Barry L. Werley[1]

Phase Issues in Thermo-Chemical Equilibrium Analysis Software

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ABSTRACT: ASTM G4 has been not only disinterested but resistant to incorporating thermo-chemical equilibrium combustion analysis in it standards and teachings. Thermo-chemical equilibrium (TCE) theory was an onerous but well-established tool for analyzing chemical reactions including combustion when first broached to the ASTM Committee G4 oxygen safety community in 1992. TCE had been key in numerous fields including in understanding internal combustion engine operations and control of its emissions and in rocket combustion analysis. Yet in the oxygen fire-safety community at the time, only Glassman's criteria and the concept of burn-ratios were loosely related to TCE principles. Yet when broached for wider use in "discussing combustion of metals and alloys", a cautionary warning about its limitations hedged the suggestion and later was elevated to essentially discredit TCE use. Such use has been minimal during the 30+ years since. Among its limitations were allegations that NASA software at the time could not cope adequately with phase issues. Other software did address at least some phase issues and that is examined herein in an effort to reinvigorate TCE use if not within G4, then elsewhere.

KEY WORDS: thermo-chemical equilibrium, phase, oxygen, oxidant, fire, combustion.

The use of thermo-chemical equilibrium [TCE] software analyses to understand oxygen fire safety was apparently first proposed within ASTM G4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres by NASA-related workers Steinberg, Wilson an Benz in 1992 [***1***][2]. The software (most noteworthy NASA's own Gordon-McBride, G-M, code later succeeded by Chemical Equilibrium for Applications (CEA) code) has been described by these NASA-related workers themselves with at least two bipolar perspectives. On the one hand it seems to offer great hope and promise, but on the other hand they argued it is woefully unable to deal with a number of important situations to the point of being nearly useless? This latter aspect appears to have greatly, even fatally, attenuated interest in their original proposal to use thermo-chemical equilibria in assessing oxygen fire safety. This examination disputes the status quo.

The bipolar perspective is cited already in that very first 1992 paper [***1***] in which Dr. Theodore Steinberg, Dr. D. Bruce Wilson and Frank Benz, proclaim both views in the very

[1]No mailing address at present.
[2]Italic numbers in brackets refer to the reference list at the end of the paper.

same paragraph after using G-M code in challenging the early (1950s) work of Dr. Irvin Glassman [***2***]:

> "The ready availability of computer codes for calculating complex chemical reaction equilibrium suggest that this thermodynamically consistent approach be used for discussing combustion of metals and alloys. Although there are limitations to the computer code used in this work, these limitations are computational and not conceptual."

Although this paragraph cites "the computer code used in this work" apparently but not certainly meaning the specific Gordon-McBride code, there were zero efforts to examine other codes (HSC, FactSage, and others) that were in use. Hence this rousing endorsement of the code included the immediate disparaging hedge regarding the "limitations" that would later be magnified upon with scant explanation, exploration, and no remediation. The "limitations" alluded to were soon and several times implied to thwart much, nearly all, of the seeming value although a number of errors appear to have been made both in using the software and in drawing this conclusion. In the intervening 30+ years, a period in which much adaptation, training and implementation would have been possible, there has been little to no meaningful exploration of these codes. Efforts by this less-than-ideally-equipped writer to explore and exploit and promote this and related software within the ASTM community since 2008, and even before, have simply been declined and ignored (shunned) by the (highly NASA-influenced and perhaps too self-confident) ASTM Committee G4 leadership (NASA+)[3]. Both the pro and con advocates have at times been flawed and daunted to the point of embarrassment. Nonetheless, this has been in this "proponent's opinion the worst dereliction[4] of ASTM Committee G4 in recent decades.

Two principal limitations to the G-M code have been alleged. Perhaps the more fatal of two cited limitations is that the NASA-centric contingent (NASA+) based largely upon (early 1990s) work at NASA WSTF came to ordain the presence of copious excess oxygen in burning iron slag [***3-8***] (and perhaps some but not all other metals also) and implied that something (they concluded to be ferrite ions) had to be present to retain the "copious excess oxygen" [***6***]. Since there are no thermodynamic properties tabulated (solid, liquid, or gas specific heats, melting points, boiling or dissociation points or latent heats, etc.) for the asserted ferrite ions that they concluded would form, the software simply could not address iron combustion for lack of being able to calculate this asserted critical, if not major, component. As a three-decade skeptic (not the only one) of the "excess oxygen" thesis the entire time, this worker has finally alleged and argued elsewhere in detail [***9***] that this was/is a hugely flawed conclusion based on severely flawed experimentation. A close examination of the NASA+ work and analysis does not in this opinion prove or even suggest massive or even substantial presence of these ferrite ions/excess-oxygen beyond minor levels at most, possibly quite the reverse. Yet to this day, something, perhaps even professional embarrass-

[3] To wit: NASA White Sands Test Facility workers, former workers still associated, and those commercially, professionally, and ideologically linked to NASA and, frankly, operating at times a little like toadies and minions in a street gang.

[4] Definition of "dereliction": "The shameful failure to fulfill one's obligations."

ment and denial, has sustained this unseemly perspective.

The other principal cited apparent software limitation is cited at least twice: (1) "restrictions within the Gordon-McBride Computer Code used on handling condensed phases" [***1***] and (2) "The Gordon-McBride code is limited for application to iron burning because it does not handle multiphase systems well" [***7***]. However, these phase limitations do not appear to have been examined nor studied nor elaborated upon in any detail by these workers perhaps because of what they considered to be the other unrelated disqualifying "excess oxygen" factors. Rather, on at least some occasions, these NASA+ authors chose to cope with the alleged phase issues by selecting "input" (perhaps starting point) physical states that avoid introduction of the condensed phase (though actual formation of condensed phases was still a prospect). Namely, Instead of specifying combustion of ambient-temperature iron, they specified combustion of high-temperature iron gas, and then arrived at curious results. However in an earlier (perhaps in some ways flawed) analysis, this commentator suggested [***10***] they may well have incorrectly interpreted the results and operation of the code and in this effort will attempt to surmise and examine at least some of the issues of phase effects (while stipulating to a background not perfectly adapted to the task). The results seem to be significant but may or may not address all of the stated concerns of the NASA+ contingent.

