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An Introduction to Thermo-Chemical Equilibrium Principles for Oxygen-Compatible Hardware Designs

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ABSTRACT: Thermodynamic parameters, specifically burn ratios, have been used to understand the coarse combustion behavior of metals for more than three decades. The introduction of thermo-chemical equilibrium theory can lend a much improved perspective on this analysis of combustion, and modern commercial and consensus adjunct software can help make these analyses practical for practitioners of the art at all levels of experience.

KEY WORDS: chemical thermodynamic equilibrium, oxygen, safety, fire explosion, transient, . incremental partitioned, counter current, combustion.

The safe design of oxygen systems to minimize the occurrences and consequences of fires and explosions is based to a great extent on an extensive empirical foundation. A series of experimental tests provide actual measurements of assorted thresholds at which ignition and/or propagation or explosion may occur, and systems are designed to avoid crossing those threshold conditions. Theoretical considerations do play an important role, but perhaps more often to extrapolate these measured data rather than to substitute for actual measurements. In most cases, theoretical calculations have been inadequate as substitutes for experimental data.

Among the more theoretical and respected of currently employed parameters are "burn ratios" which suggest when metals might burn in a gaseous (and therefore high speed and explosive) combustion mode, when they might burn in a slower and less hazardous liquid combustion mode, when they might burn in the slowest solid combustion mode, and most significantly when they may not be capable of combustion at all. However, these burn ratios are not without serious limitations, limitations that may be mitigated significantly with the use of thermo-chemical equilibrium principles. Earlier papers [*1-4*][2] explored a series of issues associated with this body of study.

This present effort seeks to extract material from those earlier papers and attempts to assemble it in an introductory format, in an effort to persuade the members of ASTM Committee G4 (of diverse technical backgrounds) that these analyses are not only of great value, but that they can be formatted and simplified to a degree that they can be practical to the full range of technically diverse backgrounds within the Committee. Consequently, they can help to fulfill its primary objectives to: 1. save lives, 2. save hardware, and 3. save system mis-

[1] No addresses. This paper was prepared for self-publication and later archiving .

[2] Italic numbers in brackets refer to the reference list at the end of the paper.

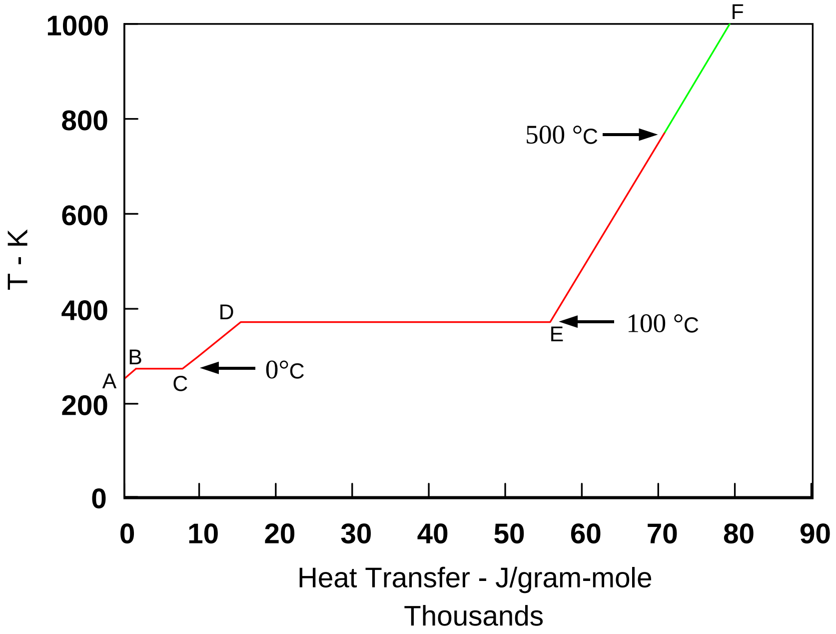

Fig. 1—*Simplistic thermo-profile for water.*

sions. ASTM G4 can better serve its own mission if it establishes a thermo-chemical equilibrium function within its ranks to simplify, document and deploy this theory and to adopt computer utilities to maximize its particular benefits and render them most practical.

Beginning Thermodynamics 101

Numerous beginner's textbooks in the sciences simplify basic thermodynamics. We learn that for many materials, such as common water, the basic information as shown in Figure 1 can be extremely useful.

We learn that to a significant degree, at low temperatures, the material is a solid (water is ice below 273 K, 0°C, 32°F), and to a good approximation if we slowly add heat energy to the solid, its temperature will rise approximately linearly. This is called a sensible heat for its amount can be determined from the uniform temperature of the solid. This is shown as the inclined line from points A to B on Fig. 1.

When the solid has attained it melting point or fusion temperature (273 K, 0°C, 32°F for water) then further heating is no longer sensible on the basis of temperature, for as more heat is added, it then converts the solid into a liquid (it melts) linearly at constant temperature, and this is called the latent heat of fusion/melting. This is depicted as the horizontal line from points B to C on Fig. 1.

When the solid is fully melted, we treat is as a liquid that can be sensibly heated linearly along the line from points C to D on Fig. 1, until it achieves the boiling point (373 K, 100°C, 212°F for water).

When the liquid is at its boiling point, any further heat addition is again no longer sensible on the basis of temperature and any addition of heat goes to linearly convert the liquid to gas, and this is called the latent heat of vaporization. This conversion is shown as the horizontal line segment from points D to E on Fig. 1.

At point E all of the liquid has been converted to gas (we call it steam) and any further heat addition once again is sensible. If pressure is constant any further addition of heat warms the gas and expands it and we approximate it as an ideal gas that warms linearly with added heat and this is valid up to at least 500°C, (shown as a dotted line from points E to F, and beyond, on Fig. 1).

At this point the initial basics we all learned in early science courses have been recapitulated. We have seen how this curve can be represented, can be drawn, knowing just these seven parameters (heat capacity of solid, liquid, and gas, latent heats of fusion and vaporization and melting- and boiling-point temperatures). And this powerful depiction is used widely. It allows very good interpretations of the operation of many other processes including heat engines (the Rankine-cycle steam engine for example). *But Fig. 1 is* ***not*** *exact.*

Flaws in Beginner Thermodynamics

Very significantly, if we apply thermo-chemical equilibrium principles, the curve of Fig. 1 would change only slightly. That is why water was chosen for this example, but very significantly, at high temperatures, water changes in some other ways that *are* important. Fortunately, a number of valuable computer software programs can make significant thermo-chemical equilibrium adjustments to Fig. 1. These include NASA's CEA program, and Outokumpu's HSC software, but there are others [*2*].

In general, the only changes that occur to the data on Fig. 1 occur at the nice sharp corners at points B, C, D and E of the melting and boiling point plateaus which would become somewhat rounded. This is because the melting and boiling effects start to kick in a little early at all four corners. It is less pronounced at the melting point corners than at the boiling point corners. But in fact as you add heat when you approach the melting point or boiling point plateaus, some of the heat will vary locally (on the molecular level) to provide some melting or vapor rather than to provide warming. As molecules knock about some will experience collisions that increase their local molecular "temperature" above that for the entire mass and some will suffer decreases. Those that experience increases will melt or evaporate early leaving those behind at a slightly lower temperature. An "equilibrium" (a balance) is set up in which some water molecules will gain energy sufficient to liquefy or leave the surface while at the same time some liquid or gaseous water molecules will solidify or condense back into the solid or liquid. The balance between these two opposite effects (their "equilibrium") affects the shape of the curve. The effects can be larger, and more complicated for other materials.

The most important changes, however, would occur at much higher temperatures. Fig. 2 estimates changes that would occur when this curve is developed with CEA and/or HSC software[3]. The scales are much larger to illustrate some important adjustments.

Notice on Fig. 2 how at about 2000 K, the software (the dotted black curve) predicts a much greater heat is demanded to produce an increase in temperature than is the case for the linear extrapolation (the green line). The reason for this is that as the temperature increases, the individual water (H_2O) molecules become less stable (that is, it becomes more

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[3] HSC Software for Windows is a product of Outokumpu Research Oy, Finland. A 1990s Version 3.0 was used and its current price is about $2000. CEA (Chemical Equilibrium for Applications) is free NASA Fortran IV (or Linux) software available as a download from the NASA Glen website. The two are compared in [*2*].

