2.   RULES OF THE THERMODYNAMICS 'GAME'

As with everything in Science and Engineering, there are rules of engagement to which one must adhere in order that *any* technical analysis remains accurate and true. Thermodynamics is no different. However, in Thermodynamics there exists certain 'rules' that at the start might appear odd (for a lack of a more descriptive term), but which in fact work for the benefit of the Engineer. To begin with, Thermodynamics is <u>very</u> precise. It is never capricious or arbitrary; what works now will work *exactly* the same, if all conditions remain as they were in the beginning, a week from now, a month, a year, a decade, even a millennium from now. There is absolute certainty in Thermodynamics, as is there a definite cause-and-effect relationship. When one grasps and accepts these truisms, one may be filled with a sense of relief that once correctly calculated, constructed and operated, a Thermodynamic system, irrespective of what it is, where it is or who is behind the controls will <u>always</u> perform *exactly* as initially intended.

The basis for Thermodynamics lies in its definition of terms of the properties of state of matter and how these definitions/properties interrelate. For *all* matter, Thermodynamics prescribes that any system that employs any specie (or species) of matter, the Thermodynamic properties of that matter as a solid, liquid or gas (or a combination of any two or even all three states of that matter) are 'set' and known. These properties of state are (in no particular order) in the English System of Units:

- Temperature T, in degrees Fahrenheit (or Rankine),
- Pressure P, in Pounds Force per unit Area absolute,
- Enthalpy H, in British Thermal Units [3] (BTU) per Pound Mass,
- Entropy S, in BTU per Pound Mass-degrees Rankine, and
- Specific Volume η, in Cubic Feet per Pound Mass.

So, in essence, there exists five <u>total</u> *independent* variables that define the Thermodynamic properties for any species of matter regardless of the state of that matter, be it a solid, liquid or gas; that's all, just five. These properties can be tabulated or graphed, and when done in a simple graphical X-Y form, for <u>any</u> two known properties, the remaining three can be easily found just by viewing the graph. The same can be said of a spreadsheet of these five properties, which are typically

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[3] As an aid to the reader in understanding how much heat a BTU represents, burning a common match, either a paper or wood stemmed match, generates approximately nine BTU's of total exothermic heat

prepared as a table with Pressure or Temperature being the major variable. Look under a specific known Temperature for example, and the value of each of the remaining four properties are listed.

In this paper and for our example, a Boiling Water Reactor (BWR) Nuclear Plant power cycle will be presented as a *modified* Rankine [4] Cycle. The Rankine Cycle is appropriate and correct for the example, and in fact it is the <u>exact</u> process cycle that was employed at the <u>very</u> earliest stages of plant engineering and design to model what was eventually built. The 'modifications' to the cycle will become readily apparent, and will be discussed, in the latter portion of this document.

For our purposes in the application that will be presented, the best and easiest format to view the Thermodynamic properties of the matter in which we will be interested, water, is in graph form. Further, the best method to visualize our system is in a graph entitled a Mollier Temperature – Entropy (T –S-) Diagram [5]. It is presented as Figure 1.

In viewing Figure 1, it is understandable that for the 'uninitiated' or those Engineers who are a bit 'rusty' in Thermodynamics, this graph may appear a bit daunting, merely due to the large number of property curves that it contains. In order to make things a bit clearer, and to provide further explanation regarding what all these lines represent, a more simplistic T – S Diagram is presented as Figure 2. In this Figure, just one property curve appears, and if the reader looks closely at Figure 1, this is the bell-shaped curve beginning at the lower LH corner, rising up and then falling back again to the lower RH corner of the Diagram. This bell-shaped curve is called the "Vapor Dome", somewhat misnamed, but this will also be explained shortly.