Additional disqualification of G-M software code use was predicated by the same NASA+ workers that centered on the results the NASA code produced in predicting dissociation of Fe 2+ oxide. Their analyses [***1,7***] appears to reveal what may be errors in what dissociation is and how it affects thermo-chemical behavior, but may also have misused the code (as this worker has also done many times, probably even embarrassingly in print) thereby compounding significant errors upon significant errors in the data used to indict the code. In this opinion there is no major validity to these last indictments (nor for that matter, the first two) of this NASA code at least for the goals of many oxygen safety workers. And this conclusion appears to be supported by analogous use here of apparently much more flexible, but with its own limitations, Outukumpu HSC 3.2 code for the same purposes.

The NASA G-M code (especially the command line version) is very difficult to use and understand and the massive instruction sheets proved of almost no value to this much less-than-optimum user. The HSC code appears to be much more flexible, but its instruction manual (3.2 version) was also of less-than-ideal use to this limited-background user. However HSC does hold promise in that it allows for the declaration of multiple separate phases some of which are to be examined herein.

The HSC manual (page 58) cites:

> "Although equilibrium calculations are easy to carry out with HSC Chemistry, previous experience and knowledge of the fundamental principles of thermodynamics is also needed. Otherwise, the probability of making serious errors in basic assumptions is high."

Consequently, can the phase issues present a remaining fatal obstacle against a robust

exploitation of TCE math in material evaluations regarding oxygen fire safety? Therefore, this commentary will attempt to identify, develop and speculate on some context for the effect of phase-related factors. These factors may or may not address the earlier cited NASA+ concerns. The writer freely admits (confesses perhaps too often herein) he is not the most skillful champion for this effort just the most (perhaps only) one willing to try, and the topic learning curve is not easy to master, but its promise is not to be ignored either. Hopefully, there are G4 members better suited and better trained to address the issues if G4 systemic bias can be overcome. So hopefully these considerations will prove at least moderately enticing and even valid and can be refined and improved or even corrected if too flawed. And thankfully, just as Glassman's criteria and the SRI burn-ratio parameters are used by rank-and-file oxygen safety practitioners, similar practical low-complexity TCE-based parameters can be developed that should be similarly easy to use.

The writer has been in touch with the team at NASA Glenn who are responsible for the current CEA implementation of and modifications to the G-M code. They have not indicated any interest in this effort and as a result, this exploration of phase issues will not focus on the CEA code and its specific issues. Indeed, his past fledgling efforts (that ignored multi-phase issues) will need examination for flaws related to this or other material. Sadly, these and other issues have been met by strong opposition qualifying as passive-aggressive, if not active, censorship.[5] Hence the early HSC code will be the overwhelming focus here. Prior efforts will be extended to develop and advance a simplified perspective that should appeal to the rank and file but may be at great risk of error needing correction later. But hopefully the oxygen safety community can be motivated to take on this important topic.

TCE Math

Dr. Irvin Glassman's standard text "Combustion" [***11***] describes thermo-chemical equilibrium math as it applies to combustion. It ain't pretty. In the writer's dated judgment, the oxygen safety community may have a number of highly specialized members who could and indeed should translate and hopefully simplify the big picture for a large peer sector, but they haven't stepped up so far. As already noted, in this judgment, the biggest dereliction of the past three decades has been this avoidance of exploiting this theory, even if just qualitatively, for it is worthwhile knowing things like "water seeks its own level", even if one does not know exactly how water does it.

Glassman's text [***11***] and also his former student Dr. Ken Kuo's text [***12***] discuss thermo-chemical equilibrium and software. Glassman specifically describes the calculation of adiabatic combustion temperatures as the reheating of a materials combustion products with the heat that it released (its standard or nonstandard heat of combustion, standard or nonstandard heat of formation as the case may be). However one can calculate other useful parameters similarly (such as the NASA+ disdained burn-ratios). This is nontrivial because as one heats combustion products they not only warm but can break up into numerous other

[5] This analysis assumes that metal combustion is not highly secretive for competitive purposes and that that is not a factor in the current scenario.

materials and phases with differing heat capacities and the way in which they do that is predicted by which combination of materials yield the minimum Gibbs (or other applicable) free energy. That is where things get ugly and the math gets oppressive.

Hence if a system has two or more regions (for example "phases") that differ then one must calculate the free energies separately and find the temperature that yields the minimum *sum* of their individual free energies which may be different from what they would be if the components were uniformly mixed. So in effect one must consider all of the possible ways in which differing regions my evolve so that one can estimate that scenario which would yield the lowest combined free energy and therefore the thermo-chemical equilibrium. This is what NASA's CEA code is accused of not doing well, but which might not be entirely correct and indeed, the CEA results may be far more useful than some claim.

Thermo-chemical equilibrium concepts have been crucial in analyzing numerous combustion behaviors (in the automotive, pollution, and other fields) and has provided vital data not easily developed nor measured,[6] inferred or even surmised otherwise. These concepts are crucial to the air separation industry that represent a major fraction of the oxygen safety need and some even have their own TCE codes not just for safety reasons but for basic competitive product development. Yes there are nature's glitches. In one famous example glitch, nitric oxide is a gas that forms quickly at high temperature in internal combustion engines but when temperature is rapidly reduced during the expansion stroke, it is slow to reverse itself and so equilibrium calculations can way-under-predict the presence of nitric oxide in the consequently non-equilibrium exhaust gas. But these glitches can often be reconciled and even so, the benefits outweigh the trauma they inflict.

