

# The Art & Science of Aquarium Management

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More and more of my time is spent answering questions from hobbyists. I believe this is happening because the options for aquarium management are growing at such a dizzying pace that the art and science of it has not kept up. Here is one sampling of some of the more frequently asked and more important questions asked.

## WHAT'S THE DIFFERENCE BETWEEN IODINE AND IODIDE, CHLORINE AND CHLORIDE, AMMONIA AND AMMONIUM?

All matter is made up of atoms consisting of a core of positively charged particles called protons and neutral particles called neutrons, surrounded by an orbital field of an equal number of negatively charged particles called electrons. Forces in the orbital field of electrons drive atoms to acquire orbital stability. There are two mechanisms to achieve orbital stability: 1) the gain or loss of electrons, or 2) the sharing of electrons between atoms. The first mechanism leads to the formation of ions. Since ions have more or less electrons than protons, they have either a negative or positive charge, respectively. Negative ions (called anions) associate with positive ions (called cations) to form ionic compounds. The second mechanism, sharing of electron between atoms, leads to the formation of uncharged covalent molecules. Sodium is an example of an atom which can give up an electron to achieve stability, acquiring a positive charge ( $\text{Na}^+$ ). Chlorine stabilizes by gaining an electron and acquires a negative charge ( $\text{Cl}^-$ ). Sodium ions associate with chloride ions to form sodium chloride, an ionic salt, common table salt. If, on the other hand, chlorine atoms acquire stability by sharing electrons then they form a covalent compound,  $\text{Cl}_2$ , elemental chlorine. The same is true for iodine and bromine. Ions have properties totally different from their elemental forms. Chlorine, iodine, and bromine are highly

toxic, even at extremely low concentrations, whereas chloride, iodide, and bromide are essential for life and are relatively non-toxic. Chloride ions are a major dissolved component of sea water. Hydrogen consists of a single proton, no neutron, with a single orbital electron. If hydrogen gives up its electron, it acquires a positive charge and becomes a hydrogen ion ( $\text{H}^+$ ). Hydrogen is unique in that its ion is a proton, although hydrogen ions or protons do not exist as such, but protonate a solvent, usually water, to form a hydronium ion,  $\text{H}_3\text{O}^+$ . If hydrogen shares an electron with another hydrogen, it forms a covalent bond or elemental hydrogen ( $\text{H}_2$ ). Oxygen can share

electrons with another oxygen and form elemental oxygen ( $\text{O}_2$ ) or it can share electrons with hydrogens and form a covalent compound  $\text{H}_2\text{O}$ , water.

Water ( $\text{H}_2\text{O}$ ) is entirely innocuous when compared to hydronium ( $\text{H}_3\text{O}^+$ ), which is corrosive at even low concentrations. Hydrogens can share electrons with nitrogen and form a covalent compound  $\text{NH}_3$ , ammonia. When ammonia gas is added to water, it removes protons from hydronium water and forms ammonium ions,  $\text{NH}_4^+$ . The extent to which this takes place is dependent on the hydronium concentration (pH): the higher the hydronium concentration (the lower the pH), the more ammonium is formed. Ammonia ( $\text{NH}_3$ ) is very toxic, but ammonium ( $\text{NH}_4^+$ ) is relatively safe.

## WHAT IS pH

Water is a covalent compound and, like other covalent compounds, does not extensively dissociate. Its limited dissociation takes place according to the equilibria:



The extent of dissociation is expressed as a rate constant  $K = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$ , which is equal to  $1.0 \times 10^{-14}$ . In such an equation, [ ] designate concentration. At the equivalence point, the hydronium concentration is  $1.0 \times 10^{-7}$  moles per liter or 0.0000001 moles/liter. This is usually expressed as pH, or the negative log of the hydronium concentration, 7.0. pH is a very useful expression for expressing cumbersome concentrations. Each pH unit represents a 10-fold concentration difference of hydronium ions, the number of decimal places in moles/L of hydronium ions. The most reliable measurement of pH is that obtained with a functioning, calibrated electrode under proper conditions. The most unreliable measurement of pH is that obtained with a poorly functional or miscalibrated electrode or one obtained under improper conditions. A steady and reproducible digital reading is not assurance of accuracy. If you are not trained to recognize the inadequacies of pH meter measurements, you are better off with pH dye methods. pH electrodes may appear to function, but have a clogged reference junction. An electrode which jumps around with the approach of static charge or ground (your hand) cannot reliably measure pH. An electrode should have rapid and consistent response to not only strong pH reference buffers, but diluted buffers as well. An electrode should be calibrated at two points on both sides of the target pH and it should behave linearly between those points. Always remove a sample of water from the aquarium to measure pH. Measurement by immersing the electrode directly in the tank can be severely compromised by otherwise undetectable stray electrical currents. Very soft water (e.g., distilled water) cannot be measured reliably unless a small amount of potassium chloride is added to improve conductivity. pH dye measurements work well, but have two limitations: measurement is dependent on visual perception, and dye response is subject to error from protein interference, salt concentrations, inadequate buffering or any combination of these. For that reason, only dyes with clear color changes around the target pH should be used. Otherwise, try to use two different dyes to help visual judgment and also catch interference.

#### **WHAT IS THE DIFFERENCE BETWEEN DISTILLED, DEIONIZED, AND R/O WATER?**

Distilled water is obtained by condensing water from its vapor form to its liquid form. It is a relatively pure form of water, free of dissolved solids. It will, however, contain gases and vapors. Distillation does not free water of carbon dioxide, ammonia, or other vaporous contaminants. For that reason, distilled water rarely has the theoretically pure pH of 7.0. Deionized water is obtained by filtering it through ion-exchange materials that remove cations (sodium, calcium, magnesium, potassium, ammonium) and anions (chloride, sulfate, bicarbonate, nitrate). Deionization results in very pure water, but it retains non-ionized contaminants such as organics, carbon dioxide, oxygen, nitrogen, chlorine, silica. Water for deionization is usually pretreated with activated carbon or organic scavenging resins to remove organics and some gases. Either distillation or deionization produces water suitable for most of the more demanding water needs of hobbyists. Such water usually has a pH of about 6.0, due to dissolved carbon dioxide. Reverse osmosis water is obtained by filtering a slow moving stream of water under high pressure against a fast moving stream under relatively reduced pressure. The purity of R/O water is variable, depending on the source water and the performance characteristics of the R/O unit. Some sophisticated laboratory systems can produce water that approaches either distillation or deionization, but, due to the inability to maintain adequate pressures, most home or hobby units produce only marginally improved water over the source water, even when operated conservatively. Many hobbyist units are not realistically rated.

#### **IS IT NECESSARY TO USE DISTILLED OR R/O WATER IN AN AQUARIUM OR IS TAP WATER GOOD ENOUGH?**

The use of tap water, once chlorine and chloramines have been removed should prove satisfactory for most hobbyists. Sometimes, tap water may contain excessive phosphates or nitrates or both for use in reef tanks or with more delicate juvenile freshwater fish. Soft acid water may also be contaminated with copper extracted

from pipes. In such situations, processed water may be a good choice. If you wish to set up a soft water environment for Discus or Tetras, and your tap water is very alkaline and hard, processed water may be necessary. If processed water is used in a freshwater aquarium it may be advisable to replace some of the essential salts that have been removed.

#### **HOW DO NATURAL WATER ENVIRONMENTS DIFFER?**

Native water environments are freshwater, spanning a full spectrum from very soft to very hard, from acidic to alkaline. By comparison, marine water, although it varies somewhat, is relatively consistent. Estuaries generally represent brackish waters, variable mixtures of fresh and marine waters. Soft water has a low calcium and magnesium content and such water usually has an acid pH with low acidity and low alkalinity. It may, however, have a high pH or a high acidity, but high alkalinity is very rare in soft waters. Hard water, in contrast, has elevated calcium and magnesium concentrations, usually with high pH and high alkalinity, although high acidity may also be possible, but low pH is unusual. It is a mistake to assume that, if water has a high pH, it must be hard water.

