur trioxide to form sulfuric acid, this reaction is not employed when sulfuric acid is made.
  a Explain why not.
  b Describe the process that is used.
  c Write equations for the reactions that occur in the process described in part b above.