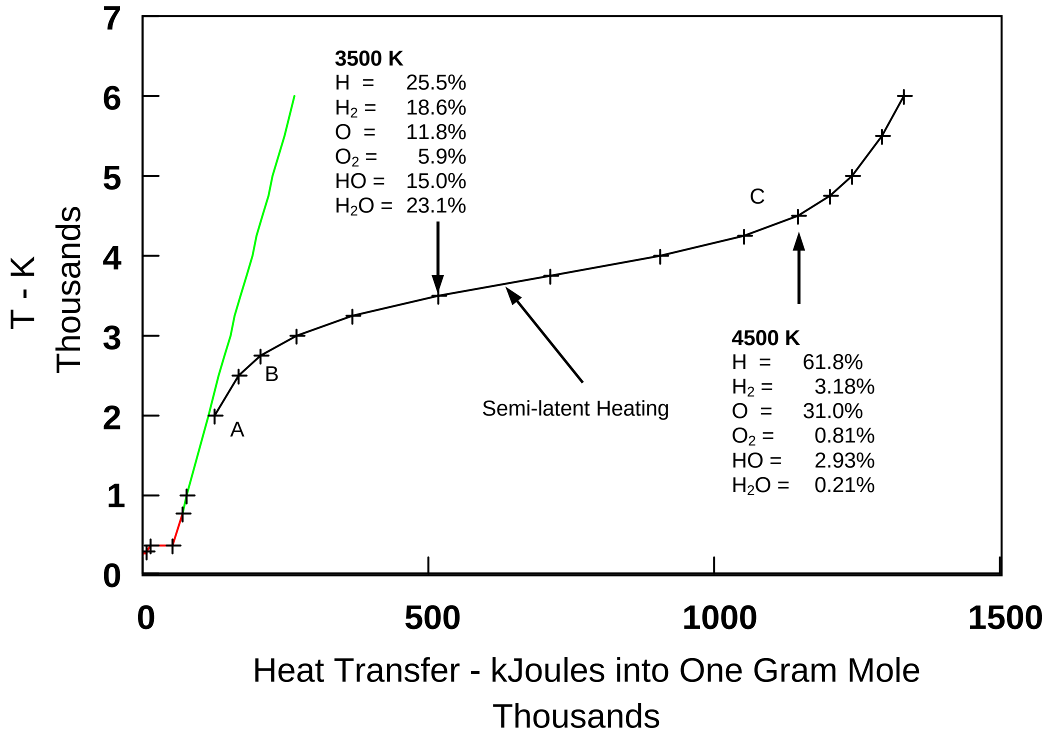

Fig. 2—*Thermo-profile for water from Outokumpu HSC and NASA CEA software.*

easy to "knock" each other apart). The atoms are vibrating and bouncing around and colliding more intensely and sometimes some will experience collisions that increase their energy or actually split them apart, breaking them into H and OH, or even H, H, and O, and other, possibilities (not all are shown). Similarly some that have broken apart earlier are finding each other and coming back together. These particular molecules absorb heat when they come apart (when they are chemically reduced) and they will return that heat when they come back together (when they re-combust). Indeed as the temperature increases, between points B and C, as the fraction of the molecules that are broken apart increases, the slope of the curve bends down towards level where a semi-latent ("less sensible effect") limits the rate of temperature rise but does not achieve full constant-temperature behavior. At the highest temperatures, beyond point C, the heat of decomposition (the reverse of heat of combustion) has been almost supplied, the curve bends back upward again and reflects sensible heating of the fully decomposed atoms. Still other effects can further absorb heat and are neglected here, for example electrons can separate from individual atom to produce a very ionic "soup" of nuclei, and free electrons. This too sets up another equilibrium between atoms that are losing electrons and those that are regaining them. Calculated estimates of the equilibrium composition (ignoring ionization) are shown for the approximate temperatures 3500 K and 4500 K, and at the highest temperature, the components of the gases are nearly all monatomic hydrogen and oxygen.

The mathematics to generate these more detailed, if still not exact, curves is all quite daunting. It is a potent incentive to stick with the simplistic approach. It involves solving simultaneously many, many equations, each estimating the heating of a single constituent, to

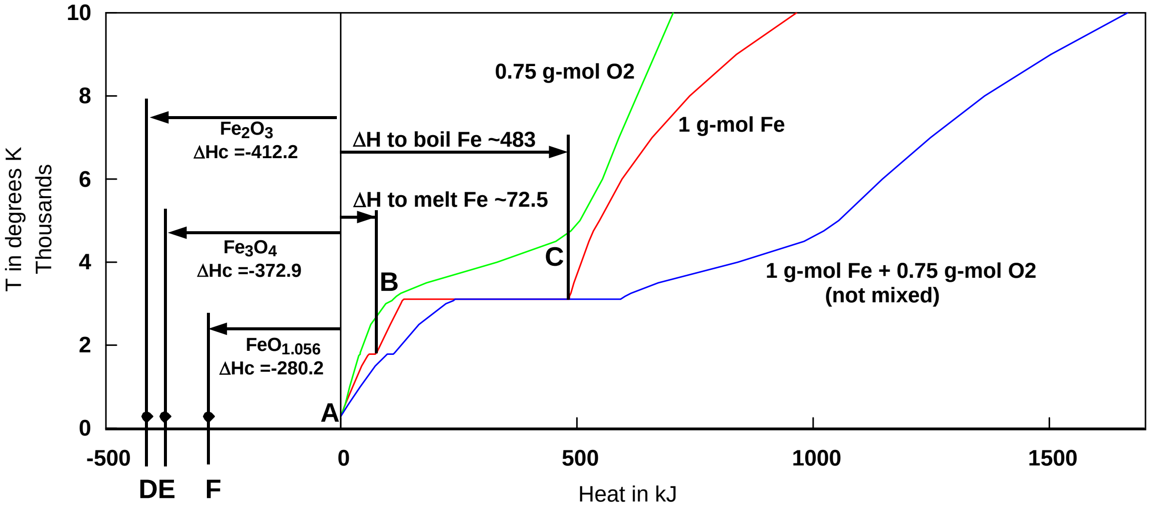

Fig. 3—*Thermo-profiles for 1 g-mol iron and iron plus 0.75 g-mol diatomic oxygen.*

find a minimum in the total free energy (as opposed to merely the mechanical or thermal energy) of the system. But since there is modern software to do that daunting math, curves like Figure 2 can be developed and can be practical, and once in hand can be exploited with a much less specialized background demanded from the user. And we shall see that is good news for every oxygen safety practitioner.

Enter Oxygen Safety Needs

For many of the materials of interest to oxygen and oxidant systems, the curves that relate thermo-chemical behavior are much less “ideal”, less well-behaved, than that for water as in Fig. 1 or even Fig. 2. However, we will consider an example that is not too different, namely the most common material used in oxygen systems: to wit, iron. Iron has been a bone of contention in many ways for many years and is thermo-chemically fairly well behaved. Some of the controversy is a matter of perception but some is clear controversy that thermo-chemical equilibrium principles can help resolve.

Fig 3 exhibits a red solid curve consistent with that of Fig. 2 based upon Outokumpu HSC and NASA CEA software for iron. It has many similar characteristics, but the temperatures involved are higher. Indeed it behaves even better than the curve for water, exhibiting melting and boiling points and yet no similar semi-latency region, because iron can not decompose. It can ionize but those smaller effects are not included here.

Figure 3 also exhibits a green solid curve for oxygen covering the same temperature range as that for the iron, and the amount of oxygen is equivalent to that which would be needed to form the most stable oxide of iron, hematite, Fe_2O_3. At these temperatures oxygen shown as a green line, starts out as a gas at point A and as its temperature is raised, it experiences a semi-latency region between points B and C where the diatomic oxygen molecule breaks apart into monatomic oxygen atoms. This heat of decomposition acts like a heat of combustion in reverse that is being added back into it (as for the water of Fig 2) but this requires one to think monatomic oxygen can “burn” with itself. Indeed, Figure 3 indicates monatomic oxygen is quite reactive with itself and yields a heat of formation of about 400 kJ/0.75 gram-mol, about the same as one would recover burning a gram-mole of iron in oxygen at room temperature.

Finally, Figure 3 exhibits a dotted blue curve which is the sum of the combined heats required to bring both the iron of Fig 3 with the oxygen of Fig. 3 to any given temperature *separately,* so that reaction between them is not a consideration. In this case the combined curve exhibits distortions of all the characteristic features. If this iron were to be fully combusted (as a batch) with this oxygen to form hematite (Fe_2O_3, with no oxygen left over), or magnetite (Fe_3O_4, with about 11.11 percent of the starting diatomic oxygen leftover), or wustite ($FeO_{1.056}$ or $1.056Fe_{0.947}O$) with about 29.6% percent of the starting diatomic oxygen left over) and if the system were then returned to the starting temperature, then it would release heats of formation (which are also defined as the heats of combustion at room temperature), of about 412.2, 372.9, and 280.2 kJ. Heats of combustion are considered negative by convention and so these are plotted, respectively, at points D, E, and F on Figure 3. Indeed, in the real world many different final products that are mixtures of all three oxides and which may contain un-reacted iron also are possibilities. So if this iron were to burn with this oxygen what would the expected combustion be like? How would the iron and oxygen get from point A to points D, E, F, or anywhere else on the plot?

