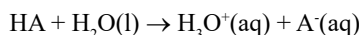



All the Ps: pH, pOH, pK_a, pK_b and pK_w

Acids in aqueous solutions donate a proton or hydrogen ion, H⁺(aq), to a water molecule. In this reaction water is described as acting as a base, i.e., a water molecule accepts a proton, or hydrogen ion, H⁺(aq). This process is described using the following equation.



 The formation of the hydronium ion, H₃O⁺, is often simplified to the hydrogen ion, H⁺. The use of H⁺ ions when describing acid-base reactions is an accepted convention. In aqueous solutions this is used to represent the hydronium ion, H₃O⁺, formed.

The pH scale provides a means for measuring the acidity of a solution. This is often provided as a simple linear scale running from 1 to 14, see Fig. 1. For very concentrated acids and bases, pH values will lie outside this range. At 298 K, a pH value below 7 indicates an acidic solution while a pH value above 7 indicates an alkaline solution. Solutions with a pH equal to 7 at 298 K are described as neutral. Figure 1, includes reference to familiar chemical indicators, e.g. red litmus with acidic solutions, and blue litmus with basic solutions.

Fig. 1

pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
[H ⁺] mol dm ⁻³	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
Litmus	Red						Blue							
Universal Indicator	Red	Orange	Yellow		Green		Blue			Purple				
examples	Gastric Acids		Fruit Juices		Coffee	Water	Sea Water	Antacids		Soaps		Drain Cleaner		


pH

The pH is related to the concentration of hydrogen ions, [H⁺(aq)], in aqueous solution. It is presented as a common logarithm, i.e. log₁₀. The logarithm of a number is the exponent to which another fixed number must be raised to produce that number. For example, the log₁₀ value of 1000 is 3, written as 10 to the power 3, or 10³, i.e.; 10 × 10 × 10 = 1000.

The pH of a solution is defined as the common logarithm, that is, log₁₀, of the reciprocal of the hydrogen ion concentration, [H⁺(aq)]. This is written as:

$$\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$$

Example 1: If an aqueous solution has a hydrogen ion concentration, [H⁺(aq)], of 0.01 mol dm⁻³, then its log₁₀ value is -2, or 10⁻².
The pH of the solution is: pH = -log₁₀(0.01) = 2

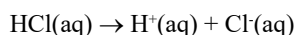
 When using common logarithm, log₁₀, the value has no units. This applies to all occurrences for pH, pOH, pK_a, pK_b, and pK_w.

The inverse function of log₁₀ is called the antilogarithm. This is used to determine the hydrogen ion concentration, [H⁺(aq)], of an aqueous solution.

$$[\text{H}^+(\text{aq})] = 10^{-\text{pH}}$$

Example 2: A pH meter gives a pH reading of 1.98 for the solution described in Example 1.
This pH value can be used to determine a more precise concentration for the solution,
i.e. [H⁺(aq)] = 10^{-pH} = 10^{-1.98} = **1.05 × 10⁻² mol dm⁻³**


Brønsted–Lowry acids are substances that dissociate in aqueous solutions to produce hydrogen ions, H⁺(aq). Strong acids fully dissociate, i.e. the concentration of hydrogen ions, [H⁺(aq)], directly relates to the concentration of the acid.



As the acid fully dissociates, it can be assumed that the concentration of hydrogen ions, [H⁺(aq)], in aqueous solution is the same as the original molar concentration of the acid, [HCl].

Example 3 shows the simple calculation required to determine the pH of a strong acid.

