Concentration, Acidity and Neutralization

By Wade Cheng, PhD

In the past, aestheticians, dermatologists and other skin care professionals paid little attention to acidity and neutralization. Only cosmetic chemists dealt with acidity and neutralization in cosmetic production or development.

Recently alpha hydroxyl acids (AHAs) have become a very popular technology in the cosmetic industries. The concept of concentration, acidity and neutralization are closely involved in AHA technology. Therefore, these terms are often mentioned by dermatologists, aestheticians, other skin care professionals and even some consumers.

Concentration, acidity and neutralization are technical terms in chemistry pertaining to some basic chemistry knowledge. Aestheticians, cosmetologists and even dermatologists usually do not have a clear understanding of these terms. There is substantial confusion and misinformation about these terms in the skin care market. This article will provide a simple and understandable depiction of these chemistry terms for aestheticians and skin care professionals.

Acid is a substance which is able to release hydrogen ions. An acid molecule can be expressed by HA. Through ionization HA becomes hydrogen ion (H+) bearing a positive charge and a corresponding acid anion (A-) bearing negative charge. The ionization is usually achieved in a polar solvent such as water. The process is shown in **Figure 1**.

Acids are commonly classified as strong or weak, to indicate the approximate degree of ionization. The strong acids include hydrochloric acid, nitric acid, and sulfuric acid among others. These strong acids have 100% of the molecules ionized in a dilute aqueous solution. In contrast, weak acids have small portions of the molecules ionized in solution. For instance, acetic acid is the active ingredient in vinegar which gives it a distinct odor and sour taste. There is only 0.42% of acetic acid molecules ionized (4.2 molecules per 1000 molecules). The ionization of a strong acid and a weak acid is shown in **Figure 2**.

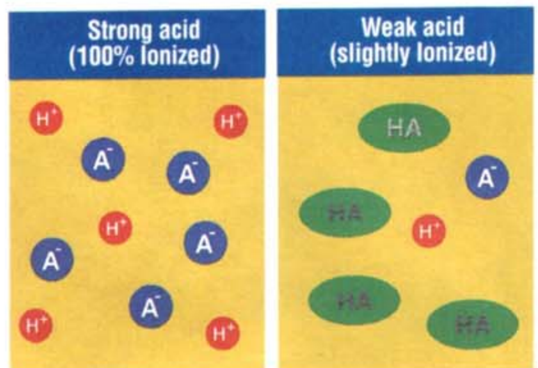

Figure 2. Strong Acid and Weak Acid

In the cosmetic industry, the concentration traditionally used is weight-percent, i.e., % (w/w).

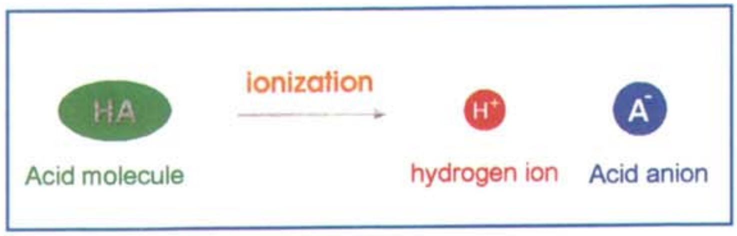

Figure 1. Acid ionization

The concentration in weight-percent is defined as: % (w/w) = Weight of an ingredient ÷ Total weight.

For instance, there are 5 grams of glycolic acid (100% pure) in 50 grams of solution. The concentration (w/w) is 5÷50 = 10% (w/w). This is illustrated in **Figure 3**. Often, the symbol (w/w) is omitted for simplicity.

As we know, the number of voters is the most important factor in an election and the weight or age of a voter (over 18) does not make any difference. Similarly in chemistry, the number of molecules per unit of weight or volume is far more important than the weight concentration for its chemical and physical properties. Therefore, a concentration with an equal number of molecules provides a reasonable and unbiased comparison.