Combustion From Davy to Munroe

Perhaps one of the earliest and most important efforts to understand and predict the nature of combustion traces to the work of Sir Humphry Davy [*5*], in 1817, when he wrote that for a material to burn:

> “The ratio of the combustibility of the different gaseous matters are likewise to a certain extent as the masses of heated matter required to inflame them.”
>
> " ...flame...is extinguished.. only when the heat it produces is insufficient to keep up with the combustion, which appears to be when it is incapable of communicating visible ignition... ...as this is the temperature required for the inflammation ....."

This has often been “translated” from the original English to mean that a material can only burn if its heat of combustion is sufficient to raise the material to its ignition temperature. This is not to predict it *will* burn (sufficient heat allows but does not imply combustion), but rather to exclude the possibility of burning if the condition is not met (insufficient heat precludes combustion).

This basic idea underpins the work of Munroe et al. [*6*]. Whereas Davy was studying gas combustion, Munroe et al. were studying metal combustion. They formulated two parameters similarly: the burn ratio at the melting point, BR_{mp}, and the burn ratio at the boiling point, BR_{bp}., as follows.

$$BR_{mp} = \Delta H_{combustion} / (\Delta H_{rt\text{-}mp} + \Delta H_{fusion})$$

$$BR_{bp} = \Delta H_{combustion} / (\Delta H_{rt\text{-}mp} + \Delta H_{fusion} + \Delta H_{mp\text{-}bp} + \Delta H_{vap})$$

Where

$\Delta H_{combustion}$ = heat of combustion
ΔH_{rt-mp} = heat to warm metal from room temperature to melting point
ΔH_{fusion} = latent heat of fusion
ΔH_{mp-bp} = heat to warm metal from melting point to boiling point
ΔH_{vap} = latent heat of vaporization

And they proposed that for the metal to burn as a liquid it must have a $BR_{mp} \geq 1$, and for it to burn as a gas it must have $BR_{bp} \geq 1$. Perhaps most significant of all, if the metal has $BR_{mp} < 1$, it may be unlikely to "burn" at any appreciable rate (it might still oxidize as in rusting at slow or even appreciable rates). This predicts metals fall into three rough categories. Notice that for iron, Figure 3 contains all the data necessary to calculate these variables. For the three oxides: Fe_2O_3, Fe_3O_4 and $FeO_{1.056}$, the BR_{mp} is given by the equation: $\Delta H_c/(\Delta H$ to melt Fe) = 5.7, 5.1, and 3.9 respectively, and BR_{bp} is given by $\Delta H_c/(\Delta H$ to boil Fe) = 0.85, 0.77 and 0.58, respectively, and compare to burn ratios of 5.1 and 0.5, respectively reported by Munroe et al. [*6*], unfortunately Monroe does not cite the oxides or mix of oxides his calculations are based upon.

Indeed, many metals that have $BR_{mp} \ll 1$ (e.g. gold, silver) are predicted to be among the least flammable, some other metals with $BR_{mp} \geq 1$ (e.g. cobalt, nickel, iron,) are predicted to burn slowly as liquids and rank roughly in the order of their burn ratios, and still other metals with the highest BR_{mp} and $BR_{bp} \geq > 1$ (titanium, aluminum, tin, zinc) are predicted to exhibit extremely rapid combustion and present a hazard that must be carefully considered if they are used. And these results validate the use of these parameters to gain at least a coarse perspective on metals that have little experience in oxygen service.

These parameters in combination with other data have been very useful in gaining a perspective on metals, and some are tabulated in ASTM G 94-92 Tables X.1.6 and X.1.7. However they are coarse (blunt) tools and are not precise. And they are only published for a few metals at room temperature. They have still other limitations that are worth exploring here. Nonetheless, one trying to decide between platinum and zirconium for a new metal to use would be pleased to find that Platinum has a low melting-point BR , while they would be seriously discouraged to find that Zr has a high boiling-point BR.

Quest for Better Burn Ratios?

Traditional burn ratios are not perfect. Among questions that surfaced about burn ratios is whether they should be calculated for the heat to warm the metal to its ignition temperature, and must metals burn entirely as a single phase? Could they somehow partition their combustion into different mechanisms either simultaneously or sequentially in time? Could a metal burn partially as a solid and/or partially as a liquid and/or partially as a gas? If so should the burn ratios be calculated at the onset of ignition, melting, or boiling instead of the completion? Mathematically these prospects are not excluded. Indeed, a 1992 paper [*7*] argued that two-phase combustion of magnesium had been observed. Magnesium has a heat of combustion much greater than would be required to vaporize itself and indeed was seen to produce large quantities of magnesium oxide dust consistent with gas phase combustion and yet also produced a solid residue that might dictate solid phase or fused liquid-phase combustion, yet it has also been pointed out that the residue may be also be a result of "reverse phoresis" in which gas phase combustion products may condense back onto the source magnesium specimen.

And these prospects raise a question of some importance: Can burn ratios as currently formulated be improved? If mixed-phase combustion or partitioned combustion is possible, how might that occur? Earlier papers, solved the equations to predict that if such combustion is possible, what the maximum amounts that might burn as a liquid or gas would be [*8*] and examined more burn ratio possibilities than are reproduced here.

These nagging questions suggest that burn ratios might be improved and thermo-chemical equilibrium principles can go a long way toward making those improvements valid.

Examining the BR Theme

Thermo-chemical equilibrium data allow for a much better appreciation of what Davy and Munro were attempting to do and can perhaps lead to new and improved formulations of Munroe's "burn ratios".

First notice that none of the original burn ratios adjust for the scale or process of combustion. As a result, the original burn ratio formulations compare the heat of combustion of an *entire* specimen to the heat needed to melt or vaporize that same *entire* specimen. The whole specimen is treated as a batch. This leads to two serious conflicts:

1. The heat of combustion of any atom is *never* transferred into that same atom. It is transferred into the products of combustion of that atom. In other words, in order to release heat, oxygen must react with the metal and at that instant the metal ceases to exist and becomes an oxide with elevated temperature and thermodynamic properties differing from those of the metal. However, if the metal is not treated as a batch, then this heated oxide may transfer a portion of its heat of combustion to other as yet un-reacted metal atoms to melt or vaporize them, but can never transfer all of it. No portion of a metal atom's heat of combustion is ever transferred into that same metal atom, hence treating the burn ratio as the entire heat of combustion transferring into the entire native metal is flawed.

2. This key observation begs for a more precise consideration of three potential boundary combustion processes, one in which a batch combusts (as if simultaneously) to produce one form of oxide, something more easily accomplished among single or small numbers of atoms, the other two, transient combustion, in which an incremental sequence of atoms reacts (in potentially several differing ways) while being in heat transfer with the remaining other atoms of metal and/or oxidant in many assorted ways (something more likely to occur in among large numbers of atoms).

"Single" Atom (Bulk) Combustion.

Single-atom combustion is the most elemental form of batch combustion and can be examined with the theory of flammable-gas combustion. When a flammable gas is combusted, leading textbooks [*9-12*] teach that the heat of combustion is transferred (quite