Example 3: What is the pH of a 0.050 mol dm⁻³ hydrochloric acid solution?
 HCl fully dissociates producing 0.050 mol dm⁻³ H⁺(aq) ions.
 $\text{pH} = -\log_{10} [\text{H}^+(\text{aq})] = -\log_{10} (0.050)$
 $\text{pH} = 1.30$

 When using very small numbers and their common logarithm, avoid rounding numbers as even small variances will lead to large errors being introduced. Ensure that final answers are recorded to an appropriate number of significant figures.

pOH

Bases may dissociate in aqueous solutions to produce hydroxide ions, OH⁻(aq). The concentration of hydroxide ions, [OH⁻(aq)], can also be presented as a common logarithm. For a strong base, which fully dissociates, the concentration of hydroxide ions formed will directly relate to the original concentration of the base.

$$\text{pOH} = -\log_{10}[\text{OH}^-(\text{aq})]$$

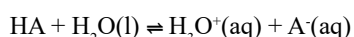
The pH of an alkaline solution can be calculated by determining its pOH value. At 298 K,

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

Example 4: What is the pH of a 0.2 M solution of potassium hydroxide?
 KOH is strong base and fully dissociates producing 0.2 mol dm⁻³ OH⁻(aq) ions.
 $\text{pOH} = -\log_{10}[\text{OH}^-(\text{aq})] = -\log_{10}(0.2)$
 $\text{pOH} = 0.70$
 $\text{pH} = 14 - \text{pOH} = 14 - 0.70 = 13.3$

pK_a

Weak acids will only partially dissociate in aqueous solution. This means only a small proportion of the acid molecules dissociates and therefore the concentration of hydrogen ions, H⁺(aq), produced in the solution is a fraction of the concentration of the original acid.



For acids, the equilibrium constant is defined as the acid dissociation constant, K_a. This provides a quantitative measure of the strength of the acid in aqueous solution.

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

HA represents a generic acid that dissociates in aqueous solution to produce a hydrogen ion, H⁺(aq), and the conjugate base of the acid, A⁻(aq). The hydrogen ion, H⁺(aq), combines with a water molecule, H₂O, to make an hydronium ion, H₃O⁺(aq), which can be represented as H⁺(aq) in the expression. The concentration of water can be taken as constant and can be ignored, hence its absence in the expression.

The acid dissociation constant, K_a, is dependent on temperature. Values are provided for weak acids under standard conditions, i.e. at 25 °C (298 K). Acid dissociation constants tend to be very small numbers. For practical purposes, it is convenient to use the logarithmic constant, pK_a.

$$\text{pK}_a = -\log_{10} K_a$$

The larger the value for pK_a, the smaller the extent of dissociation and the weaker the acid. Table 1 gives the pK_a value for some weak acids.


Note that methanoic acid, with a smaller pK_a value, is a stronger acid than both benzoic acid and ethanoic acid.

Table 1

Carboxylic Acid	Equilibrium	K _a (25 °C)	pK _a (25 °C)
Methanoic Acid	$\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{COO}^-$	1.6×10^{-4}	3.8
Benzoic Acid	$\text{C}_6\text{H}_5\text{COOH} \rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{COO}^-$	6.3×10^{-5}	4.2
Ethanoic Acid	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	1.7×10^{-5}	4.8

The inverse function, or antilogarithm, is used to determine the acid dissociation, K_a, from its pK_a value, i.e. $K_a = 10^{-\text{pK}_a}$, see Example 5.

Example 5: Propanoic acid is a weak acid with a pK_a value of 4.9, at 25 °C.
 The dissociation constant, K_a, can be determined as follows:
 $K_a = 10^{-\text{pK}_a} = 10^{-4.9} = 1.26 \times 10^{-5}$

 Although values for equilibrium constants, and thus K_a and K_b, should technically have no units, you will see these regularly given units in A level texts and exams. The units for K_a and K_b are often given as mol dm⁻³ and the units for K_w are given as mol² dm⁻⁶. You should also give units when answering questions.

The dissociation associated with weak acids is so small that it is reasonable to assume the overall concentration of the original acid is unchanged when at equilibrium. It can also be assumed that the concentration of dissociated hydrogen ions, [H⁺(aq)], and the concentration of the conjugated base, [A⁻(aq)], are equal, i.e., [H⁺(aq)] = [A⁻(aq)].