There most certainly are similar idiosyncrasies manifest in metal combustion, and if TCE were to be explored in earnest, they would need to be identified and warned about to support both tyros and even the experienced oxygen safety practitioner. However, that should be completely do-able. What's more, that is ASTM G4's mission and G4 has shown itself quite successful in the delivery of tutorial instruction and should play to this strength.

Phase Malaise

The NASA documentation for its Gordon McBride code (also applicable to the later CEA version) [***13,14***] is massive and not for the faint of heart. For the sake of this attempt at a "simplified" discussion, it appears the software and others like it (1) calculates the obligatory free energy (Gibbs or Helmholtz as needed) for massive numbers of mixtures of possible species that might form, seeking (with a massive amount of repetitive math) to locate the minimum that would represent equilibrium. This can be risky since there might be the previ-

[6] It has always been a major challenge to test alloy combustion. Alloys are often application specific and sold in physical shapes and sizes that require massive machining to convert into test specimens, if even possible to do. At one time (1980s), the NASA WSTF facility actually considered creating a melt-shop to prepare custom alloys for fire testing, ...apparently long ago abandoned. The writer has argued that while alloys are difficult to invent, then prepare, the constituents of alloys are almost always available as powders that can be mixed in any proportions (even in proportions that could not be actually related to bulk alloys for phase and other reasons. These mixtures could be subjected with less difficulty to testing as flammable dusts (although a correlation between dust and bulk flammability would need to be validated). Actual alloys might also be ground into dusts.

ously mentioned “glitches” but also because local minima might be mistaken or missed if the software does not test every potential region (called in some papers local chemical equilibrium [LCE]).

Glassman describes the G-M technique as using a “descent Newton-Raphson method” (page 20 in [***11***]). He then points out that in calculating an adiabatic flame temperature, one can merely take the measured heat of combustion and add it back into the combustion products to theoretically project the conditions of adiabatic combustion (for a system in equilibrium) and thereby estimate the temperature (or any other temperature of interest during heat-up or cool-down. Of course adding the heat back is a nontrivial task. This is in effect what the oxygen safety community has been doing to generate approximations of its Burn Ratio ranking of elemental metals and estimate whether a given element has enough heat of combustion to either completely melt or vaporize itself. TCE software can upgrade these estimates (most importantly to mixtures of elements) and as will be attempted later to help to understand them.

This can be more than a little complicated when a gas, liquid, or solid mixture combusts to produce assorted materials and mixtures. However, the complexity multiplies in some combustion cases with more than one phase. And these multiple phases may involve segregated local regions of the same physical nature (solid, liquid or gas). Some equilibrium combustion products might be gaseous, some liquid, and some might even be solid. It appears the NASA software starts with a single combination “input condition”. Then heat variations and entropy variations are tried using ideal gas and ideal gas-like natures. After all, the software was intended for evaluation of rocket performance (which might explain why it often does not seem to complete calculations at lower temperatures). Then depending upon temperature it may suggest a second phase (for example a condensed phase might form and) should be “inserted” into the math (though this may not be the exact intended completely correct description for their “insertions”). It also allows for the discrete insertion and omission of specific molecules though this user has not nearly mastered that feature). Then it has to do more than one massive calculation. It has to calculate the free energy of the distinct regions (in each gaseous or condensed phase) for various proportions to determine how much of each would form to produce a minimum overall free energy . The more of these phases that are present, the more challenging is the math for every phase must have its own free energy at equilibrium and in combination must form an overall minimum.

In the early 1990s the TCE Software Outukumpu HSC for Windows 3.0 became available and it (if not its predecessors) allows for the specification, inclusion or exclusion, of multiple phases (solid, liquid, and gas[7]) and apparently deals well with these issues while having it own set of challenges. When you specify (impose) several phase possibilities it appears to calculate an overall minimum free energy equilibrium for the separate species and in some cases (with exceptions) one can use it (against instructions) to treat incompatible separate phases (gases, liquids, and solids) as a single homogenous mixture (even though there does not appear to be any real-world hybrid that can form of solids, liquids and gases that do not appear to mix in nature). How it does this math is uncertain to the writer (perhaps successive approximations) but the results it produces are both interesting and seem to be informa-

[7] The writer has not explored how it handles supercritical fluids.

tive and so will be presented without enough explanation. Hence it can do calculations (albeit possibly flawed calculations) for fictitious scenarios that are not found in the real world (additional examples include solids above their melting points, liquids below their melting points, and gases below the boiling and melting points of their source liquids and solids). And when dissociation enters the picture the complexity multiplies even more as will be seen below.

In the case of the very important iron combustion in oxygen [iron being the most used and often only practical material by far in contact with oxygen], we know a solid rod (one phase) can burn in gaseous oxygen (a second phase). Many workers, writer included, have produced and studied this result in the lab (though some obviously desirable test scenarios have been curiously avoided). Furthermore, during these tests, a bulk liquid product results (molten droplets) which if quickly quenched (forced to solidify, at least at atmospheric pressure) or slowly quenched in a non-reactive atmosphere will principally contain Fe and Fe^{2+} oxide (apparently FeO at liquid and higher temperatures). The solid oxide fraction upon cooling in oxygen will contain a range of solid stoichiometries from about $Fe_{0.92}O$ to $Fe_{0.99}O$ with $Fe_{0.947}O$ being most commonly cited. These solid crystals are apparently literally a simple cubic form with various regular amounts of Fe atoms missing from the crystal structure, and in the case of $Fe_{0.947}O$ there is one Fe atom missing for every 20 oxygen. $Fe_{0.947}O$ is actually $Fe_{19}O_{20}$. Indeed. this *solid* molecular formation (with about 5% more oxygen atoms than iron) appears to be the origin of early comments of "excess oxygen" in iron slag (solid slag) that may have inspired a number of faulty experiments. What this may imply is that every cooled FeO slag may contain 5% excess oxygen (excess relative to FeO) in the molten oxide.