#### **WHAT IS HARDNESS, ALKALINITY, CONDUCTIVITY, SPECIFIC GRAVITY?**

Soft water, by definition, is water which contains very little dissolved divalent cations, specifically, calcium and magnesium, whereas hard water contains high concentrations of these. Water that contains less than 35 mg/L calcium/magnesium (equivalent to about 90 mg/L calcium carbonate or 5 German degrees) is generally considered soft, whereas water containing more than 175 mg/L calcium (equivalent to 446 mg/L calcium carbonate or 25 German degrees) is considered hard. Despite the much confused state of misinformation prevalent in the hobby, hardness has absolutely nothing to do with carbonates. The terms "permanent" and "general" hardness and "carbonate" hardness are obsolete and should be discarded. "Permanent" or "general" hardness is true hardness; "carbonate" hardness is not hardness at all but

alkalinity. Conductivity is another parameter that confuses the picture even more. A solution of sodium chloride has high conductivity, but no hardness or alkalinity. A concentrated solution of calcium chloride is very hard, but has no carbonate or alkalinity, but has high conductivity. A concentrated solution of sodium bicarbonate or sodium diphosphate has a very high alkalinity, but no hardness, but high conductivity. Hardness, alkalinity, and acidity contribute to conductivity, but conductivity is not any of them. Conductivity is a measure of the water's ability to conduct an electrical current and reflects the concentration of dissolved ions. Hardness is assessed by measuring calcium and magnesium. Historically, hardness was an assessment of water's ability to precipitate soap, a property directly dependent on the calcium and magnesium concentrations. The problems arise with test kits and conventions that report hardness as some unit of calcium carbonate. Worse, some so-called hardness test kits actually measure alkalinity. The consequence of this is that many a hobbyist confuses hardness with alkalinity, a measure of the water's ability to resist a drop in pH, also misguidedly expressed as a unit of calcium carbonate or calcium oxide. To avert this problem, manufacturers and hobbyists should avoid the usage of units that utilize calcium carbonate or calcium oxide as a point of reference. Forget grains or mg of calcium carbonate! Forget German degrees or KH! Hardness should be expressed for what it is, a concentration of divalent metal ions as mg/L. Likewise, alkalinity should be expressed for what it is, the ability to resist change in pH on the measured addition of acid, meq/L (milli-equivalents per liter). An often overlooked parameter is acidity, which is a measure of the water's ability to resist change in pH on the addition of base. Likewise, acidity should be expressed for what it is, the ability to resist change in pH on the measured addition of base, meq/L. Taken together, acidity and alkalinity constitute the buffer capacity of the water, the ability to resist change in pH from either direction. The assessment of buffer capacity should be as important as the measurement of pH, since rapid change in pH poses a greater hazard than does pH itself. Conductivity is of questionable usefulness: hard water will always have high conductivity, but high con-

ductivity does not necessarily mean hard water; high alkalinity will always give high conductivity, but, again, high conductivity does not necessarily mean high alkalinity. Conductivity tells you how much dissolved ions are in the water, but does not tell you anything about what kind they are. Any dissolved substance that ionizes will raise conductivity: sodium, calcium, chloride, sulfate, even tannic acid.

Specific gravity is the ratio of the weight of a given volume of any substance compared to the weight of an equal volume of distilled water at a defined temperature. By definition, then, pure water has a specific gravity of 1. This is a useful measurement for assessing the proper concentration of salts in seawater. As the concentration of dissolved solids heavier than water increases, the specific gravity increases. It is possible to have aquarium water with a specific gravity less than 1.0, if dissolved solids have a weight less than water, as in soft water rich with tannins or other organic acids.

#### WHAT IS A BUFFER?

A buffer is any agent or mixture that has an acid and base in equilibrium:



As before the equilibrium can be expressed as a K, where  $K = [\text{H}^+][\text{B}^-]/[\text{HB}]$ . At equivalence, the pH of this solution will be the same as the pK, which by analogy with pH, is the negative log of K. A buffer at the same pH as its pK has maximum ability to resist pH change in either direction. A buffer at this pH has its acidity equal to its alkalinity and offers maximum protection. Sea water is the most familiar buffered water: it has several buffer systems, including carbonic acid-bicarbonate, bicarbonate-carbonate-borate, and various ion-ion interactive versions of these. Commercial freshwater buffers are mixtures of monobasic and dibasic phosphates. Phosphates, however, are excellent freshwater buffers: they are highly efficient, stable, and non-toxic. Their main drawbacks are poor solubility in hard water and

they promote algae growth and proliferation (eutrophic). Sodium bicarbonate, also called acid carbonate, hydrogen carbonate, hydrocarbonate, or baking soda, is also frequently used as a freshwater buffer. Bicarbonate has a serious drawback in freshwater, however, arising from the low dissociation of carbon dioxide in water. Bicarbonate added to water creates the equilibrium:



Since  $\text{CO}_2$  does not readily dissociate or ionize to carbonic acid,  $\text{CO}_2$  is lost to the air, the net effect being that bicarbonate is gradually converted to carbonate unless an acid component is supplied. This is sometimes done by injecting  $\text{CO}_2$  in response to pH increase. The main drawback to this approach is dependence on a high maintenance electronic system which can be prone to malfunction, usually electrode-malfunction. Soft acid waters sometimes use organic acids to buffer the water. Peat, wood, and root are abundant sources of such acids, particularly tannic and gallic acids. Such acids, however, tend to discolor and haze the water. A more serious danger is the possible oxidation of these acids to phenols, which are toxic. Several organic buffers that do not have these drawbacks are available.

#### IS THE SUGGESTION TO REMOVE THE WET-DRY FROM MY REEF SYSTEM TO LOWER NITRATE CONCENTRATION SOUND ADVICE?

Nitrate is the final oxidation product of ammonia and nitrogenous waste arising in the aquarium. Ammonia is released into the water by fish, invertebrates, and other living creatures. Nitrogenous chemicals such as proteins, peptides, amino acids, nucleosides, purines, pyrimidines, etc. are likewise released into the water by the living creatures in it. These nitrogenous chemicals are ultimately metabolized by heterotrophic bacteria to ammonia. Ammonia is then converted to nitrite, then nitrate by aerobic nitrifying bacteria. Aerobic nitrifying bacteria are omnipresent on all exposed surfaces in the aquarium. Anaerobic denitrifying bacteria are present wherever there is oxygen poor surface. In the reef tank, this an-

aerobic surface is present primarily inside the porous structure of the “live rock.”

At first glance, it may seem to make sense to decrease nitrate formation by removing some nitrification capacity. And, in fact, if you do it, it may actually seem to work, provided you leave enough nitrifying surface to take care of the ammonia directly released by fish and invertebrates. The problem is that the organic nitrogenous compounds are no longer efficiently converted to ammonia and thus accumulate more rapidly. Their removal becomes much more dependent on skimming and chemical filtration. Since less ammonia is being formed and denitrification is constant, nitrate concentration either drops or remains constant or increases at a reduced rate, depending on the biology of the specific aquarium. Unfortunately, the concentration of nitrogenous organic matter (which is not measured by test kits and some of which is more toxic than nitrate ) will increase and the nitrification of ammonia, while it may remain adequate, will decrease and may reach a critical capacity that is inadequate to handle sudden surges of ammonia. There are no magic reef bacteria that bypass nitrification and directly remove ammonia and other nitrogenous compounds. No matter how much we may wish it, the reef aquarium is not the open ocean.

The only alternate route for ammonia and nitrogenous waste is algae and plants. The more algae (coral, macro, and others) the better. Algae in an external scrubber is even better, because it allows for harvesting and thus actually removes nitrogen products from the system.

It seems more intelligent not to short circuit nitrification and heterotrophic metabolism of organics by removing filter area, but to increase denitrification instead, so that it can keep up with nitrification. How can this be done? Water changes, of course, are labor intensive, but definitely lower nitrate and organics, and should be a routine of intelligent reef management. Increase the quantity of reef rock to increase denitrification. Use properly porous materials such as porous glass, lava rock, or de\*nitrate

(Seachem), either as bottom substrate or in a separate filter. Some commercial denitrifying filters are available. Those that require feeding with methanol (wood alcohol) or similar materials are probably best avoided. Algae scrubbing is also an effective way to decrease nitrate concentration as well as the concentration of many nitrogenous chemicals. Years ago, before reef aquaria were popular, I maintained successfully for years until a move was required, a combination reef and fish aquarium with an undergravel filter (heresy today!), no wet-dry, but an efficient algae scrubber, with virtually no nitrate.