These assumptions are required when determining the pH of a weak acid solution, see Example 6.

Example 6: Calculate the pH of a 0.750 mol dm⁻³ solution of propanoic acid at 25 °C, given that the acid dissociation constant, K_a, for propanoic acid is 1.26×10^{-5} .

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} = \frac{[\text{H}^+(\text{aq})]^2}{[\text{HA}(\text{aq})]}$$

Rearrange in terms of K_a

$$[\text{H}^+(\text{aq})] = \sqrt{K_a \times [\text{HA}(\text{aq})]}$$

$$[\text{H}^+(\text{aq})] = \sqrt{(1.26 \times 10^{-5} \times 0.750)} = 3.07 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10} [\text{H}^+(\text{aq})] = -\log_{10} (3.07 \times 10^{-3})$$

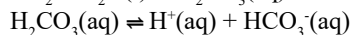
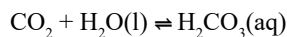
$$\text{pH} = 2.52$$

The Henderson-Hasselbalch equation, below, uses pK_a values to determine the pH of buffering solutions and the equilibrium pH in acid-base reactions.

$$\text{pH} = \text{pK}_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

These important calculations are required in measuring and managing conditions where pH sensitivities are critical, for example, involving biological or environmental systems. Example 7 outlines the use of the Henderson-Hasselbalch equation in monitoring pH in blood.

Example 7: Carbon dioxide, CO₂, dissolves in water to form carbonic acid, H₂CO₃, which has a pK_a value of 6.40.



This equilibrium occurs in blood and is one of the main contributors regulating the pH of blood.

A blood sample is obtained that contains $1.2 \times 10^{-3} \text{ mol dm}^{-3}$ of carbon dioxide, CO₂, and $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ hydrogencarbonate ions, HCO₃⁻. The pH of this blood sample can be determined using the Henderson-Hasselbalch equation.

$$\text{pH} = \text{pK}_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

$$\text{pH} = 6.40 + \log_{10} \left(\frac{1.5 \times 10^{-2}}{1.3 \times 10^{-3}} \right) = 7.46$$

pK_b

The equilibrium constant, K_b, is defined as the association constant for the protonation of a base, B, to form the conjugate acid, BH⁺.



$$K_b = \frac{[\text{BH}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{B}(\text{aq})]}$$

$$\text{and, } \text{pK}_b = -\log_{10} K_b$$

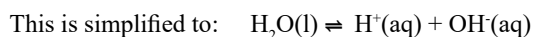
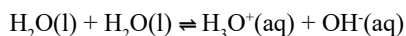
For a conjugate acid-base pair, the pK_a of the acid and the pK_b of its conjugate base are related according to:

$$\text{pK}_a + \text{pK}_b = 14 \text{ at } 298 \text{ K}$$

For example, the pK_a of ethanoic acid, CH₃COOH, is 4.75. The pK_b of its conjugate base, the ethanoate ion, CH₃COO⁻, is 9.25 (14 – 4.75).

pK_w

The ionic product of water, K_w, describes the dissociation of water in aqueous solution. This process is described in the equation below. In this reaction, water is described as acting as an acid and as a base.



The equilibrium expression for this process is:

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

As the amount of water ionised is so small, at any given time, its concentration is taken as unchanged and so it does not appear in the expression. At 25 °C (298K) the value for K_w is 1.00×10^{-14} .

The relationship between K_w and pK_w is the same as that between K_a and pK_a, or [H⁺] and pH,

$$\text{pK}_w = -\log_{10} K_w$$

For any aqueous solution at 298 K, the value of K_w remains constant at 1.00×10^{-14} . This allows for the determination of the hydrogen ion concentration, [H⁺(aq)], in basic aqueous solutions.

Example 8: Sodium hydroxide, NaOH, is a strong base that fully dissociates in aqueous solution.