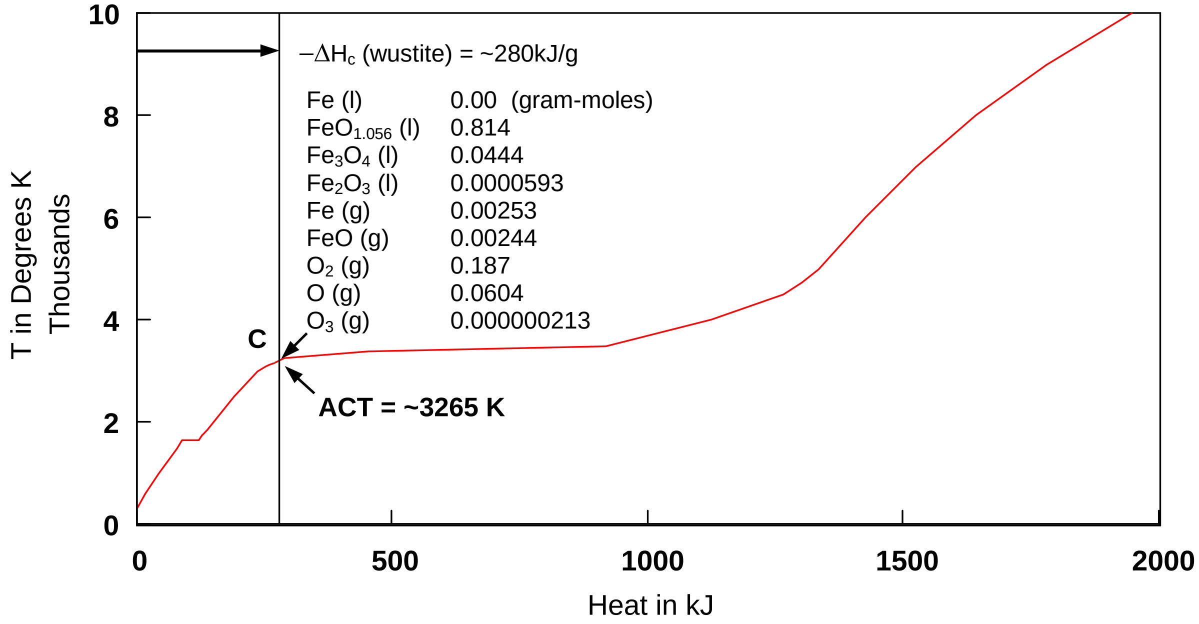

Fig. 4—*Thermo-profile for wustite,* $1.056Fe_{0.947}O/FeO_{1.056} + 0.222O_2$*, containing 1 gram-mole of iron.*

quickly) into the reaction products. The texts (and Kuo [*9*] is perhaps the most thorough in this regard) then perform a calculation based upon thermo-chemical equilibrium principles to estimate the resulting adiabatic combustion temperature (ACT). They take the heat of combustion that is evolved from the combustion products when they have been cooled to room temperature, analyze what the precise products are, then calculate what their temperature would be if those products were reheated with the same heat of combustion. It is not a trivial calculation to do.

In the case of a burning iron, the combustion product of a single iron atom with a single oxygen atom can be viewed as producing a single wustite, FeO, molecule[4]. Figure 4 exhibits the thermodynamic and thermo-chemical equilibrium profiles for bulk wustite[4]. Tabulated values for the heat of formation (the reverse of *in-situ* heat of combustion for a specific scenario) of iron to form wustite is about 280 kJ per gram-mole Fe, per 1.056 g-mole of $Fe_{0.947}O$, or per g-mole $FeO_{1.056}$. Hence the adiabatic combustion temperature can be estimated by adding this amount of heat to wustite containing one gram-mole of iron. Hence, Fig. 4 indicates that if iron is burned in oxygen and if its combustion products can be limited to just wustite (which is indeed possible), then the adiabatic combustion temperature (ACT) will be at point C and will be about 3265 K. Furthermore, Fig. 4 indicates the combustion products would principally be 81.4% of $FeO_{1.056}$ (liquid wustite) and 18.7% gaseous diatomic oxygen gas.

Figures 3 and 4 can be merged into Figure 5. In this case, the room temperature heat shown for wustite is shown at the point (-280.2 kcal/gram iron) where one would plot the final heat evolved, the heat of combustion. The two curves marry nicely. For if starting with the one gram-mole of iron at point A, the origin, adding heat to both the one gram mole of iron and

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[4] The thermo-chemical programs HSC and CEA both treat wustite as a gas as being FeO. As a condensed state, liquid or solid, CEA treats it as having one extra oxygen atom for every twenty Fe atoms, in other words as $Fe_{0.947}O$ or the equivalent $FeO_{1.056}$. HSC software can also treat it as $Fe_{0.947}O$, but also includes data for FeO as a solid (sourced to Barin [*13*,*14*] and Saxena [*15*]), but this writer is unsure if these are experimental data or theoretical. Condensed phase FeO was not included as a possible constituent herein..

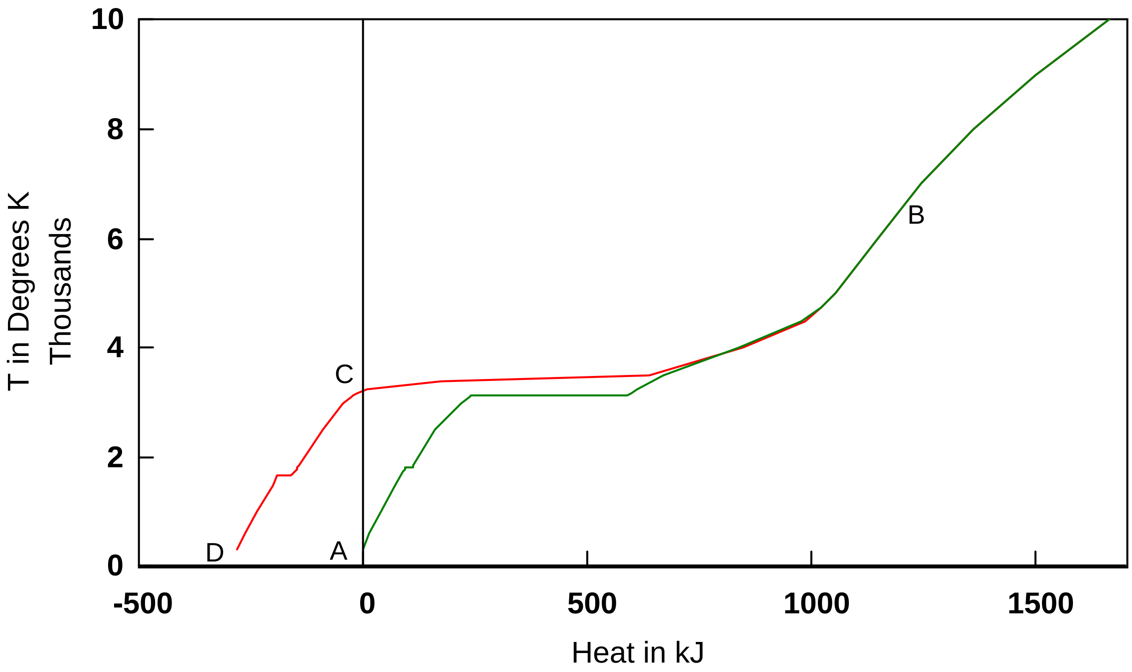

Fig. 5—*Thermo-profiles for about 1 gram-mole of iron with 1.5 mole monatomic oxygen and 1 gram mole of wustite (FeO$_{1.056}$) with leftover oxygen separated by the heat of combustion .*

separate oxygen more than sufficient to produce wustite (0.75 g-mole O_2), the materials will warm accordingly following the dotted green curve until they are at point B whereat they will be extremely hot. The electrons may be stripped away, the oxygen will be dissociated and this is essentially the same circumstance that would prevail if we heated wustite from its room temperature starting point at D. Hence, we can then mix the oxygen and iron, and they would not react and would be the same arrangement as is the wustite. If we then allowed them to cool (maintaining the constraint that no higher oxide of iron may form), then the materials would cool to point C and ultimately to point D. However, this is not necessarily the path that actual combustion of real specimens (which might not have a uniform temperature throughout) might take.

One very affirming feature of this composite thermal profile is the way the two curves merge at the highest heats and temperatures. It allows us to verify the adiabatic combustion temperature through two routes. The textbook approach, that involves reheating the cooled and analyzed product to go from point D to point C and the route that heats the separate iron and oxygen till they are fully dissociated, then mixes them at point B and cools and reacts them to the same point C. Hence when a single iron and oxygen atom “batch” react, they jump from point A to Point C.

Michael Lanyi taught the writer to plot these data this way, in the later 1990s, but the writer lacked data and skill to connect the two at high temperatures. Thermo-chemical equilibrium software calculations allow for that. This paper intends to argue that this Figure 5 is a source of excellent insight and yet, although the writer maintained an oxygen compatibility library of hundreds of documents for more than two decades, he can not recall ever seeing this very useful figure presented in any of them, for any material.

Transient/Incremental/Partitioned (TIP) Combustion

The treatment of iron combustion as the reaction of a single iron atom or a collection of simultaneous reactions as in the previous section can be viewed as the quintessential batch process. It has a “before” and an “after” and no “in-between”. At the first instant the separate iron and oxygen atom(s) are at point “A” on Fig 5 and an instant later they have all combined and jumped up to point C. The before and after conditions for any equally rapid batch collection are the same as for the single iron atom.

However, we know that every atom of iron in a normal specimen does not burn at precisely the same time. Combustion passes (propagates) through an iron specimen over a quite easily observable period. Hence although the heat of combustion of iron atoms never transfers into the same metal atoms themselves, they may serve to heat other nearby iron atoms and so transient burn ratios can be calculated that differ from the traditional bulk formulations of Munroe. Furthermore, the atoms of a bulk specimen may interact and then be divided to further react in two or more different places each with its own, and different, behavior. One extreme example will be of most interest here, though one can envision many different potential combustion schemes that might all be useful and yet might analyze quite differently.