In chemistry, it is called one mole if the weight (in grams) of a pure substance is equal to its molecular weight. It is very interesting that one mole of any substance contains the constant and huge number of molecules, i.e., 6.023×10^{23}. For instance, one mole of glycolic acid is 76.05 grams (molecular weight is 76.05) and contains 6.023×10^{23} molecules. Since each mole contains the constant number of the molecules, the mole concentration is popularly used in chemistry. The mole concentration is defined as number of moles per liter (called molarity) or per kg (called molality). The specific gravity is close to 1 kg/liter for most skin care products. Therefore molarity and molality are almost the same. For simplicity, mole concentration is used hereafter.

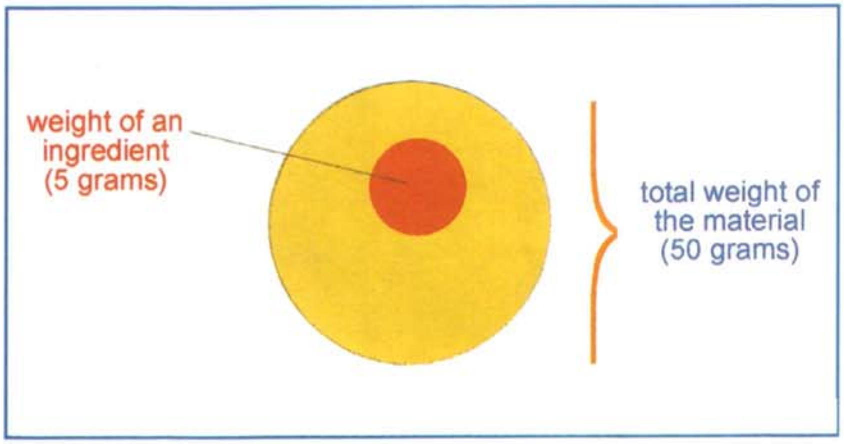

Figure 3. The Concentration of 10% (w/w).

Table I. Concentration (W/W), Molecular Weights and Mole Concentration

NAME	%(W/W)	MOLECULAR WEIGHT	MOLE CONCENTRATION
Glycolic acid	10%	76.05	0.00132
Lactic acid	10%	90.08	0.00111
Citric acid	10%	192.12	0.00052

The relation between concentration (w/w) and mole concentration of several AHAs is shown in **Table I.**

In Table I, the concentrations of three common AHAs are all 10% (w/w). However, their mole concentrations are quite different due to the different molecular weight. It is very clear that a lower molecular weight would have a higher mole concentration at the same concentration (w/w).

Acidity is the measure of hydrogen ion concentration in an aqueous media. The mole concentration of hydrogen ions is expressed by [H+]. For convenience, acidity is expressed by a scale called pH. Mathematically pH is defined as: pH = - log [H+].

Log is called common logarithm in math. What is common logarithm? Let us see the following two simple mathematical expressions: $100=10^2$ $\log 100 = 2$

Logarithm is an expression for

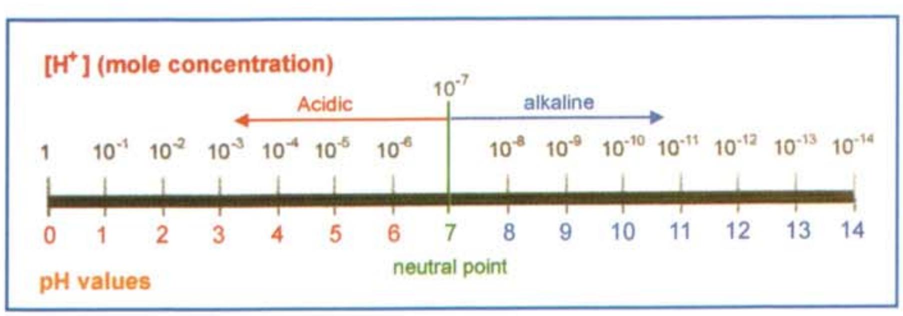

Figure 4. The Relation between pH value and (H+).

the power of 10 for convenience of huge or small numbers. For instance, log 10,000 (10^4) = 4 and log 0.001 (10^{-3}) = - 3. Note: 0.1 = 10^{-1}, 0.01 = 10^{-2} and so forth. **Figure 4** shows the relationship between pH and the mole concentration of hydrogen ion ([H+]).