However, if quenching of the molten slag (or the reaction itself) is slow in oxygen atmosphere it appears Fe_3O_4 liquid (considered by some to be an equal parts mixture of FeO and Fe_2O_3) may form and at still lower temperatures, Fe_3O_4 and Fe_2O_3 solids in various proportions may form that is at least in part, perhaps entirely, related to the quenching event. The extra cooling time may be necessary to give oxygen time to work its way into the molecules, perhaps even into the liquid or solid material, though elevated pressure should also facilitate formation of the higher oxides). Therefore slow reactions (which can often mean large scale reactions that are slower to cool) can increase heat release (and damage potential) of an oxygen-metal fire but for the most part it is the rapid initial combustion event (the formation of FeO) that is referred to as "fire" that poses a principal hazard (including explosions) that one seeks to prevent, that determines whether an event will proceed, and apparently tends to involve only the formation of the 2+ oxide which will be focused upon herein[8].

FeO (as solid, liquid or gas) and/or Fe_3O_4 (as solid or liquid: apparently a gaseous molecule has not been observed to form in nature) and/or a form of Fe_2O_3 (as solid only, for apparently neither a liquid nor gaseous molecule have been observed to form in nature) can form from combustion, and so any tendencies to separate out, to form homogenous segre-

[8] Un-reacted oxygen may be dissolved into the melt and may be the source of some oxygen that produces the change. A NASA+ contingent [***3-6***] has asserted since the 1980s that this "excess oxygen" can be so massive that it off-gasses from the slag. The claims have been disputed. But this dispute has been a major factor in why TCE software use was disdained as the conviction of the very influential group.

gated mixtures, produce at least some of the phase issues. And any of the forms may fuse to form separate or solid phases. All of this may take place in contact with a nearby gaseous mixture that may contain regions of diatomic oxygen gas, gaseous iron, gaseous FeO, mono, di, and tri-atomic oxygen gas. Note how the apparent absence in nature of gaseous Fe_3O_4 and Fe_2O_3 and liquid Fe_2O_3 , subtle facts, both complicates some things but simplifies other things by eliminating the need to calculate their free energies. Also note that while such things as homogenous mixtures of the combined three phases do not exist, the software may indeed nonetheless be calculating useful results that allow insight into whether such anomalous entities would be likely to form were it possible, ...and HSC allows for some options like this though they may not be meaningful.

So in calculating equilibrium, the minimum free energy must be determined for the range of possible or hypothetical real phases that might form especially during the rapid stages of combustion. And this is important if each possibility is different and can alter the way metal burns and thereby affects its suitability for use in oxygen systems. Clearly many more complex variations can be conceived and would warrant future analysis and abundant scholarly papers. However, where one has the data, these calculations can still be informative, probably more informative than traditional "burn ratios" and similar estimates that are in common use and have served the safety community well.

So what does the more flexible (if flawed in some cases) HSC software program predict for potential selected scenarios, and how might those variations affect material design and selection procedures? This analysis can only try to peek behind the curtain. However, such speculation has a worthy goal even if flawed, even if badly flawed. Oxidant safety practitioners have always had to contend with less than perfect combustion models and incomplete data. The insight provided even by imperfect perspectives (as has been the case with "burn ratios") holds substantial promise of being similarly useful even if not exact.

Phase Talk

Despite historical simplifications as will be examined here, Thermo-Chemical Equilibrium is a nontrivial subject. It warrants the efforts of some of the small oxygen safety communities top technical intellects. Yet, none seem interested in promoting this cause and so the present (possibly flawed) effort is what you get here. This analysis and interpretation even if seriously flawed hearkens to the bigger picture and can hopefully bring some semblance of the need and benefit of the theory to the oxygen safety practitioner audience.

One apparent problem in coping with equilibrium issues is the tidy simplified yet incomplete way that some watered-down (the simplest) aspects of equilibrium are being taught. Some aspects are widely and commonly known even in grade schools, others are virtually impossible to find covered in even advanced texts. Figure 1 shows how we all have been taught and so often seen how three of the phases of water behave. Solid water (ice phase at point "A") can be heated to its melting point "B" (0ºC, 273 K, 32ºF) at which point