In a typical pseudo-oxygen index test or promoted combustion test, a vertical rod of iron would be ignited at the bottom, and as the ignited region burns upward, it forms a molten droplet at the bottom. At some point the molten droplet becomes too heavy to remain attached to the test specimen and it falls away dividing (partitioning) the combustion into two locations, each with differing behaviors, and removing both some heat capacity and some heat from the rod. The rod may continue to burn, or may accelerate in rate, if its bottom is still at an ignition point (above both its minimum ignition temperature and minimum ignition energy values) and combustion will ultimately decay or extinguish if it is not.

When even one iron atom combusts with oxygen it can transfer heat, and that heat can serve to promote further combustion. Indeed the viability of combustion relies upon the management of combustion heat so as to facilitate further combustion. The concept of fire prevention relies upon interfering with and preventing that same facilitation.

Previous papers [*1-4*] have sought to go from the complex to the elementary in dealing with propagation. This continues to limit [yet maximize] the role of heat transfer so as to simplify analysis, and perhaps define an ideal conservative model case for TIP combustion, while recognizing other possibilities may behave differently. Vaporization of a metal may allow it to exhibit rapid combustion. Melting of a metal may allow it to exhibit a slower, typically less hazardous, mode of combustion. This is why we ask if it can melt or vaporize itself——whatever that question exactly means.

Consider Fig. 6 which shows an adiabatic specimen at that is marked into four equal segments. The thermal conductivities have been individually turned off (possible since this is a hypothetical worst-case construct only). We will contrive this extreme example on an assumption here that the bottom segment initially experiences what a previous paper [*3*] has called “miraculous combustion [5]”. Assume the bottom segment without an ignition source, spontane-

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[5] “Miraculous combustion” is not *un*realistic. Just as there is a probability that all the air in a room will go to one corner leaving all the occupants sitting in a vacuum, there is also a probability that oxygen might suddenly impact a rod causing a reaction to convert the tip to oxide. These odds are less favorable than playing the lottery.

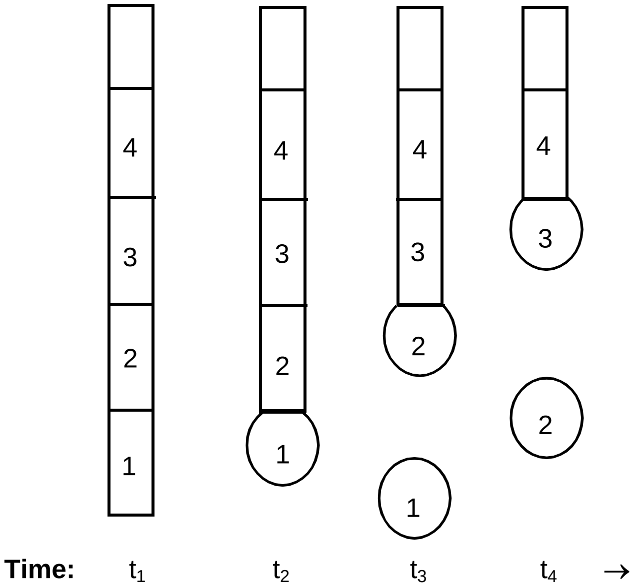

Fig. 6—*Typical test specimen divided into independent combustion segments .*

ously melts and batch reacts completely to become a molten attached droplet. The most favorable condition for further combustion in this scenario (still other hypothetical scenarios can be more severe) is if this molten droplet transfers as much heat as it can to an identical segment above with no losses elsewhere, including no losses to subsequent segments further above. As a result at one instant, time t_1, the bottom segment 1 is room-temperature iron and an instant later, time t_2, it is fully batch reacted adiabatically into an attached molten droplet 1. It has moved from point A to point C on Figure 5.

We next turn on the thermal conductivity to the segment 2 above so that the attached droplet can transfer as much heat as it can into it, which we take as being initially at room temperature, condition A of Figure 5, as its starting point. No heat transfers to segment 3 before the droplet falls away and partitions the combustion into two locations. Then at time t_3, segment 2 batch reacts completely to become a molten droplet 2, and thermal conductivity is turned on to segment 3 to transfers a maximum heat to it with no transfer to segment 4 and with no other losses, before it drops away. And this sequence repeats itself indefinitely and has many worst-case elements in it.

Figure 7 exhibits details of this sequence. The first droplet forms upon miraculous ignition beginning at point A_1, and it batch combusts to shift to point C_1. As heat transfers out of the first droplet, its state moves from point C_1 on Fig 7 along the curve to the left. Adiabatic heat transfer is assumed (for worst-case reasons) to result in transfer from any gases present as well, and so initially its temperature falls slowly but the rate increases at greater heat transfer levels. Three red arrows labeled “heats out” pointing to the left indicate three successive stages of heat transfer. These stages of heat are transferred into the second segment starting at room temperature (point A_1) and are shown as three green arrows pointing to the right labeled “heats back in”. Notice that the third arrow of each set is at the same temperature, and they are of the same length.

The third arrows shows where the heat transfer *from* the slag matches the heat transfer *into* the second segment. At this temperature-equilibration point, heat transfer ceases by the Ze-

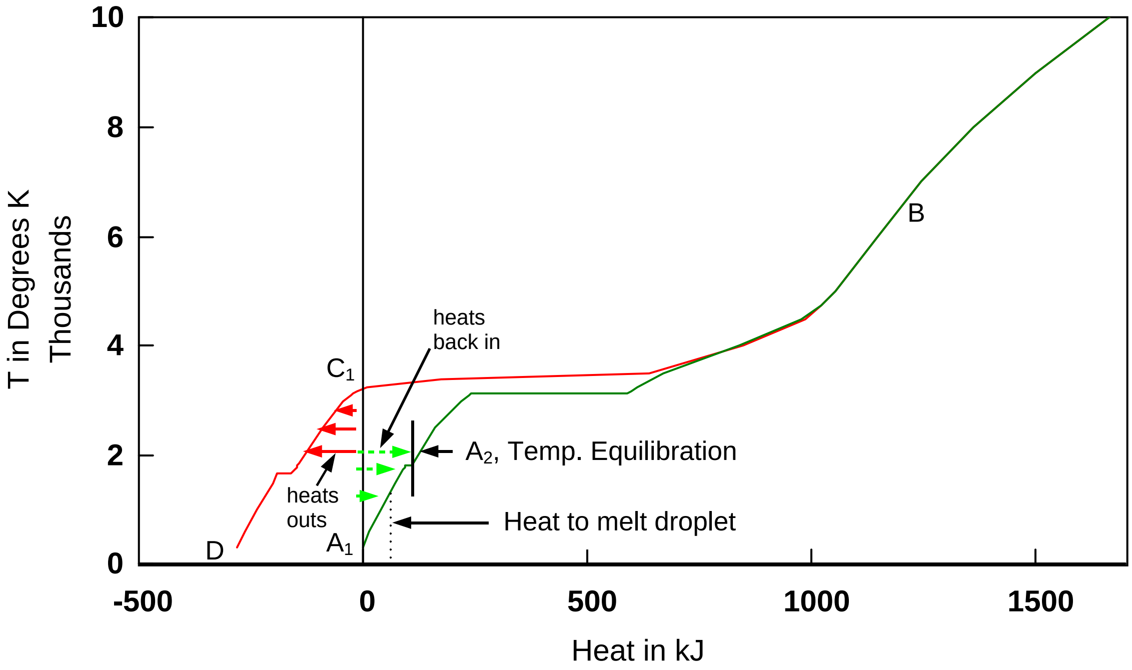

Fig. 7—*Typical test specimen divided into independent combustion segments* .