The pH scale is from 0 to 14. The middle point, 7 is considered to be the neutral point in chemistry. The left side from neutral point (pH value below 7.0) is considered to be acidic. In contrast, the right side (pH value above 7.0) is considered to be alkaline. Evidently, the hydrogen ion concentration decreases from 1 to 10^{-14}. Accordingly, pH value increases from 0 to 14. In other words, the higher the concentration of hydrogen ions, the lower the pH value. The skin's pH value is in the range of 5.3 to 6.1[1]. Therefore, skin is slightly acidic and also is called acid mantle. During the contact, an aqueous media with a significantly different pH value from skin's pH would cause discomfort or irritation to the skin. A very low pH value (below 2.0) or a very high pH value (above 12.0) may cause skin burning after significant length of contact. It is advisable to use routine skin care products with a pH range of 5.0 to 8.0. Bear in mind, 1.0 difference in pH value means 10 times difference in hydrogen ion concentration.

For strong acids, the [H+] is the same as the acid mole concentration [HA] because 100% HA are ionized to hydrogen ions and corresponding acid anions. Therefore, pH is directly related to the acid concentration [HA]. For instance, 0.01 mole concentration of nitric acid, pH value will be 2.0 (-log 10^{-2}).

However, weak acids only have a very small portion of molecules ionized so that the [H+] is usually very low compared with [HA]. For instance, 0.01 mole concentration of glycolic acid has pH value 2.915 instead of 2.0 for a strong acid.

Table II. Ionization Constant, Mole Concentration, Concentration and pH Value

ACID	IONIZATION CONSTANT (25°)	MOLE CONCENTRATION	W/W%	pH
Glycolic acid	0.0001475	1	7.61	1.92
Lactic acid	0.0001374	1	9.01	1.93
Malic acid*	0.0003900	1	13.41	1.70
Citric acid*	0.0007450	1	19.21	1.56

*can release more than 1 hydrogen ion but only the first ionization constant is shown.

Table III. Concentration (W/W) of Various AHAs at Same pH Value

ACID	IONIZATION CONSTANT (25°C)	MOLE CONCENTRATION	W/W%	pH
Glycolic acid	0.0001475	1.31	10.00	1.86
Lactic acid	0.0001374	1.40	12.60	1.86
Malic acid*	0.0003900	0.49	6.60	1.86
Citric acid*	0.0007450	0.26	5.00	1.86

The ionization degree is not the same for all weak acids but varies individually. Ionization degree means how many weak acid molecules ionized or how many hydrogen ions can be released. It is interesting that the ionization degree (percentage of molecule ionized) for each acid is a constant at a certain temperature. The ionization degree is expressed by ionization constant.

The ionization constants for several typical fruit acids are compared in **Table II**[2].

Evidently, the higher the ionization constant, the more hydrogen ions will be released so as to have a lower pH value. From Table II, at the 1 mole concentration, lactic acid has the highest pH (1.93) and citric acid has the lowest pH value (1.56). Citric acid has hydrogen ion concentration 2.33 times that of lactic acid at the same mole concentration. The acid strength for these AHAs can be expressed by: citric acid > malic acid > glycolic acid > lactic acid.

Therefore, citric acid has the most skin stimulation among these AHAs. Lactic acid is slightly weaker than glycolic acid. Since skin care professionals are more familiar with the concentration by weight-percent, the % (w/w) of AHAs are listed under the same pH value in **Table III.**

In Table III, 10% (w/w) of glycolic acid with pH = 1.86 is used as the reference. The different concentrations (w/w) of the other three AHAs are listed to achieve the same pH value. The same pH value means the same hydrogen ion concentration or acidity regardless of the difference in acid concentrations.