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[4] **S**o named after William Macquorn Rankine, who published this cycle (and others) in his paper entitled "*Manual of Steam Engines and Other Prime Movers*" in 1859. In his honor, the Absolute Fahrenheit Temperature Scale is also named after him.
[5] So named after Robert Mollier (1863 – 1935), a German Professor of Mechanical Engineering, who spent his entire career researching Thermodynamics, specifically the Thermodynamic properties of water
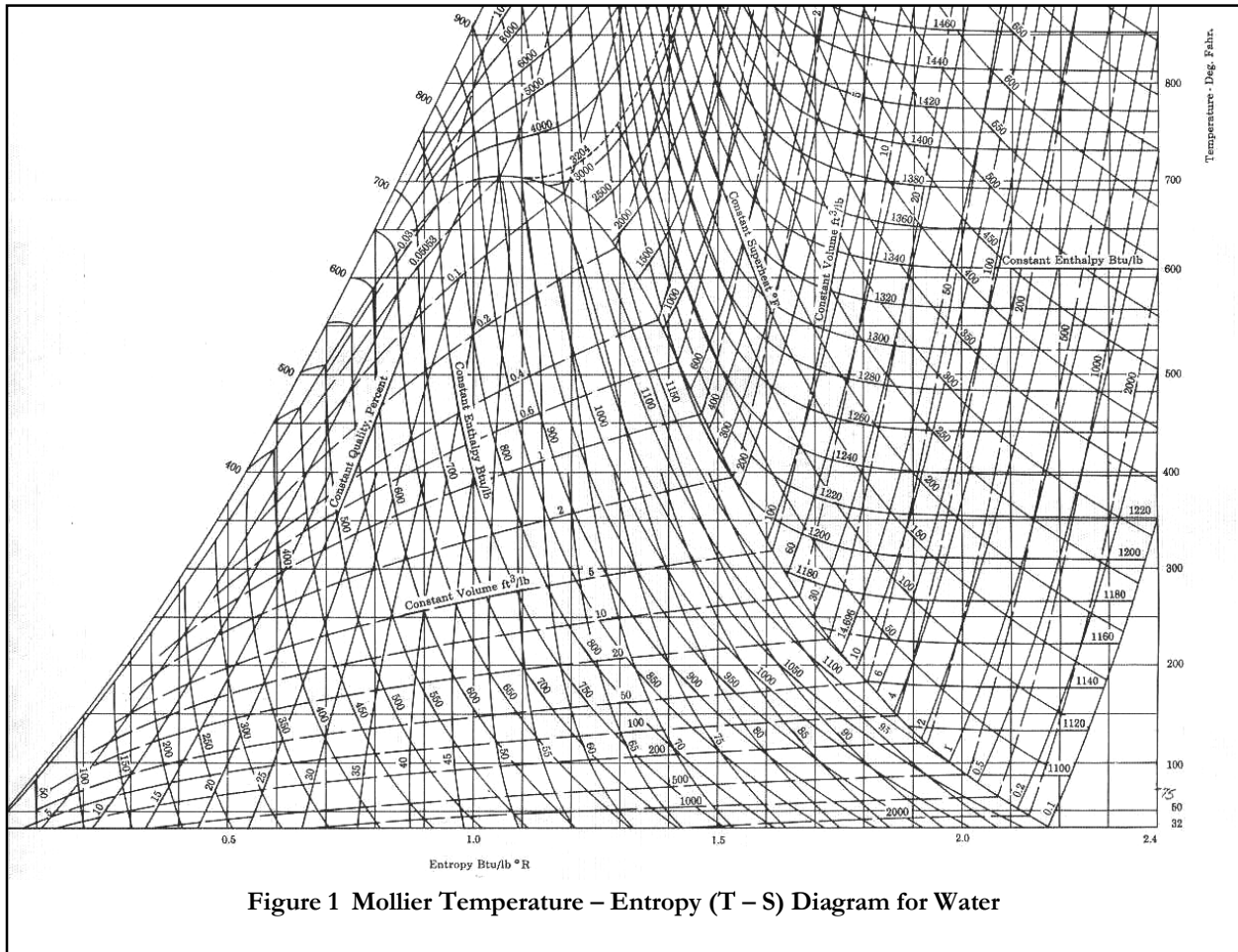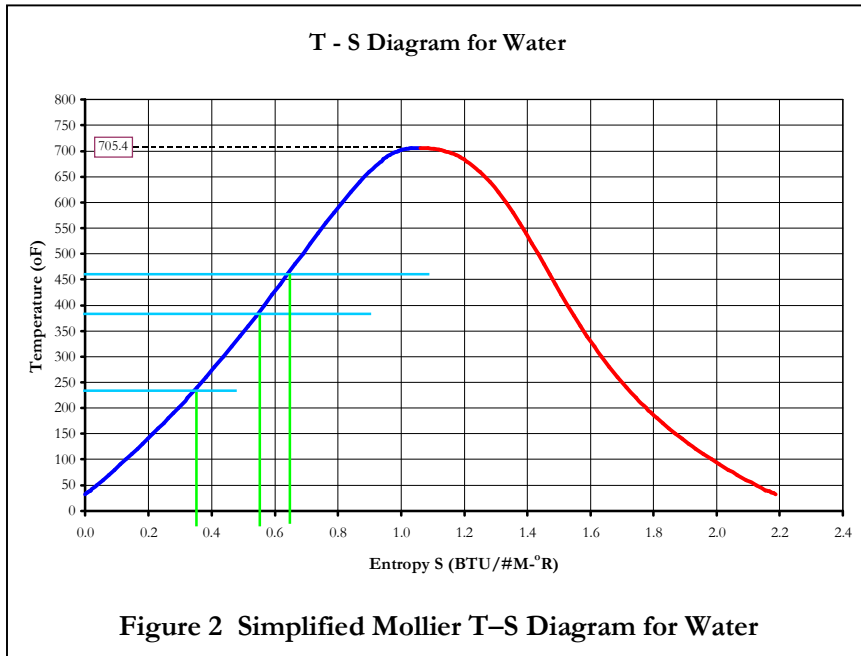
Figure 1 Mollier Temperature – Entropy (T – S) Diagram for Water