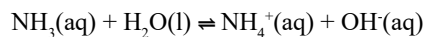
The molar concentration of a given sodium hydroxide solution, NaOH, is $0.0250 \text{ mol dm}^{-3}$.

$$\text{As } K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.00 \times 10^{-14}$$

$$[\text{H}^+(\text{aq})] = \frac{K_w}{[\text{OH}^-(\text{aq})]} = \frac{1.00 \times 10^{-14}}{0.0250} = 4.00 \times 10^{-13} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(4.00 \times 10^{-13}) = 12.4$$

Example 9: Ammonia is a weak base that dissociates in aqueous solution. The equilibrium constant, K_b, is 1.8×10^{-5} at 25 °C.



The pH of an aqueous 1.50 mol dm^{-3} ammonia solution can be determined using the following expressions:

$$K_b = \frac{[\text{NH}_4^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_3(\text{aq})]} = \frac{[\text{OH}^-(\text{aq})]^2}{[\text{NH}_3(\text{aq})]} \quad \text{Assuming: } [\text{NH}_4^+] = [\text{OH}^-]$$

Rearrange in terms of [OH⁻(aq)]

$$[\text{OH}^-(\text{aq})] = \sqrt{K_b \times [\text{NH}_3(\text{aq})]} = \sqrt{(1.8 \times 10^{-5} \times 1.5)}$$

$$[\text{OH}^-(\text{aq})] = 5.20 \times 10^{-3} \text{ mol dm}^{-3}$$

Using the expression, $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.00 \times 10^{-14}$

$$[\text{H}^+(\text{aq})] = \frac{K_w}{[\text{OH}^-(\text{aq})]} = \frac{1.00 \times 10^{-14}}{5.20 \times 10^{-3}} = 1.92 \times 10^{-12} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(1.92 \times 10^{-12}) = 11.7$$

pK_w can be related to the other 'ps' according to the following expressions:

$$\text{pH} + \text{pOH} = \text{pK}_w$$

$$\text{pK}_a + \text{pK}_b = \text{pK}_w$$

At 298 K, pK_w is equal to 14.

Questions

- Determine the pH of the following solutions, given the hydrogen ion concentration:
(a) $0.0275 \text{ mol dm}^{-3}$ (b) $1.40 \times 10^{-9} \text{ mol dm}^{-3}$
- Convert the following pHs into hydrogen ion concentrations in mol dm^{-3} .
(a) 4.32 (b) 2.15
- (a) Nitric acid, HNO₃, is a strong acid.
Calculate the pH of $0.850 \text{ mol dm}^{-3}$ nitric acid, HNO₃.
(b) Methanoic acid, HCOOH, is a weak acid. What is the pH of $0.500 \text{ mol dm}^{-3}$ HCOOH solution, given the pK_a for methanoic acid, HCOOH, is 3.75 at 25 °C?
- Calculate the pH of pure water at the following temperatures:
(a) 10 °C (pK_w = 14.5) (b) 50 °C (pK_w = 13.3)
- (a) Sodium hydroxide, NaOH, is a strong base.
Calculate the pH of a $0.400 \text{ mol dm}^{-3}$ sodium hydroxide solution, NaOH.
(b) What is the pH of 1.00 mol dm^{-3} ammonia solution, NH₃(aq), at 25 °C?
 $\text{NH}_3(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
Given that pK_w = 14.0 at 25 °C and pK_a for the dissociation of the ammonium ion, NH₄⁺, is 9.25 at 25 °C.

Answers

- (a) 1.56 (b) 8.85
- (a) $4.79 \times 10^{-5} \text{ mol dm}^{-3}$
(b) $7.08 \times 10^{-3} \text{ mol dm}^{-3}$
- (a) 0.07 (b) 2.03
- (a) 7.25 (b) 6.65
- (a) 13.6 (b) 11.6

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