#### **HOW CONCERNED SHOULD I BE ABOUT PHOSPHATES? ARE THEY TOXIC?**

With the exception of a few organophosphate insecticides, phosphates are not toxic. Monosodium and disodium phosphates are routinely used as freshwater buffers and pH adjusters. In seawater, phosphates are only slightly soluble and precipitate as detritus. Phosphates are inhibitory to hard corals and for that reason are undesirable in reef aquaria. Phosphate is an essential plant nutrient and tends to promote proliferation of algae, particularly undesirable hair algae, in both freshwater and seawater. Algae proliferation, however, also depends on nitrate and potassium concentrations, as well as nitrogenous organics, carbon dioxide, trace elements, and competing plants and macroalgae. To avoid both coral inhibition and algae proliferation in seawater, phosphate concentration should be kept below 0.2 mg/L (ppm). In freshwater, phosphate at less than 5 mg/L should pose no problem. Common sources of phosphate in the aquarium are the municipal water supply, fish waste, food, phosphate buffers or pH adjusters, some gravels, and carbon. Phosphate in carbon arises from the organic origin of all carbons (anything that was once living will contain phosphate) and not from acid washing (as is often mis-stated). All carbons, regardless of the manufacturer's claim to the contrary, contain and leach phosphate, albeit not all to same extent. Unfortunately, the carbons that are better for water purification are usually the carbons that contain the most phosphate, unless they have been pre-washed to remove some of the leachable

content. If you are concerned about phosphate and use carbon, pre-soak and wash it for several days in distilled water with a small amount of muriatic acid (enough to keep the pH of the water acid). Remember that phosphate is not at all toxic and that, unless you have either hard corals or have a hair algae problem, there is no need to get neurotic about phosphate. There are phosphate removing products on the market. These products are based on the precipitation of phosphate on the surface of either aluminum oxide (aluminum rust) or iron oxide (iron rust). The aluminum products are white while the iron products are brown. Some aquatic suppliers try to conceal the identity of these materials by giving them other generic identities such as “ceramic.” Aluminum oxide is manufactured as spherical beads. Some aquatic companies sell the intact beads while others sell broken beads that appear as granules rather than beads. For water flow dynamics, the intact beads are geometrically superior. These materials are generally safe and effective. They do, however, remove more than just phosphate. Silicates, organic acids, some amino acids, and some vitamins are also removed. They are more effective in seawater than in freshwater, at higher pH than lower pH. Once something has been bound, it is not released. Once exhausted, none of these materials can be regenerated, regardless of any manufacturer’s claim to the contrary. Phosphate cannot be baked away. If not exhausted, they can be removed, allowed to dry, and reused until exhausted, but this is not regeneration. If you find that you are not exhausting your phosphate remover in bringing your phosphate level to an acceptable level, then use less than the recommended amount rather than repeatedly removing and replacing the material.

**WHAT ABOUT VITAMINS AND TRACE ADDITIVES? ARE THEY REALLY NECESSARY? OR ARE THEY HARMFUL?**

Two vitamins, C and B<sub>12</sub>, have been reported as beneficial to corals. Plants and macroalgae usually benefit from vitamins B<sub>12</sub>, biotin, thiamine, and riboflavin. Plants and algae also require potassium, magnesium, manganese, iron, calcium, strontium, zinc, molybdenum, copper, nickel, cobalt, selenium, rubidium, vanadium, and tin.

Some of these are best delivered as chelates to make them more biologically available and prevent rapid precipitation, particularly in seawater. Some are quite toxic at any concentration greater than trace. Corals and some invertebrates, as well as plants and algae, can benefit from supplements in the water. It is important not to overdose, particularly with trace elements products. This, after all, is why they are called “trace” elements. The two main vitamins beneficial in the aquarium are vitamins C and B<sub>12</sub>. A product high in vitamin C, ascorbic acid, will significantly lower redox when added, because vitamin C is a powerful anti-oxidant or reducing agent. Vitamin B<sub>12</sub> is very intensely red and even small quantities of it will color the product that contains it pink to red or brown, depending on other components present. If a product claims to contain B<sub>12</sub>, it should be some shade of red or brown, not blue or green. The only natural components of such a product that would impart a blue or green color are copper and nickel, and if present at a concentration high enough to impart such a color, these products would be toxic. A synthetic dye could also impart such a color. A crude vitamin source such as algae or cyanobacteria (*Spirulina*) would also impart a green color from the chlorophyll content. Such a source, however, would be inadequately low in critical vitamins, particularly B<sub>12</sub>, without further processing. B<sub>12</sub> should be the most important component of an aquatic vitamin supplement and when present at suitable concentration it must impart some kind of red coloring to the product. Liquid vitamin products are highly susceptible to oxidation and microbial contamination. It is important that they contain chemically stabilized components, and incorporate preservatives, or be sterile, or both. You may think you prefer a product that is “all natural” and without preservatives, but such a liquid vitamin product would quickly spoil unless sterile and refrigerated.