Referring to Figure 2, one can clearly see the Vapor Dome, but it is divided into a left hand blue curve and a right hand red curve. What does this mean? It indicates that <u>by definition</u> the state of matter <u>on</u> the blue line is what is called "Saturated (liquid) Water". <u>On</u> that line <u>and to its left</u>, water is <u>always</u> and only a liquid. The state of matter <u>on</u> the red line, again <u>by definition</u>, is called "Saturated Gas". <u>On</u> this line <u>and to its right</u>, water is <u>always</u> and only a gas. Three horizontal lines of constant Temperature are shown (in light blue). At the precise point where each constant light blue Temperature line intersects the darker blue Saturation curve, a corresponding orthogonal light green line is shown. Each green line indicates the Entropy of Saturated Liquid at *that specific* Temperature. Collectively, the green lines also tell us that as the Temperature of Saturated Liquid *increases*, so does its Entropy. Conversely (though not explicitly drawn in the Figure), as the Temperature of Saturated Gas *decreases*, so does its Entropy.

T - S Diagram for Water

Temperature (oF)

Entropy S (BTU/#M-°R)

Figure 2 Simplified Mollier T–S Diagram for Water

This begs the question, what is Entropy, or for that matter the definition of the four other properties of state? Entropy is commonly described in simplistic terms as "…that amount of energy that is lost..." Though somewhat true, the <u>actual</u> meaning of Entropy is 'that amount of energy which cannot be made available for our use no matter what method(s) or physical technique(s) is/are used when the process is *irreversible* '. In essence Entropy represents atomic (or in water's case, molecular) vibrational energy that we cannot extract for practical use no matter how hard we try or by what means we attempt [6].

The definitions of Temperature and Pressure are fundamental, and their definitions will be left to the reader to uncover (if necessary).

Enthalpy [7] is the total intrinsic amount of energy within a substance (in our case gaseous or liquid water) in the form of molecular vibration and expansion energy that *can* be extracted for our use.

