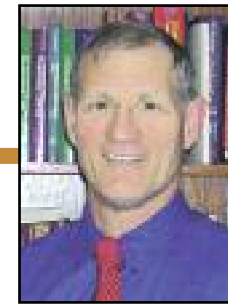

ACID-BASE CONCEPTS AND THE HENDERSON-HASSELBALCH EQUATION

by Bill Wojciechowski, MS, RRT

The physiologic importance of limiting the change in hydrogen ion concentration within the body fluid compartments is well recognized. Wide pH shifts can interfere with various metabolic processes. Hydrogen (H+) ions are continually generated by these metabolic processes. H+ ions are highly reactive species. They react with negatively charged protein molecules, and in high concentrations alter the protein's charge, configuration, and function. The body has elaborate mechanisms to maintain acid-base homeostasis, especially in the arterial blood where the pH is preserved within a narrow range of 7.35 to 7.45.

Most of the H+ ions in the body come from fat and carbohydrate metabolism, which produce 15,000 to 20,000 millimoles (mM) of carbon dioxide per day. Carbon dioxide itself is not an acid, but when it combines with water (especially in the presence of the catalyst carbonic anhydrase), the weak acid carbonic acid forms. Carbonic acid (H2CO3), in turn, dissociates to form H+ ions and ions.

The Henderson-Hasselbalch equation, a buffer equation, is based on the law of mass action

Expressions for H+ Ion Concentrations

The concentration of H+ ions in a solution can be expressed a number of ways, that is, moles/liter, pH, and nanomoles/liter. Recall from your college chemistry courses that a mole of a substance is its molecular weight in grams. For example, the molecular weight of sodium chloride is 58 daltons; therefore, a mole of sodium chloride weighs 58 grams. When 58 grams of sodium chloride are dissolved in 1 liter of water, the result is a 1.0 molar solution of sodium chloride, or a sodium chloride solution with a molarity of 1.0. For H+ ion concentrations, the unit moles/liter is extremely unwieldy. For example, the H+ ion concentration in normal arterial blood is 0.00000004 mole/liter, which is a rather abstract and intangible number.

To avoid using such awkward and cumbersome numbers, the Danish biochemist Søren Sørensen devised the pH scale and introduced the pH definition. The letters "pH" represent the power of hydrogen. Mathematically, he defined pH as

pH = -log [H+]

The pH is the negative logarithm of the H+ ion concentration expressed in moles per liter. The brackets in the representation [H+] signify the units moles/liter, or molarity. The formula developed by Sørensen enables one to simplify the transition from expressing H+ ion concentrations in moles/liter to pH. Consider the calculation that follows. Determine the pH of a solution having a H+ ion concentration of 0.00000004 M (M = molarity).

pH = -log (0.00000004)
= -log (4.0 x 10-7)
= -0.60 –(-7)
= -0.60 + 7
= 7.40

For hydrogen ions, the concentration is conventionally described as a pH value. Interestingly, a pH change of 1 represents a 10-fold change in H+ ion concentration. For example, a pH reduction from 7.40 to 6.40 is equivalent to a 10-fold increase in the H+ ion concentration. As the H+ ion concentration of a solution becomes higher, its pH becomes lower — more acidic. The converse is also true.

The third expression for the H+ ion concentration is nanomoles/liter. Nanomoles/liter is used to avoid using logarithms. The Greek prefix "nano" means one-billionth, or 10-9. The unit nanomole, therefore, indicates one one-billionth of a mole, or 10-9 mole. A normal arterial blood pH of 7.40 corresponds with 40 nanomoles/liter (nmol/liter), or 40 x 10-9 nmol/L. The normal arterial blood pH range of 7.35 to 7.45 is equivalent to a nmol/L range of 45 to 35, respectively. As the pH decreases, the numbers of nanomoles/liter increases. The H+ ion concentration given in nmol/L can be easily converted to pH as follows:

pH = 9 – log of the H+ ion concentration in nmol/L

Thus, to convert 40 nmol/L to its corresponding pH unit:

pH = 9 – log 40
= 9 – 1.60
= 7.40

pK Concepts

The pK is defined as the negative logarithm of the dissociation constant KD of an acid, that is,

pK = -log KD

Acids are categorized as either weak or strong. Weak acids tend not to dissociate readily; therefore, they liberate few free H+ ions. Carbonic acid (H2CO3) is a good example of a weak acid, which does not readily associate. The dissociation of H2CO3 is shown below.