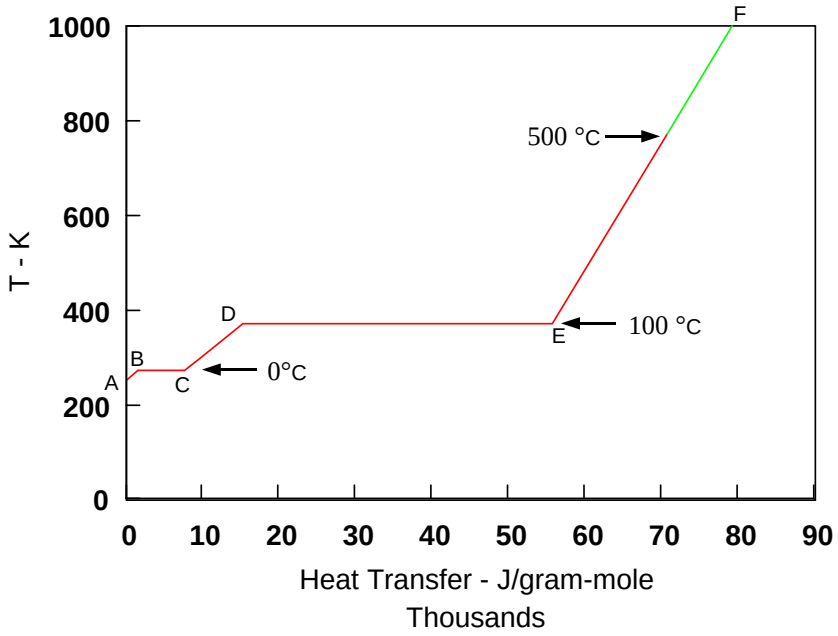


Fig. 1—*Simplistic thermo-profile for water.*

we have all been taught and have observed for ourselves how further warming makes liquid water phase form *at constant temperature* that forms puddles (automatically segregates into a separate phase) around the solid until all is liquefied at point "C". Still further heating warms the liquid to the boiling point "D" (100ºC, 373 K, 212ºF) and leads to the production of gaseous water (steam phase) and continued heating converts all of the liquid into gas phase at point "E" which similarly segregates into a separate phase again *at constant temperature*. Then the gas can be heated to still higher temperatures and pressures and can do work in steam engines and other useful equipment and some much less well known things can happen at the highest temperatures, including breaking (dissociation) into what could be differing phases. Virtually everyone knows this, it is beyond dispute *yet as we shall see may not obtain similarly in every case of every material that is heated*. TCE theory and software appear to nicely explain much if not all of this well known, if complicated, behavior.

Note that the segregation of the water phases during these phase changes is not only important it is apparently crucial. When ice melts it collects automatically as a *separate segregated* liquid. When water boils, it collects automatically as separate bubbles within the liquid or as a gas layer next to a *separate* liquid surface. Figure 2 exhibits calculations with HSC software (which calculates for room temperature and above) for the liquid to steam transition of water where the free energies are calculated for separate phases.

Curve ABC is for a single liquid phase at atmospheric pressure and is generated from the heat capacity of liquid water as the temperature rises. The curvature (decreasing slope compared to the linear extrapolation) to the right as temperature increases implies an increasing heat capacity, and the section above point "B" 373°C (the boiling point) is likely generated from theory rather than measured data since liquid water is not observed at temperatures above its boiling point.

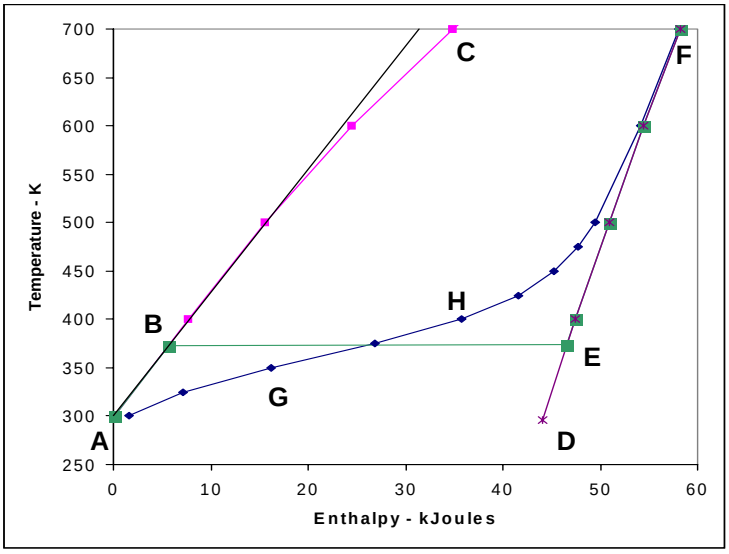


Fig. 2—*Liquid-to-gas phase changes for H_2O per HSC software.*

Curve DEF is for a single steam phase. Again it is generated from the heat capacity of steam as temperature rises. In this case the upper section EF is based upon measured data and the low section (below the boiling point "E") is likely either theoretical, extrapolated or inferred (for example teased from humidity measurements).

Curve ABEF is for a transition that HSC calculates when there are two separate segregated (latent) phases specified: one gas, one liquid. This is also the behavior we have been taught (Fig. 1) to expect and have witnessed in untold numbers of ways. It is declared to be caused by a segregated system having a minimum free energy compared to a homogenous system (a system formed of a fictitious uniformly mixed liquid and gas).

However, curve AGHF is the curve HSC calculates when a single phase is declared and both the gas and liquid species are listed within it (albeit a violation of the HSC instructions). Might this calculation be phase mixture? HSC does not appear to declare phases to be gas, liquid or solid, so this might be a generic result for two materials with differing temperature versus enthalpy curves? Might this reflect a homogenous combined phase transition (liquid and gas being taken as mixed rather than separate despite violation of HSC instructions). This type of "S-shaped" curve does indeed occur in other circumstances for some phase transitions in nature as will be seen below.

Alas, what happens if liquid water is included in the phase with gaseous water but also in a second phase by itself? Alternatively what happens if gas phase water is placed in a first phase and then also included in a second phase with liquid water? Turns out HSC produces the same curve AGHF results.

So when HSC is used to calculate phase change between segregated liquid and gaseous phases, it appears to calculate a latent (constant temperature) transition. When it calculates phase change between segregated liquid and gas or adds a non-real mixture of liquid and gas, it calculates lower free energies for the "nonexistent" mixture. Hence the inclusion