Temperature has a certain effect

Table IV. The Temperature Effect on Ionization Constant and pH value

GLYCOLIC ACID	IONIZATION CONSTANT	PH FOR 1 MOLE CONCENTRATION
0°C (32°F)	1.334×10^{-4}	1.94
25°C (77°F)	1.475×10^{-4}	1.92
LACTIC ACID	**IONIZATION CONSTANT**	**PH FOR 1 MOLE CONCENTRATION**
25°C (77°F)	1.374×10^{-4}	1.93
100°C (212°F)	8.4×10^{-4}	1.54

Table V. The Concentration vs pH for Glycolic Acid and Lactic Acid

CONCENTRATION (W/W)	0.1%	0.5%	1%	5%	10%	15%	20%
pH (glycolic acid) @25°C	2.86	2.51	2.36	2.01	1.86	1.77	1.71
pH (lactic acid) @25°C	2.91	2.56	2.41	2.06	1.91	1.82	1.76

on pH values. Usually pH decreases slightly as the temperature increases. This is mainly due to the increase of the ionization constant. The temperature, ionization constant and pH value of glycolic acid and lactic acid are shown in **Table IV**[3].

In Table IV, glycolic acid has a pH difference of 0.02 between 0°C and 25°C. Lactic acid has a huge pH difference of 0.39 between 25°C and 100°C. Therefore, pH comparison must be made at the same temperature. Otherwise, inaccurate or incorrect conclusions would be derived. Aestheticians should utilize the temperature effect on pH to reduce possible skin irritation during AHA treatments. It is recommended to use cool water to wash skin before an AHA Treatment and to rinse off after the AHA treatment. Cool water could lower the temperature so as to obtain a higher pH value.

Although a weak acid has low degree of ionization, the pH is still quite low at a fairly low concentration. The % (w/w) and pH for glycolic acid and lactic acid is shown in Table IV.

Extensive studies reveal that skin irritation is mainly determined by the pH value of AHAs. The Cosmetic Ingredient Review panel (CIR) recently recommended that the safety pH values of AHA products is ≥ 3.5 for home care products and ≥ 3.0 for rinse-off salon treatment products. Evidently the pH is below 3.0 even at 0.1% concentration (w/w) for glycolic acid or lactic acid. Therefore, AHAs must be neutralized appropriately for safety.

What is neutralization? Neutralization is a process in which an acid is mixed with an appropriate amount of a base so that the final pH is close to the neutral point (7.0). In chemistry, the neutralization is a hydrogen ion combined with a hydroxyl anion to become a neutral water molecule. Hydroxyl anion (OH^-) is characteristic for alkali, whose aqueous solution is bitter, slippery and caustic. This is shown in **Figure 5**.

In general, an equal mole of hydroxyl anion can neutralize hydrogen ion to pH close to 7.0. The pure water is considered to be neutral, i.e., pH = 7.0. It is called partially neutralized if acid's pH is still below 7.0 after mixing with an alkali. Extensive studies show that the AHAs' skin effect dramatically decreases as pH increases, particularly when close to 7.0. Therefore, the pH value of commercial AHA products is generally controlled between the 2.5 to 5.0 range. Therefore, the partial neutralization is widely used in AHA products.

Sometimes the terms "buffered or unbuffered" are used to represent "neutralized or unneutralized". In chemistry, a buffer is a solution capable of keeping pH value unchanged or changed slightly after mixing with a small amount of acid or base. AHAs partially neutralized

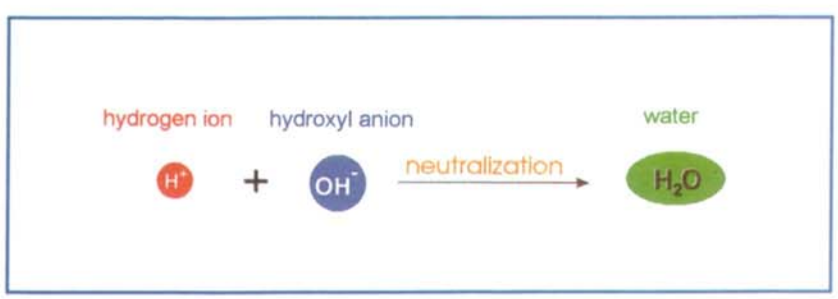

Figure 5. The Neutralization Process.

with alkali have some buffering capacity. The terms "buffered or unbuffered" are somewhat vague compared with "neutralized or unneutralized." Therefore, the terms "neutralized or unneutralized" are much more precise and are recommended for use in AHA chemistry.