$$H2CO3 \leftrightarrow H^{+} + HCO3^{-}$$

Strong acids, on the other hand, readily dissociate and liberate many free H+ ions. Sulfuric acid (H2SO4) is a strong acid

continued on next page

because it readily dissociates into its component ions. The dissociation of H_2SO_4 is

$$H_2SO_4 \leftrightarrow 2H^+ + SO_4^{2-}$$

The equilibrium constant for a generic acid (HA) will further illustrate the difference between weak and strong acids.

$$HA \leftrightarrow H^+ + A^-$$

Where, HA = undissociated acid; H^+ = hydrogen ion; and A^- = negative ion

For weak acids, fewer H^+ ions and A^- ions will form; therefore, more HA molecules will be present. For strong acids, more H^+ ions and A^- ions will be liberated; consequently, fewer HA molecules will exist.

The pK value of an acid represnts the pH at which the acid is 50% dissociated and 50% undissociated. In other words, the pK is the pH corresponding to half neutralization. That means equal concentrations of acid and base will be present. Different acids have different pK values,depending on the acid's tendency to dissociate. In practical terms, when the pK is low, the acid is stronger, and the higher the pK, the weaker the acid. Conversely, when the pH is greater than the pK, the acid is more than 50% dissociated.

Chemical Equilibrium and Law of Mass Action

When two or more chemical substances react, one or more of the substances different from the reacting species will form. As an example, consider the reaction,

$$A + B \rightarrow C + D$$

Substances A and B chemically react to form the products C and D. Assuming that the reaction $A + B \rightarrow C + D$ is reversible, then the reaction $C + D \rightarrow A + B$ would need to be considered. After establishing that the reaction is reversible, it can now be represented as:

$$A + B \leftrightarrow C + D$$

As a reaction proceeds, the concentration of the reactants decreases. The reactants are usually present in definite concentrations. As time passes, their concentrations stabilize and become constant. This state in which concentrations no longer change is called chemical equilibrium. The law of mass action refers to the condition when the rate of the forward reaction equals the rate of the reverse reaction.

Buffers and the Henderson-Hasselbalch Equation

Chemical systems that resist large shifts in pH are called buffer solutions. A buffer is a mixture of a weak acid and the salt of that weak acid. Carbonic acid (H_2CO_3) is a weak acid and sodium bicarbonate ($NaHCO_3$) is the salt of H_2CO_3. As H+ ions are produced during metabolism, these H+ ions are buffered by the anion of the salt of the weak acid. That anion is HCO_3^-. It can capture free H+ ions and form more of the weak acid H_2CO_3, thereby neutralizing the H+ ions and limiting the pH change of the solution.

The Henderson-Hasselbalch equation is based on the law of mass action. The Henderson-Hasselbalch equation can also be called a buffer equation because It can be used for pH calculation of a solution containing an acid and its conjugate base, e.g., $H_2CO_3/H^+/HCO_3^-$.

$$pH = 6.10 + \log \frac{[HCO_3^-]}{(PaCO_2)(0.03\ mEq/L/torr)}$$

The Henderson-Hasselbalch equation is Under normal acid-base conditions, the pH of the arterial blood is

$$pH = 6.10 + \log \frac{24\ mEq/L/torr}{(40\ torr)(0.03\ mEq/L/torr)}$$

$$= 6.10 + \log \frac{20}{1} = 6.10 + 1.3 \quad = 7.40$$

Human physiology provides protective mechanisms against significant pH shifts throughout the body. A variety of buffer systems contribute toward the maintenance of acid-base homeostasis, safeguarding against extreme acidosis and alkalosis conditions that could cause serious cellular dysfunction or even death.

Bill Wojciechowski, MS, RRT is Chairman and Associate Professor of the Department of Cardio-Respiratory Care at the University of South Alabama in Mobile, Alabama. He can be reached at wwojciec@usouthal.edu