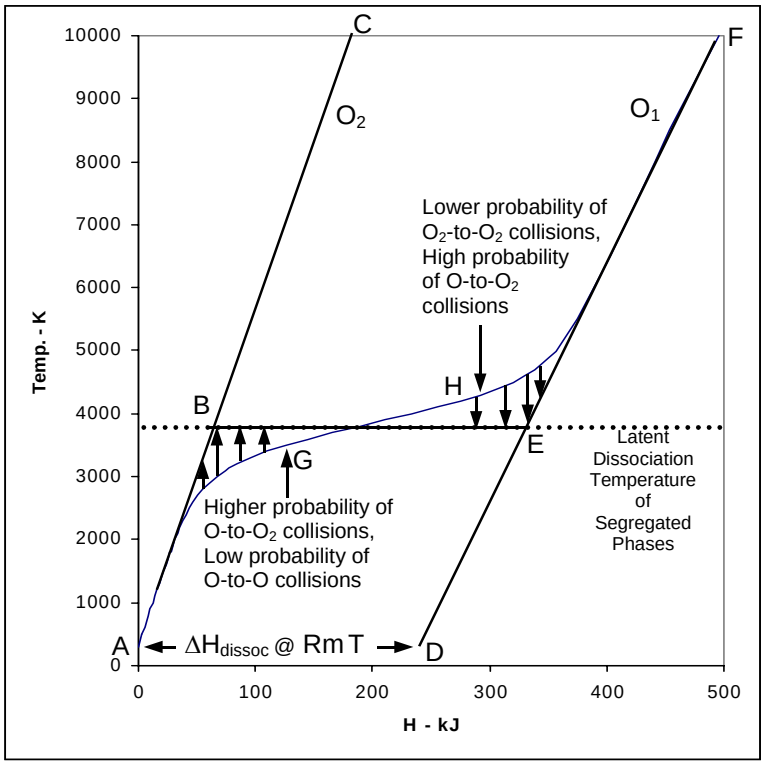


Fig. 3—Effect of *Segregated O_2 and O_1 phases ala Fig. 1*.

of liquid and gas (or liquid-solid or solid-gas or all three combined) materials in a single phase designation in HSC is potentially problematic and discouraged.

In nature we do not know of any scenario where liquids mix freely with gases, or gases mix completely with solids, or liquids mix completely with solids, ...or all three mix together, ...unless that is what happens in so-called "super-critical systems". Consider a thought experiment in which a liquid phase has been broken into a near molecular-size aerosol so that the resulting "near-homogeneous" mixture would allow nearly every gas atom to interact with liquid atoms and vice versa. Might perhaps the latent transition behavior be lost? Ditto a system where a solid material has been ground into a near-molecular sized dust that is dispersed in a liquid or gas? The writer has no answer for this at present.

Consider next in comparison what happens when one heats diatomic gaseous oxygen sufficiently. At some high temperature, it will perhaps gradually or abruptly break into monatomic oxygen (dissociate), and then one has two gases that would be mixed upon formation and in most cases one would *not* expect it to self-segregate into separate phases.[9] Figure 3 exhibits how HSC software predicts the transitions of oxygen that would obtain analogous to those for the H_2O of Figure 2. Curve ABC is for the diatomic gas and curve DEF is for the monatomic gas. Curve AGHF is for the inherently mixed gases (both gases are listed in HSC in the same phase and having the "S-shaped form" of mixed liquid and

[9] While one would expect mono– and diatomic oxygen gas to readily mix there can be cases where gases or their situations are so different that they might indeed separate into distinct gas phases or even just form physical layers. This might be expected to act similarly to differing phases?

gaseous water of Fig. 2) and curve ABEF is the estimate if the monatomic oxygen that forms must separate from the diatomic precursor (monatomic and diatomic gases listed in separate phases in HSC in separate phases yielding a “latent”) transition and “dissociation point” and dissociation temperature akin to melting and boiling point transitions. And if HSC is allowed to predict a system where the oxygen can form into either a monatomic gas phase with a segregated diatomic gas phase or a mixed gas phase, ...it predicts it will all form into the single mixed phase (curve AGHF) that is apparently observed in real systems.

Next, consider the prospect that the diatomic oxygen gases were being heated in a centrifuge that would separate the two gases? It might be quite practical to cause segregation of the O_2 and O in a gas system, for example in a centrifuge there is after all a 2:1 difference in their masses. It might also be practical to exploit the paramagnetism of oxygen if there is a difference between the diatomic and monatomic forms. Instances like these are exotic and should be rare, but there is a prospect one might be able to force a latent transition with a defined dissociation temperature (fully akin to a melting or boiling point) as shown on Figure 3.

The writer is wont at situations like this to speculate on factors uncertain to him that may be responsible for the variations in free energy that seem to produce this phenomena. Such speculation has been especially abhorrent to cognoscente in G4 and is being limited.

While there are cases where gases can layer or separate, ordinarily gases are taken to intermix fully especially at high temperatures including during combustion. However, if one takes a liquid and heats it to dissociation or decomposition, if a new liquid forms, it can be important whether that new liquid separates out (or is immiscible) into a second phase or if it dissolves (is miscible) fully or partially in its parent liquid the way sugar dissolves in hot coffee. Both latter scenarios can occur in nature.

Melting and boiling and dissociation of gases are not the only phase transitions that can occur. Dissociation and structure changes in crystals, and chemical reactions (e.g. ammonium nitrate to form nitrous oxide and water), may or may not also produce segregated phases or homogeneous mixtures, or both. Ditto ionization. Ditto “excitation” that is cited in which electrons in an atom’s orbitals will shift around and absorb or release energy in the process. All of these changes, some overlapping magnify the complexity and so it is vital for the core workers in ASTM G4 participate and help form positions so that practical tools like Fig. 1 can become available to rank-and-file oxygen safety practitioners everywhere.

And so this effort seeks to once again both urge and demand ASTM G4 step up and shoulder this need. This is central to G4’s bailiwick. The following example for iron seeks to again make this case compelling and to upgrade the writers past efforts to climb this learning curve with a still more useful and less flawed, less amateurish product, but perhaps still not yet perfect, exercise based upon HSC 3.0. Yes some instances will be horribly complex but as is argued here, and exemplified with Figure 1, there are instances that are tractable and can serve as baby steps.

Example: Iron Combustion

Countless numbers of workers have for hundreds of years found the data of Figure 1 for water to have been useful, despite not knowing why those data (latent melting and boiling phase changes) obtain rather than single-phase change data as HSC produces for dissociation of oxygen gas. For a few decades, this less-than-optimum worker has sought to promote the development of similar "thermal profiles" for assessing the combustion tendencies of metals, albeit a much more complex scenario but one that seems quite possible if skilled workers behind the curtain do the onerous work of generating those thermal profiles and flagging potential exceptional problems. A practical thermal profile for iron akin to Figure 1 for water has been sought in the past [***10***] and shall again be reworked[10] here with the perhaps more advanced if still not perfect phase insights covered in this paper.