Specific Volume is the reciprocal of Mass Density, and it represents the volume of a unit mass of the substance being evaluated, in our case liquid and gaseous water.

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[6] The Second Law of Thermodynamics defines Entropy. If a process is *reversible* (100% efficient), then the change in Entropy from the start to the end of that process is <u>zero</u>, and when *irreversible* the amount of Heat transferred is equal to $\int TdS$. In practice, <u>no</u> process is strictly *reversible*, so Entropy must always *increase*.

[7] Technically, H is equal to U + PV, where U is 'Internal Energy' and PV is the product of Pressure and Volume

Returning to Figure 2, the reader should notice that there is an intersection of the blue and red curves at the point of greatest temperature on the Vapor Dome, precisely at 705.47° F. So, if the blue curve defines *liquid* water, and the red curve defines *gaseous* water, what state of water exists at their intersection? Good question. The answer is that the point of intersection of the Saturated Liquid curve and Saturated Gas curve on the Vapor Dome is called the "Critical Point", and it is at this point that the state of matter, water, is neither, and both, a gas and a liquid. In essence, it is at this point that water exhibits the properties of both a gas and a liquid.

There is one final point to be made regarding Figure 2, and that is the space between the blue and red curves within the Vapor Dome. What exists there? Once again, a good question. For the answer, the reader is asked to select any one of the three horizontal constant Temperature lines. Now, beginning at the far left side where the chosen constant Temperature line intersects the darker blue Saturation curve, this as we now know is the point where 100% of the water exists as a Saturated Liquid. At this point, <u>no</u> water exists in a gaseous state. Now, if the reader moves to the right just a fraction of an inch along the constant Temperature line, a small percentage of water will exist as a gas because a corresponding small amount of energy, as heat, will have been applied. The remaining large percentage of mass still exists as a Saturated Liquid. And, as one moves farther and farther to the right along this same constant Temperature line, more and more water will exist as a gas (because increasing amounts of energy will have been incrementally applied), while less and less will exist as a liquid. At the farthest edge of any constant Temperature line, where it intersects the red Saturated Gas curve, <u>all</u> of the water will exist as a gas <u>by definition</u>. <u>No</u> liquid water exists at this point, nor at any point along this Temperature line farther to the right of the Vapor Dome. So, in summary, any horizontal constant Temperature line through the Vapor Dome represents the process where increasing amounts of heat are applied to a unit mass of liquid water *at that Temperature*, resulting in more and more of this liquid being converted into a gas, which we call *steam*. The process continues until 100% of the water is converted into steam, this point is where the constant Temperature line intersects the Saturated Gas curve. Steam, <u>by definition</u> is gaseous water; it is colorless, odorless and invisible to the eye. Water *vapor* by contrast is <u>not</u> steam, but microscopic droplets of liquid water that we <u>can</u> physically see and feel. In this regard, the distinction between water vapor and water as steam makes the aforementioned term 'Vapor Dome' somewhat of a misnomer, because the outline and internal volume of the Vapor Dome represents the entirety of the Thermodynamic properties of liquid water and gaseous water as <u>steam</u> (not vapor) all of which coexist at an array of various Temperatures. Again, vaporous water is actually liquid water in microscopic droplets; steam is contiguous water existing <u>entirely</u> as a gas.

As an aside, two of this author's technical 'annoyances' are that of the media displaying a Nuclear Power Plant's Cooling Tower during which the reporter orally states or implies that 1) the Plant's Nuclear Reactor actually resides within the Tower – it most certainly does <u>not</u>, and 2) that the plume of white vapor emanating from the Tower's top is 'steam', which it certainly is <u>not</u>. Every modern era Nuclear Reactor in the United States actually resides within its own incredibly robust Containment Structure, this Structure in turn resides within the Reactor Building, that is located adjacent to the Turbine Building. The visible plume spewing from the Cooling Tower is merely clean liquid water as a vapor. Farther above this visible vapor plume is where the water vapor changes state to completely gaseous water - steam. But, by definition, one can readily see the vapor, and <u>not</u> the steam; both *are* there, visible or not, in massive quantities. The next time you too witness any reporter stating either or both of the aforementioned mistruths, feel free to add them to your own list of technical pet peeves!