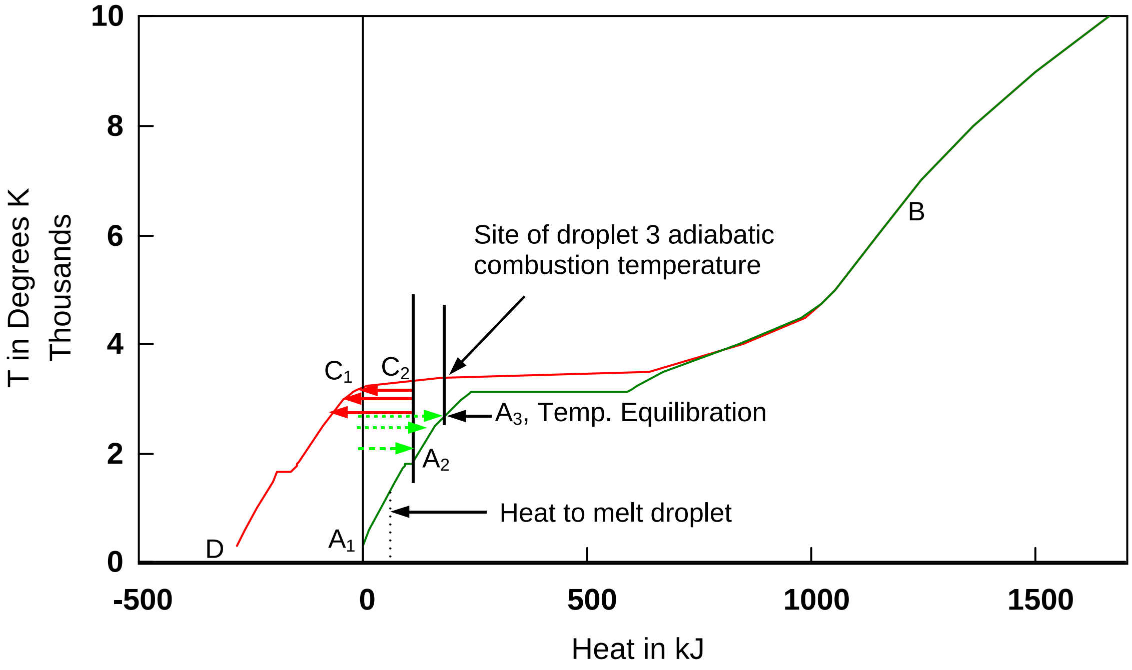

Fig. 8—*Typical test specimen divided into independent combustion segments* .

roeth Law of Thermodynamics. We now allow the slag to fall away, at time t_3 on Figure 6 because it has become a drag on the heat capacity.

Notice at this point of detachment that the maximum heat that can transfer out of the droplet (and its gases) has been sufficient to exceed the indicated heat to melt the second segment into droplet 2 (indicated with a black dotted line), but it is much less than the BR_{mp} would predict. Figure 7 suggests the heat required to melt the droplet and it is only slightly smaller than the heat represented by the third arrow, not more than five times smaller as the BR_{mp} would suggest. A new burn ratio parameter based in these data would suggest the maximum transfer possible in this situation would be more nearly 1.7 times as great.

Let us follow this mechanism through one more droplet. Figure 8 exhibits the combustion of the preheated "premelted" second droplet as a batch. Starting from, its initial preheated state at point A_2, slightly above the melting point, it combusts and its state shifts as a batch to point C_2 on a secondary axis through A_2 and is at its adiabatic combustion temperature directly above. This is at a greater enthalpy than point C_1 and so we can transfer a greater heat out of this droplet.

Again three red arrows pointed left and three green arrows pointed right show progressive heat transfers to segment three, starting with it at point A1 and ending when equal temperature is achieved with it at point A_3. This is very similar to what would be expected if segment one had been preheated by an igniter to point A_2 to achieve ignition. This would be called strong ignition (which is commonly used in experimentation) since it is above the minimum ignition temperature and energy that can actually ignite iron (which is reported to be *below* the melting point [*16*]). For segment 3, heat transferred to it at point A3 is again greater than that indicated for melting the iron and this time is again smaller than the traditional burn ratio predicts at the melting point but is still only about three times as great.

However, this is clearly a bootstrapping sequence, in which the combustion of each succeeding segment would produce a droplet (including associated gases) of greater temperature, and enthalpy, and therefore of greater flammability, until the boiling point of iron is reached and would then proceed to increase the enthalpy of each progressively more vaporized droplet until ultimately a droplet would be completely vaporized, despite the fact that the heat of combustion of iron is insufficient to vaporize itself by traditional BR_{bp} criteria. All subsequent segments could burn as vapors.

In real world testing, we know that each droplet does not transfer nearly a maximum heat, that the segments do not come to equal uniform temperatures, nor do the segments experience batch combustion, nor is the droplet devoid of un-combusted iron[6], and we know there *are* important and substantial radiation and convection losses that are significant and would grow with every droplet, and that portions of any gases that form will dissipate and their heat transfer will be lost. And finally we know the statistical probability of a miraculous initial combustion is negligibly small.

This proposal for a model of TIP combustion may need refinement. And it may be that several differing variations may be useful. However, for this metal, these thermo-chemical equilibrium data point the way to an improved understanding of the iron combustion hazard.

Equilibrium Combustion

The previous section modeled adiabatic TIP combustion, which resulted in its acceleration. Indeed this acceleration means that this specimen would be combusting above it fire limit

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[6] The observation of the high level activity apparent on the surfaces of burning iron droplets hanging from test specimens had for years supported the idea that the attached slag was thoroughly mixed and uniform. However, in 1995, the writer [*17*] quenched, literally quick-froze, droplets of steel burning above it threshold, capturing their near-spherical shape, and sectioning revealed both voids and pure-iron second phases therein.

and that, by circular reasoning, is one reason why its combustion is accelerating. The rate of combustion of its later segments should be the most rapid and could achieve vapor-phase speed. However, when real-world heat losses are factored in, one can find that with the combustion of each segment, the starting temperature may actually *decrease* with each segment. Ultimately this second scenario ends with extinction of the combustion. There is a boundary point at which the combustion will neither accelerate nor decelerate and this point is referred to as equilibrium combustion (not to be confused with thermo-chemical equilibrium). Fire limits are points of equilibrium combustion by historical definition.

Equilibrium combustion is crucial to the determination of the fire limits for flammable gas mixtures and for the combustion of polymers (in the Oxygen Index test ASTM D2863 Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (oxygen Index) and it near-clone: ASTM G 125 Measuring Liquid and Solid Material Fire Limits in Gaseous Oxygen) and equally so for the combustion of metals in ASTM G 124 Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres. A number of mechanisms are capable of producing TIP-like combustion that may yield substantial, but yet un-sustained, combustion. In equilibrium combustion, each droplet would leave the residual specimen right at its ignition condition, right at the point Davy and Munro stressed. Excess ignition energy, or any transient variable that transfers more heat or that facilitates heat transfer further along the specimen will allow a transient form of transient (a doubly transient) propagation to occur. Hence if the ignition energy is introduced slowly so that more heat conducts along the specimen before ignition, if the ignition promoter leaves unburned portions of itself behind in the residual droplet, if the chemistry of the igniter alters key physical properties (such as sulfur which alters surface tension in an iron melt), if radiation is reflected back to the specimen, then any of these and others may act to induce additional or even temporary combustions, or acting conversely, may induce premature or erratic extinction.

Figure 9 exhibits a green arrow pointed to the right representing the heat necessary to raise a segment from point A_1 to an ignition temperature at point A_2, taken as 1143 K (reported as the ignition temperature of steel [*16*]). If the ignition temperature is this low, below the melting point even as some resources indicate, then when the segment combusts, shifting to a batch-combustion droplet state at point C_2, it can then begin transferring heat to the next segment. For each segment to be just heated to its ignition temperature it must receive the same amount of heat, extracted from the previous droplet, and that is shown as a red arrow of the same length as the green arrow but pointed to the left at point D_2. The blue arrow indicates the portion of heat that is recoverable at a temperature above 1143 K that can be lost from the enthalpy of the slag droplet at point C_2 and yet just sustain combustion. Less loss would mean accelerating combustion, more loss would mean decelerating combustion.

Indeed, this suggests yet another new parameter or burn ratio formulation might be the ratio of the maximum heat loss at equilibrium combustion to the maximum available to transfer. In Figure 9, it appears the loss (the blue arrow) can be about 80% of the total (blue arrow plus red arrow) at 1143 K.

The Three-Oxides-of-Iron Quandary.