Iron is by far the material used most in oxygen service but not because of any fire resistance properties. Iron is used on a practicality basis (statistically safe practices: a long history of successful use) in limited often low-risk applications where it will, nonetheless, readily combust if ignited and ignition prevention is in realty the principal fire-safety tool. However, in some cases shielding is employed, to achieve safety needs. Use of the alternatives of shielding and barricading of systems though not massive is also not rare nor inexpensive. Nonetheless, this is not to say there can not be batch-to-batch variations in the fire risk of iron, and more so steel, that warrant study. Therefore, good understanding of its combustion behavior is still important.

As noted earlier, this commentator has argued any presence of large-scale "excess oxygen" and alleged consequential ferrite ions (for which there are no thermodynamic data available) is unproven (perhaps they are even a community urban legend or even worse a troll, if you will), and that a perspective he finds troubling on dissociation cited in some papers is also misleading[11]. Furthermore, the early Gordon-McBride code used to support some arguments may have been almost certainly incorrectly used in some cases, all of which have worked to unreasonably discredit the value of Gordon-McBride code and in turn other TCE software like HSC[12]. That leaves these several issues on how the software treats condensed and multi-phase situations as a remaining credible concern that is being explored here using the more flexible HSC 3.0 software that can address at least some multiple-phase scenarios akin to the prior examination of multiple gas-phase effects of heating water or oxygen gas. This may not allay all of the rather entrenched concerns, nor dissuade possibly errant beliefs, but may and will now be applied to iron where the presence of multiple condensed (liquid and/or solid) phases are now prospects but which may yield benefit from this methodology.

[10] In a previous series of attempts to apply G-M code and later HSC code, the subtlety of phase adjustments and impositions was simply ignored out of ignorance.

[11] In paper [***1***] it states with regard to metal oxide "...complete dissociation would produce elements and the enthalpy of dissociation would be the negative of the of the enthalpy of combustion (i.e. formation)...".

[12] It is worth noting that despite the alleged shortcomings of GM code and its early potentially flawed usage by this worker, many of the early curves for at least iron (and perhaps other metals) compare well with these latest hopefully phase sensitive results which reflect expectations to a great degree even if still imperfect.

Keep in mind, the earlier examination of oxygen gas phases revealed the consequences of how multiple gas phases might or might not tend to segregate or disperse during combustion and how that might affect oxygen behavior if it obtained but argued that such segregation could be situationally highly unlikely. In many cases it appears one need not do free energy minimizations to know what the situation will be. So does a similar though perhaps more complex situation present with iron? ...It appears it does to some degree.

This example will now again build what this worker has called a thermo-chemical equilibrium "profile' as was begun historically (albeit possibly flawed or incomplete) in efforts to understand these analyses [***10***]. This involves the generation of a curve with two very different sections: (1) the separate heating of the unmixed combustion reactants (iron and oxygen) from ambient to such a high temperature that it would produce elemental gases incapable of reacting even if mixed and (2) their subsequent cooling after a theoretical mixing of those same hot elemental gases back to ambient to see what products might be most prone to form based on free energy along the way [without the encumbrance of mythic "excess oxygen" and the other cited distractions].

This assumes that mixing of the high temperature reactant gases would yield little or no assumed free energy change (that the heat and entropy of mixing would be negligible at very high temperature). This is akin to and extrapolates the approach Glassman describes of feeding the heat of combustion back into the cooled products of combustion to compute the adiabatic combustion condition but then continuing the re-heating of the products beyond the adiabatic combustion temperature point until they resolve back into high-temperature elements relatable to the materials that began the reverse process. This worker's earlier versions without conscious phase consideration using both CEA and HSC softwares, are perhaps a flawed approximate version of this same approach [***10,15,16***] though both produced remarkably similar data.

HSC follows the practices of G-M code in some respects. Rock-solid-known phase transitions (specifically solid to liquid) are entries in its database as a single material. Why force massive calculations to determine a result that is virtually certain? However gases (basic and dissociated) are treated as separate materials but not separate phases. Hence an "Fe" entry covers both the solid and liquid forms (whereas an "Fe(s)" entry would cover just the solid form but there are few, maybe only carbon and tungsten, entries in the HSC V. 3.0 database that do not include the transition to liquid). "Fe(g)" is the gas form. "O_2(g)" and "O (g)" are separate entries. The software contains an editor that allows the user to split the database entries into separate entries or create wholly new entries (e.g. for exotic ferrite ions). Correct entries are not easy to create and the software may not always contain the correct code to use for estimating every equilibrium.[13]

Iron Properties.

Figure 4 exhibits the HSC estimated heating of iron from solid-to-gas with the liquid to gas transitions shown for both segregated and hypothetical homogeneous phases to

[13] Additional ambitious efforts that seem do-able would be to consider single phase homogeneous solid/liquid/gas systems since sublimation is a known mechanism. Furthermore, the matter of melting point range materials (lead-tin) bear consideration for another time. For now baby steps are still being taken.