The remaining Thermodynamic properties not illustrated in Figure 2 or yet discussed, Pressure, Enthalpy and Specific Volume are illustrated in Figure 3. Lines of constant Pressure (P) are shown in light brown, while Enthalpy (H) is shown in violet, and Specific Volume (η) in plum.

Beginning with Pressure, the reader should note that where water is *in the liquid state* [8], lines of constant Pressure, *isobars,* are <u>very</u> close together, and increase from <u>right to left</u>. In fact, comparing Figure 3 to Figure 1, one readily sees in Figure 1 that there is only one line of constant Pressure to the left of the Saturated Water
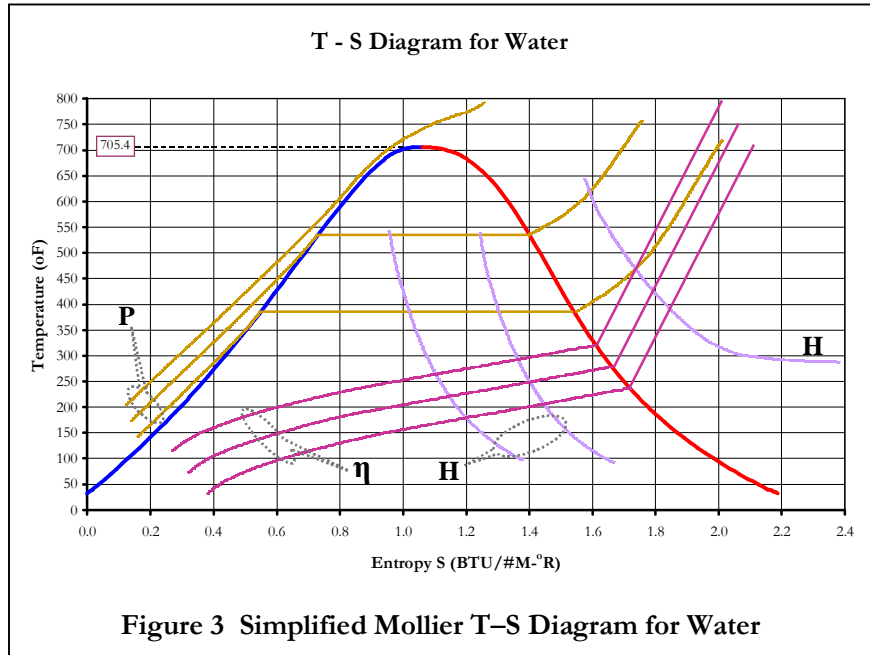

Figure 3 Simplified Mollier T–S Diagram for Water

curve, while the first numerically identified constant Pressure curve (which begins just to the left of

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[8] This 'zone' is comprised of the entirety of area to the left of the Saturated Liquid line which is called '*Subcooled Water'* area, up to and including the Saturated Liquid line

the Critical Point) is identified as 4,000 psia. As identified in Figure 1, the actual value of the lone constant Pressure line to the left of the Saturated Water curve is actually 15,000 psia!

The fact of constant Pressure values being so large and lines of equal Pressure being so close together when water is a liquid should shock no one – it is common knowledge that liquids are, for practical purposes, incompressible, and water is not exempt from this caveat. Being the case, it takes very little energy to raise the Pressure of liquid water. Conversely, steam, can possess an *enormous* amount of energy depending upon its Temperature and Pressure. Due to incompressibility, as Mollier's Diagram indicates, lines of constant Pressure of *liquid water* are very close together to the left of the Saturated Water curve and above the Dome where water exists entirely as a liquid. Because of the compressibility of steam, a *gas*, lines of constant Pressure in areas where water is strictly a gas, on the Saturated Gas curve and to its right, isobars are farther apart. Also of note are two additional facts concerning Pressure. First, within the Vapor Dome, lines of constant Pressure run parallel to lines of constant Temperature. Secondly, lines of constant Pressure *increments/decrements* are farther apart in chart areas that represent steam, this fact should also by now be self-evident to the reader because steam, as already stated, *is* compressible while liquid water is not. Therefore, because steam can be compressed, to do so requires a comparatively far greater amount of energy. Conversely, steam is able to supply far greater amounts of useful energy to the user than liquid water, and in this truism remains the reason for water being the motive fluid in most large power generating facilities.