The final combustion products of iron and the heat released by each can differ. So

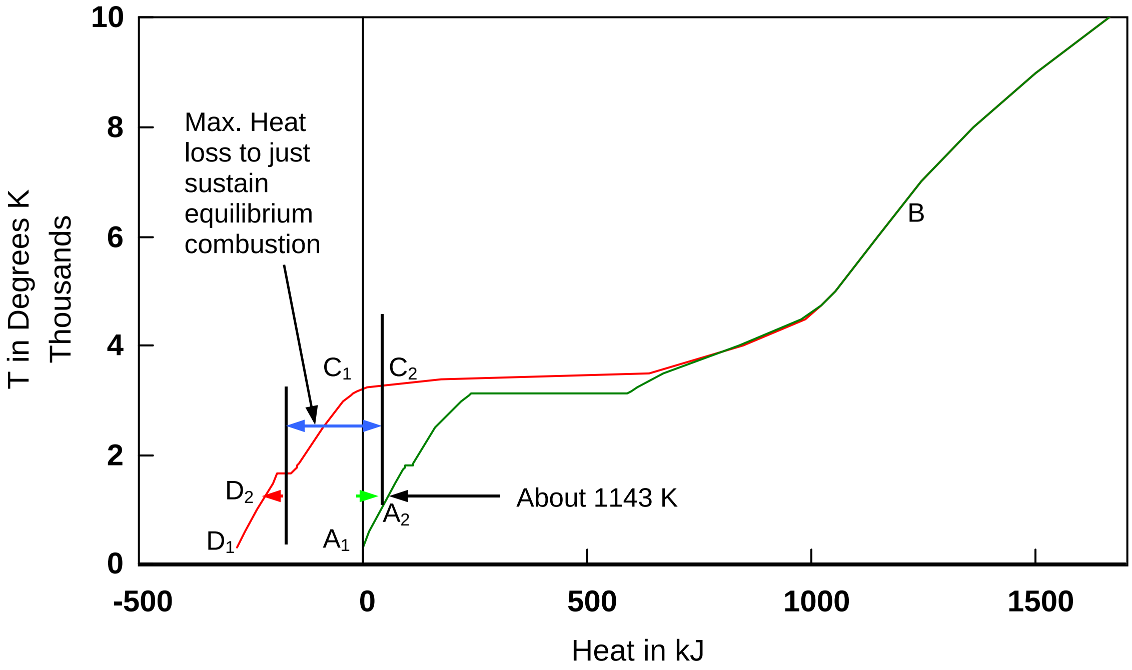

Fig. 9—*Maximum heat losses to just allow equilibrium combustion.*

far, we have constrained our iron mathematically to burn to produce only one oxide ($Fe_{0.947}O$, aka $FeO_{1.056}$). This can be done with real iron and the writer has done it in the tests alluded to in footnote 6. It required the combustion be quenched at high temperature, thus freezing the combustion products and their equilibrium. But there are also magnetite, Fe_3O_4, and hematite, Fe_2O_3, forms, and their heats of combustion are greater than for wustite. And these have caused some consternation over the years with the use of traditional burn ratios and again point out the shortcomings of traditional burn-ratio formulations.

If the ultimate products of iron combustion are wustite, $Fe_{0.947}O/FeO_{1.056}$, the heat of combustion is about 280.2 kJ per gram-mole of iron content, and the traditional melting-point burn ratio is about 3.9. If they are magnetite, Fe_3O_4, the heat of combustion is about 372.9 kJ gram-mole of iron content, and the traditional melting-point burn ratio is about 5.1. If they are hematite, Fe_2O_3, the heat of combustion is about 412.2 kJ per gram-mole of iron content, and the melting-point burn ratio is about 5.7. What if an application that should be acceptable if its iron could combust only to produce wustite, were suddenly changed so that hematite might be the product and suddenly the system might become unacceptable? These suggest the flammability of iron is extremely dependent on what it's final products are and that is not nearly correct. These are all misleading, and thermo-chemical equilibrium data provide an explanation.

Fig 10 again exhibits iron with enough separate oxygen to produce hematite as the green curve. In addition, three curves are shown for the three equilibrium oxides of iron that can form in this amount of oxygen beginning at points D, E, and F for hematite, $0.5Fe_2O_3$, magnetite ($0.333Fe_3O_4$) and wustite ($1.056Fe_{0.947}O/FeO_{1.056}$), respectively. For the magnetite and wustite forms, more than enough gaseous oxygen is present because the total oxygen is consistent with that for hematite.

Notice that as one adds heat to hematite, it warms and then at one point shifts to a semi-latent plateau at which it decomposes into magnetite and wustite. At this point the extra heat in

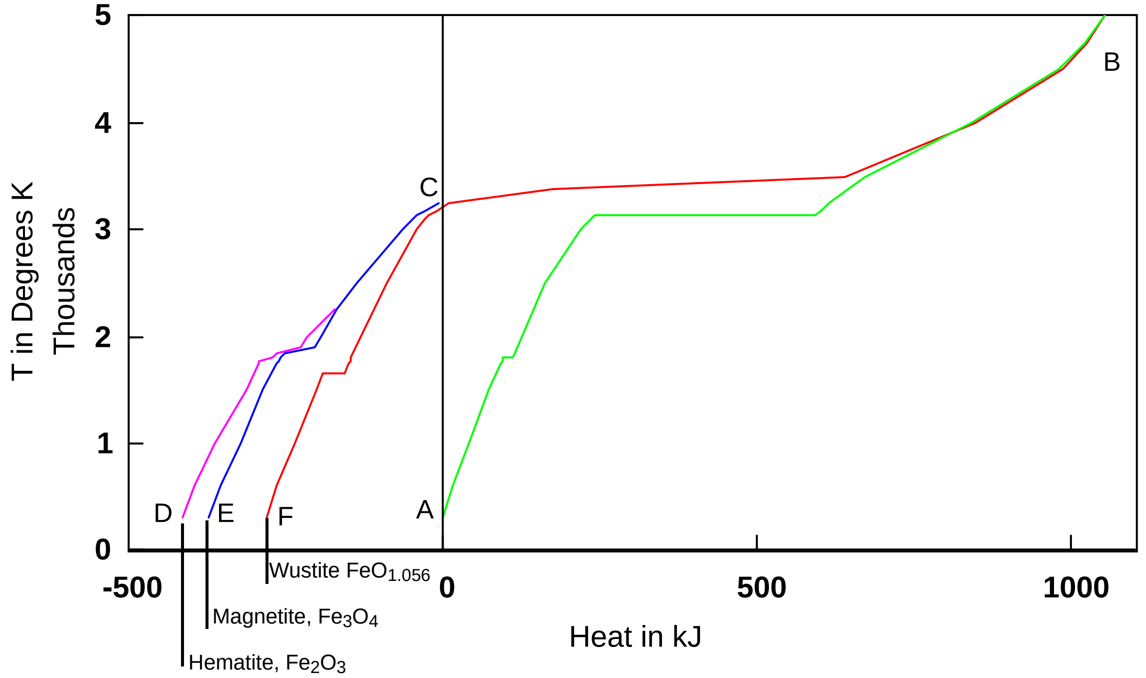

Fig. 10—*The Three Oxides of Iron Issue.*

its heat of combustion has been used to convert it into these other forms. If one warms magnetite, instead, it warms to where it intercepts the hematite curve and later merges with it. Ultimately the merged curves meets with the curve for wustite at point C (the miraculous batch combustion point). And at that point the extra heat of combustion that one obtains from a magnetite final product has been used to convert it into wustite. Therefore although, the three oxides produce differing heats of combustion and therefore differing burn ratios, the adiabatic combustion temperature and products calculated from all three and indeed for any combination of these oxides that might form is, as it must be, the same.

Indeed, in many situations the rate at which any slag would cool could well be too fast for magnetite and hematite to form. Hence burn ratios may often be most applicable based upon wustite products.

This is not to say that the three oxides are identical. If the slag from combusting iron were to fall onto a surface, then the amount of heat transferred from any higher oxides to that surface would be greater and the damage could be greater. It might also help spread a fire at a greater rate even if it did not alter the combustion nature. However, if the surface were massive, it might lead to such rapid cooling of the slag that it could freeze the equilibrium at wustite. In laboratory testing in which the slags were allowed to accumulate in a concentrated pile (which protract its cooling time), widely varying mixtures (1:2, 2:1) of only the higher oxides have been reported [*18*].

Counter-Current Combustion.

Scenarios in which formation of the higher oxides could be a problem to system designs because they might affect the combustion nature as well as any fire-spread are those where the slag may act like it is in a counter-current heat exchanger. A counter-current heat exchanger is shown at the top of Figure 11.