**HOW CAN I RECOGNIZE SELF-SERVING PSEUDO-SCIENTIFIC GOOBLEDY-GOOK WHEN I SEE IT?**

First, consider the source. What are the credentials or experience? Does the author have a financial interest or political agenda in persuading you to buy something you

may not need or following a specific course? This is not to say that everyone associated with or owning stock in a commercial aquatic enterprise is out to deceive you, but you should exercise a critical eye. Remember that hobbyist magazines are not what the scientific community refers to as “peer reviewed” journals. It is not unusual for a lot of nonsense to make it into print. Seeing an assertion in print does not make it true. These magazines serve a very useful function and I do not suggest that they should be replaced by peer reviewed journals or that you should not avail yourself of them, only that articles that appear in them reflect the perceptions and misperceptions, judgments and misjudgments, views and biases of the authors and do not necessarily reflect a consensus of experts or even that of the magazine. Bear in mind, too, that even the “experts” are not always as expert as they may seem.

Does the author rely on well reasoned, logical thought sequence to back up his assertions or does he rely on name dropping or supposed citations from authority figures? If citations to the literature are made, are they citations to the scientific literature or to other unsubstantiated articles? Are the citations relevant? Beware of materials taken out of context: e.g., the chemistry of nitrogen compounds in air under extreme conditions or on radiation exposure does not apply to aqueous conditions.

Does the author just guess that something is effective or does he actually do the arithmetic? For example, has anyone recommending the use of calcium hydroxide (limewater) to raise calcium ever computed the actual calcium content of limewater and what impact a given volume will have on a given aquarium volume? I have and it is remarkably insignificant. Assuming a maximum content of 270 mg/L calcium (under the best conditions!), adding half a gallon of limewater to 10 gallons of seawater will raise the calcium by less than 14 mg/L, not counting what it would do to the pH.

Are assertions based on anecdotal evidence involving few people who have not actually conducted controlled experiments but instead have changed multiple variables at

the same time such that it is impossible to discern what is actually occurring? Does the author recommend the use of certain materials without identifying them or recommending some generic sources, or does he recommend some expensive aquatic version? For example, if limewater is recommended, are you told it is generally available cheaply as “pickling lime” at any grocery store; or calcium chloride, are you told it is available very cheaply as “road salt” pellets at your local hardware store? Or are you told these sources are not sufficiently pure? The facts are that these materials are no less pure than sources bottled specifically for the hobbyist.

Does the author make inconsistent recommendations? For example, that you use a vitamin C additive on a regular basis and that you use potassium permanganate to raise your redox whenever it falls below a recommended value. This is inconsistent, because vitamin C, being a very powerful anti-oxidant, if it is active, will sharply lower the redox, and adding permanganate, a powerful oxidizer, will destroy the vitamin C. Another example: on the one hand condemns the use of chelating agents as rendering trace elements useless through sequestration, but on the other endorses the use of chelated iron for maximum availability.

Does the author make universal recommendations or condemnations without making distinctions? For example, that all organics in the aquarium are bad, without consideration to the benefits of some amino acids, chelating agents, vitamins C, B<sub>12</sub>, other vitamins, all of which are organic.

Does the author use faulty reasoning? For example, the detrimental waste removed by protein skimming is organic, vitamin supplement products are organic, therefore, vitamin supplements should be avoided.

Does the author make claims and assumptions that are no more than wishful thinking? For example, that zeolites or other ion exchangers can remove nitrate from seawater. Or, that a particular carbon is phosphate-free, when there is no such thing. Or, that vitamins are com-

patible with oxidizers like ozone or permanganate. Or, any other desirable selling point that requires the suspension of fundamental physical or chemical principles.

It has become increasingly difficult to discern fact from fiction in the rising tide of pseudo-technical jargon, inflated claims, unverified assertions, and inconsequential observations. It is important for the hobbyist to be as informed as he can.