Curves of constant Specific Volume, being somewhat 'linked' in function to Pressure, run in numeric quantity reverse to lines of constant Pressure, and only are relevant in areas where steam exists (because liquids are virtually incompressible). As Pressure *increases*, lines of Specific Volume *decrease*, and this makes complete sense due to the fact that steam *is* compressible and raising pressure reduces steam's volume. Conversely, Specific Volume *increases* as Pressure *decreases*.

Enthalpy varies greatly across Mollier's Diagram, and this fact should by now be self-evident to the reader, since Enthalpy represents both the total quantity of energy that is inputted into matter as well as the total amount of energy *that is available* to the user to produce useful work. Similar to Entropy, throughout the entirety of Mollier's Diagram Enthalpy *increases* from left to right and from lower to higher Temperatures in *isotherm* curves nested at approximately 45° to the horizontal.

T - S Diagram for Water

Figure 4 Simplified Mollier T–S Diagram for Water
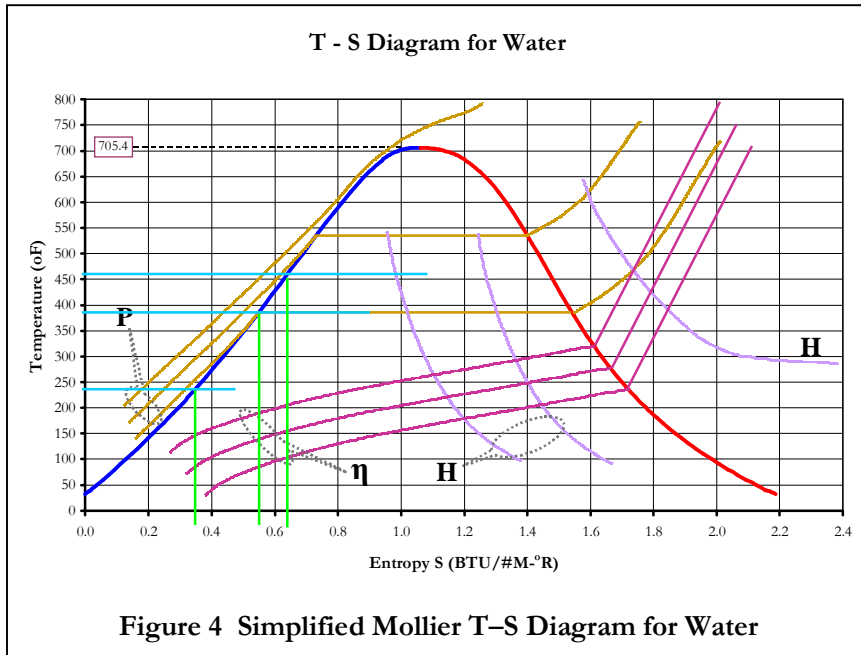
Putting every property variable discussed so far on one additional Mollier's Thermodynamic T – S Diagram for water, one sees in Figure 4 the resultant replica of all of the relevant Thermodynamic properties identified in Figure 1, but in a far more simplistic diagram. It is strongly suggested that the reader take a moment or two and compare Figures 1 and 4, so that the positioning and order of magnitude of all variable curves by type are comfortably understood. As an adjunct to Figure 1, as this paper progresses Figure 4 may be used by the reader to help simplify the understanding of the process diagram that will be discussed shortly.