

## 1

# Acids, bases and hydrogen ions (protons)

## Definition of pH

pH is defined as “the negative logarithm to the base 10 of the hydrogen ion concentration”,

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

For example, at pH 7.0, the hydrogen ion concentration is 0.000 000 1 mmol/litre or  $10^{-7}$  mmol/l.

The  $\log_{10}$  of 0.000 000 1 is  $-7.0$

Therefore, the negative  $\log_{10}$  is  $-(-7.0)$ , i.e.  $+7.0$  and hence the pH is 7.0.

$$10,000 \times 100,000 = 1,000,000,000 = 10^9$$

or

$$10^4 \times 10^5 = 10^9$$

(adding powers is the same as multiplying the original number)

$$\log \frac{x}{y} = \log x - \log y$$

$$\log \frac{1}{x} = -\log x$$

Figure 1.1 Revision of logarithms.

Number	Equivalent as 10 to the power “n”	Logarithm <sub>10</sub>
1000	$10^3$	3.0
100	$10^2$	2.0
10	$10^1$	1.0
1	$10^0$	0
0.1	$10^{-1}$	-1.0
0.01	$10^{-2}$	-2.0
0.000 000 1	$10^{-7}$	-7.0

Figure 1.2 Examples of numbers and their logarithms.

Number	Logarithm <sub>10</sub>
1	0
2	0.301
3	0.477
4	0.602
5	0.699
6	0.778
7	0.845
8	0.903
9	0.954
10	1.0
20	1.301
30	1.477
200	2.301
2000	3.301

Units	Alternative representation
1 Mole per litre	1 mol/l
0.001 Mole per litre	1 mmol/l
0.000 001 Mole per litre	1 $\mu$ mol/l
0.000 000 001 Mole per litre	1 nmol/l

Figure 1.3 Understanding units.

pH value	Equivalent in other concentration units
pH 1	0.1 Moles hydrogen ions/litre, or $10^{-1}$ Moles hydrogen ions/litre, or $10^{-1}$ g hydrogen ions per litre
pH 14	0.000 000 000 001 Moles/litre, or $10^{-14}$ Moles hydrogen ions/litre, or $10^{-14}$ g hydrogen ions /litre

Figure 1.5 pH and equivalent values.

Definition of a base:
A base is a substance that accepts a proton (i.e. a hydrogen ion, $\text{H}^+$ ) to form an acid. e.g. lactate is a conjugate base that accepts a proton to form lactic acid
Definition of an acid:
An acid is a compound that dissociates in water to release a proton (i.e. a hydrogen ion, $\text{H}^+$ ), e.g. lactic acid
A strong acid
(e.g. hydrochloric acid) is one that readily dissociates in water to release a proton.
A weak acid
(e.g. uric acid) is one that does not readily dissociate in water (e.g. to form urate and a proton)

Figure 1.4 Brønsted and Lowry definition of acids and bases.

Acidotic arterial blood pH values		Clinical examples
pH 6.8	160 nmol/l	metabolic acidosis, e.g. diabetic ketoacidosis, renal tubular acidosis  respiratory acidosis
pH 6.9	130 nmol/l	
pH 7.0	100 nmol/l	
pH 7.1	80 nmol/l	
pH 7.2	63 nmol/l	
pH 7.3	50 nmol/l	
Normal arterial blood pH values		
pH 7.35	45 nmol/l	normal arterial blood pH  pH range is 7.35 to 7.45 (45 to 35 nMoles H <sup>+</sup> /litre)
pH 7.36	44 nmol/l	
pH 7.38	42 nmol/l	
pH 7.40	40 nmol/l	
pH 7.42	38 nmol/l	
pH 7.44	36 nmol/l	
pH 7.45	35 nmol/l	
Alkalotic arterial blood pH values		Clinical examples
pH 7.5	32 nmol/l	metabolic alkalosis  respiratory alkalosis
pH 7.6	26 nmol/l	
pH 7.7	20 nmol/l	
pH 7.8	16 nmol/l	
pH 7.9	13 nmol/l	
pH 8.0	10 nmol/l	

Figure 1.6 Examples of pH values seen in clinical practice.