The alkali or bases commonly used to neutralize AHAs are sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonia (NH4OH) and triethanolamine (TEA). These bases can reduce [H+] to a desirable degree and control a certain pH value.

During the neutralization process, the hydrogen ions combine with hydroxyl anions to form water. There is another substance produced known as salts or ester. The salts or esters consist of the acid anions and metal cations which are completely ionized in the solution. When the water in the solution evaporates or is boiled off, the acid anion and metal cation will conglomerate to form solid salts or esters. The glycolic acid neutralized with sodium hydroxide is shown in **Figure 6**. Glycolic acid ionizes to acid anion and hydrogen ion. Sodium hydroxide ionizes to sodium cation and hydroxyl anion. Hydrogen ion combines with hydroxy anion to form water. The sodium cation and the acid anion are linked together to form glycolic acid ester (sodium hydroxyethanoate). However, the ester is 100% ionized in the solution.

What is the function of AHA esters ? Why not control a certain pH with a low concentration instead of partially neutralizing AHAs? Let us compare the glycolic solution with the same pH values (3.0) but at concentration (w/w) 3% and 10%, respectively. Since the hydrogen ion concentrations are the same (same pH), the safety factor for skin would be similar for both concentrations. However, the solution with 10% has the much higher concentration of the AHA ester. Some experiments reveal that 3% glycolic acid (pH=3.0) could effect the skin depth at 3-5 cell layers 30 minutes after application. In contrast, glycolic acid at 10% concentration (pH=3.0) can affect 10-20 cell layers deep within the skin under the same conditions. The higher a concentration, the more penetration it would have. This is called concentration effect and is well understood in common practice. Although AHA ester is not as effective as unneutralized AHA, a considerable penetration of AHA ester could contribute significantly to the overall skin effect of AHAs.

In summary, a concentration is not equal to the acidity for weak acids such as AHAs. The pH value represents the concentration of hydrogen ion and is critical for skin safety. The pH value of AHAs can be adjusted to a desirable degree by a partial neutralization process, which produces the corresponding AHA esters. ■

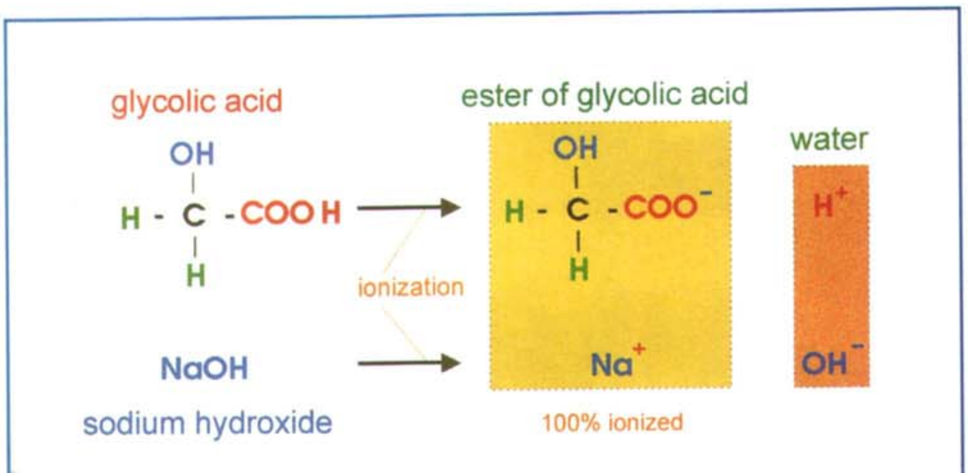

Figure 6. Glycolic Acid Neutralized with Sodium Hydroxide.

Wade Cheng is Vice President and Director of R&D, Rejuvi Laboratory, San Francisco, CA. He holds a BS degree in Chemistry and Chemical Engineering, an MS in Analytical Chemistry from University of San Francisco and a PhD in Biochemistry from University of California, Davis. For questions and inquiries, fax: (650)588-7796 or E-mail: Rejuvi@mindspring.com

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