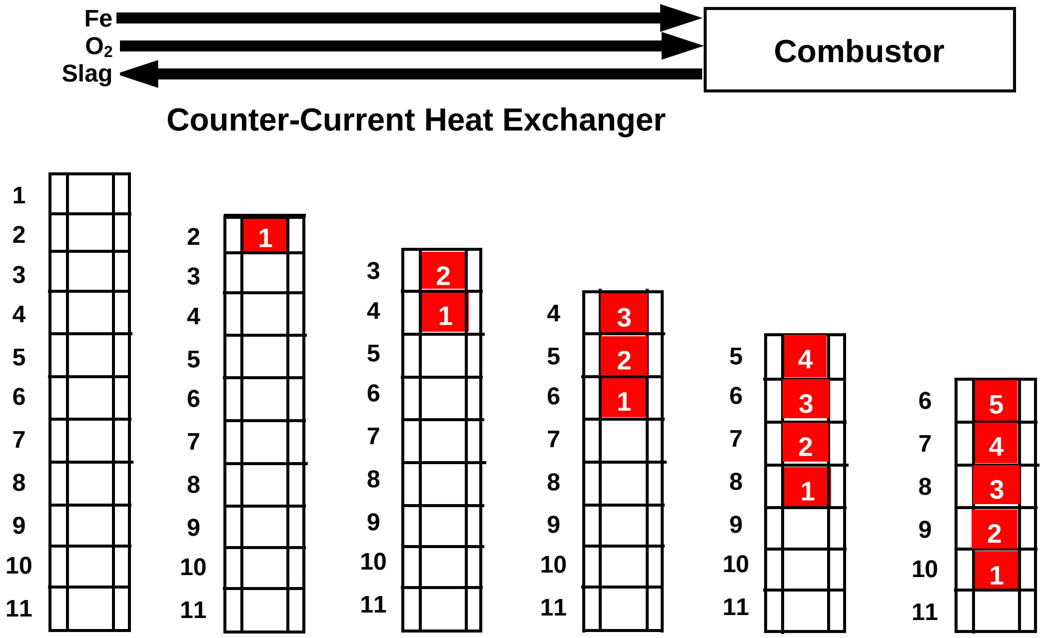

Fig. 11—*Counter-current heat exchanger combustion .*

Iron and oxygen, that may be viewed as moving in segments, are fed separately (to prevent mathematical reaction) into one side of the exchanger and then to a combustor. After combustion the adiabatic slag (with any gases) is fed back into the remaining side of the exchanger. The slag first transfers as much heat as possible to the second segments of iron and oxygen that are on their way in, then transfers as much as it can from what is left to each set of succeeding segments until in theory its temperature is returned to room temperature and all of its heat of combustion has been bootstrapped into the incoming flow. If this happens quickly its final room temperature state is likely to be wustite, and if it happens slowly it may be magnetite or hematite or mixtures thereof.

Therefore the second incoming segment and each succeeding incoming segment will be bootstrapped much as had happened for the TIP combustion scheme except detachment of droplets will not interrupt the heat recovery process and so it will achieve a point of pure vapor-phase combustion more quickly and the point where the incoming stream becomes fully gaseous will recede towards the source. In theory this allows a maximum amount of the heat of combustion to be transferred.

A real world example where this might happen is hard to imagine. The closest the writer has come is to a tube that is top ignited as in the lower portion of Figure 11. If the slag from the combustion of each segment runs into the bore of the tube it can exchange against the “incoming” tubing as is illustrated in counter-current fashion. Of course in this case, if oxygen is flowing upward, it might tend to blow the slag out of the tubing (Tilt!). And if the oxygen is flowing downward, the tube will tend to be severed and the supply of oxygen will be interrupted. Hence this tube would have to be contained within a bigger tube, something that is fairly uncommon in real oxygen systems.

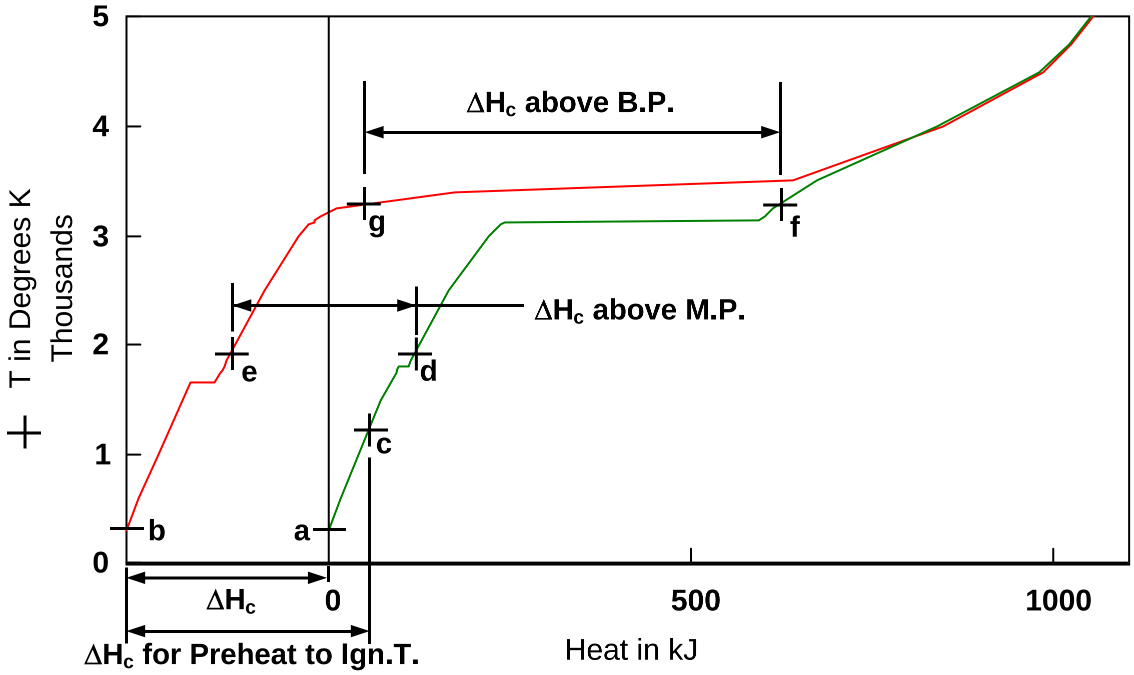

Fig. 12—*A PC Utility for Exploring Alternative Burn Ratio Formulations* .

Standards and a PC Utility.

To repeat, the mathematics to generate these thermal profiles is daunting. However we have noted that software is available to do that math for us. Nonetheless, use of that software has many challenges of its own. Its use is not nearly trivial and is also something that garden-variety OSPs should also dearly wish to avoid. One must pay many dues to generate these curves and for some metals they may require postings with precautions. However, once the resulting figures, thermal profiles, like those presented here are generated and posted with suitable precautions (assuming for a moment that they are correct—something yet to be established), they are useful and most users if not all, do not require a degree in advanced math or the payment of extreme dues to make good use of them. They provide much more insight into the nature of metal combustion than the coarse burn ratios that have served the community remarkably well thus far. And yet if these curves are not daunting to use, they can still be onerous.

The writer maintains that ASTM Committee G4 should establish a thermo-chemistry subcommittee and develop a series of simplified thermal profiles for metals, incorporating them into a standard or adjunct practice. It should examine profiles for alloys for possible inclusion as well, flagging unique aspects on each as warnings to our users.

Since calculations based on these curves can be laborious, the extraction of even these data begs for a computer utility. These thermal profile figures can be imported into an adjunct PC utility in the spirit of the ASTM G4Math.exe (a past utility now in limbo due to an ASTM aversion to software adjuncts). Consider Figure 12 as it might appear on a PC screen. The use of such a utility could be simple.

A drop-down menu could allow the selection of any of a number of burn ratio formulations or adiabatic combustion temperature calculations to be selected. Then a series of mouse clicks identify the points on the curves to be used in calculating the parameters and Presto! A report cites the burn ratio or other property for those conditions.

For example. two mouse clicks on a horizontal line such as at points a and b, would allow the utility to report the standard heat of formation (the *standard* heat of combustion of the metal). Clicks at points c and b would report the nonstandard (*in-situ*) heat of combustion at any preheated temperature, such as at the ignition temperature). Clicking points d and e, would report the nonstandard heat of combustion at a temperature above the melting point. Clicking points f and g, would produce the nonstandard heat of combustion of iron as a gas (and notice how the heat of combustion sharply increases there).

Adding the curve for iron (the red curve from Figure 3) would allow clicks to establish the heat to warm iron to any hypothetical ignition temperature, to the onset or completion of melting, to the onset or completion of boiling, relative to ambient temperature or similar differential parameters that might apply to a system operated at elevated temperature. Perhaps a bounty of other useful information remains to be found? With such a utility, the (1) lives saved, (2) hardware saved, and (3) system missions that might be saved should be greater than without such a utility.

Summary

Traditional burn ratios have been of great use to the oxygen safety community, but have been flawed and coarse. Thermo-chemical equilibrium principles have shown what some of these data's flaws are. Thermal profiles can be produced with thermo-chemical equilibrium software that can allow a much more detailed perspective on how a metal might burn, allowing better perspective on when solid, molten or gaseous combustion may obtain. The sensitivity to ignition energy might also be suggested. Development of thermal profiles for the series of metals of interest to oxygen systems has been recommended and a PC utility adjunct should be adopted to facilitate analysis of these data.

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