## What is pH?

pH is “the “power of hydrogen”. It represents “the negative logarithm<sub>10</sub> of the hydrogen ion concentration”. So why make things so complicated: why not use the plain and simple “hydrogen ion concentration”? Well, the concept was invented by a chemist for chemists and has advantages in chemistry laboratories. In clinical practice we are concerned with arterial values between pH 6.9 and 7.9. However, chemists need to span the entire range of pH values from pH 1 to pH 14. Values in terms of pH enable a convenient compression of numbers compared with the alternative which would be extremely wide-ranging as shown in Fig. 1.3. Figure 1.6 shows the normal reference range for pH in blood and, *in extremis*, fatal ranges that may be seen in acidotic or alkalotic diseases.

## The pH scale is not linear

“The patient’s blood pH has changed by 0.3 pH unit” means it has doubled (or halved) in value.

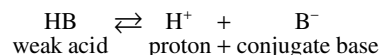
It is sometimes stated that “the patient’s arterial blood pH has increased/decreased by, for example, 0.2 pH unit”. However, notice that because of the logarithmic scale, this can misrepresent the true change in traditional concentration units. For example, a fall of 0.2 pH units from pH 7.20 to pH 7.00 represents 37 nmol/l, whereas a decrease from pH 7.00 to pH 6.8 represents a change of 60 nmol/l.

Also note that because the log<sub>10</sub> of 2 = 0.3 (that is 2 = 10<sup>0.3</sup>), a decrease in pH by 0.3, e.g. from pH 7.40 to pH 7.10, represents a two-fold increase in H<sup>+</sup> concentration, i.e. from 40 nmol/l to 80 nmol/l.

Similarly, an increase in pH from pH 7.40 to pH 7.70 represents a fall in H<sup>+</sup> concentration from 40 nmol/l to 20 nmol/l.

## The Henderson–Hasselbalch equation

A weak acid dissociates as shown:



where HB is the weak acid that dissociates to a proton H<sup>+</sup> and its conjugate base B<sup>-</sup>. NB Traditionally authors refer to the conjugate base as “A<sup>-</sup>”, i.e. the initial letter of acid, which is perhaps confusing.

Therefore from the Law of Mass Action where K = dissociation constant:

$$K = \frac{[\text{H}^+] + [\text{B}^-]}{[\text{HB}]}$$

Taking logs:

$$\begin{aligned} \log K &= \log[\text{H}^+] + \log[\text{B}^-] - \log[\text{HB}] \\ \therefore -\log[\text{H}^+] &= -\log K + \log[\text{B}^-] - \log[\text{HB}] \\ \text{i.e. pH} &= \text{pK} + \log \frac{[\text{B}^-]}{[\text{HB}]} \end{aligned}$$

Hence the Henderson–Hasselbalch equation:

$$\text{pH} = \text{pK} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

## Clinical relevance of the Henderson–Hasselbalch equation

This is illustrated by respiratory acidosis and respiratory alkalosis. The equation shows that:

$$\text{pH} = \text{pK} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Therefore in the case of the bicarbonate buffer system:

$$\text{pH} \propto \log \frac{[\text{HCO}_3^-]}{\text{pCO}_2}$$

Or, alternatively, the hydrogen ion concentration [H<sup>+</sup>] ∝  $\frac{\text{pCO}_2}{[\text{HCO}_3^-]}$ .

In other words, the hydrogen ion concentration is proportional to the ratio of the amount of CO<sub>2</sub> to bicarbonate concentration in the blood. Hence, in **hypercapnia** (high blood CO<sub>2</sub> concentration) such as in respiratory acidosis, the ratio of pCO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> is abnormally **high**, therefore the [H<sup>+</sup>] is **high** (i.e. pH is **low**).

Alternatively, **hypocapnia** caused by hyperventilation results in respiratory alkalosis. In this condition, **low** blood CO<sub>2</sub> concentrations prevail so the hydrogen ion concentration [H<sup>+</sup>] is **low** (i.e. pH is **high**).

The clinical relevance of pH and buffers will be described further in Chapters 2–5.