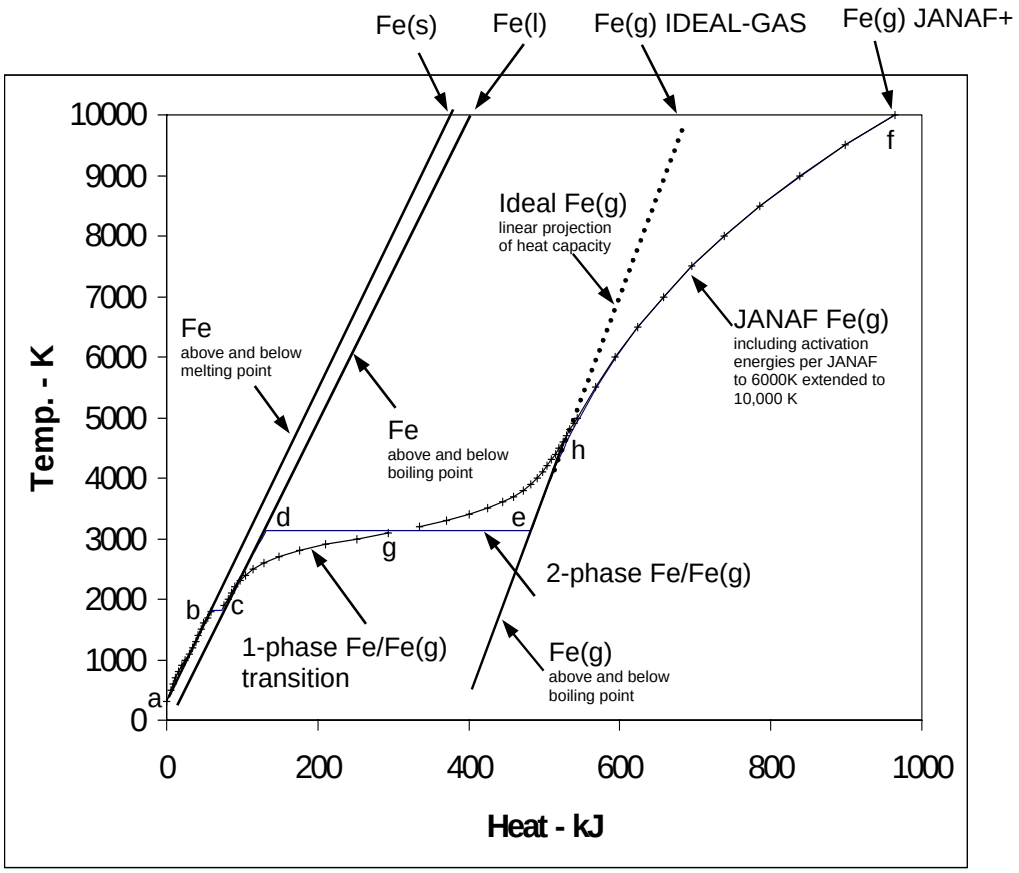


Fig. 4—*Heating curves for iron*

10,000 K as extensions of the 6,000K limit of JANAF data. A linear ideal-gas projection of the lower temperature Fe(g) data is also shown[14]. The solid-to-liquid and liquid-to-gas transitions are combined in the HSC data and produce a latent transition when inserted into a single phase. When the integral solid-to-liquid entry and iron gas entries are inserted into separate phases, the two-phase latent curve (ABCDEF) results. However, the HSC rules can be violated and the liquid to-solid entry and the iron gas entries can be inserted into a single phase and then the "S-shaped" transition (ABCGHF) results obtain. The validity of the latter is plausible but not certain nor is it expected to occur in common reality if it is valid.

Combined Properties.

Both phase-related oxygen curves were presented in Figure 3. However in stark contrast, the two-phase (segregated, ABEF) curve of Fig 3 is not expected to apply in *almost,* if not all circumstances because the two gases can, and would be expected to mix as a single phase . The single phase curve AGHF has the "S-shape" and will used herein. Figure 5 ex-

[14] Note that at high temperatures as noted in the past [***15***] (HSC data for high temperature iron gas are significantly different than NASA CEA more ideal gas data. Note that other variables affect iron oxide at very high temperatures, one of which is the formation of ions and that can absorb heat also.

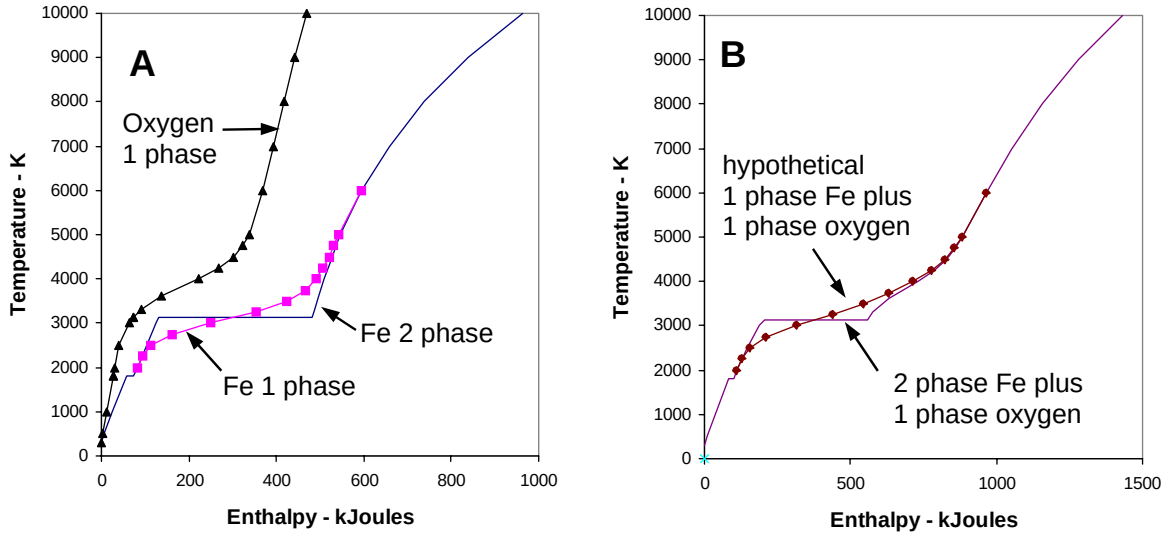


Fig. 5—*Composite heating of separate iron and oxygen to high temperatures. (Iron melting transition shown as both single phase and double (latent) phase transition.)*

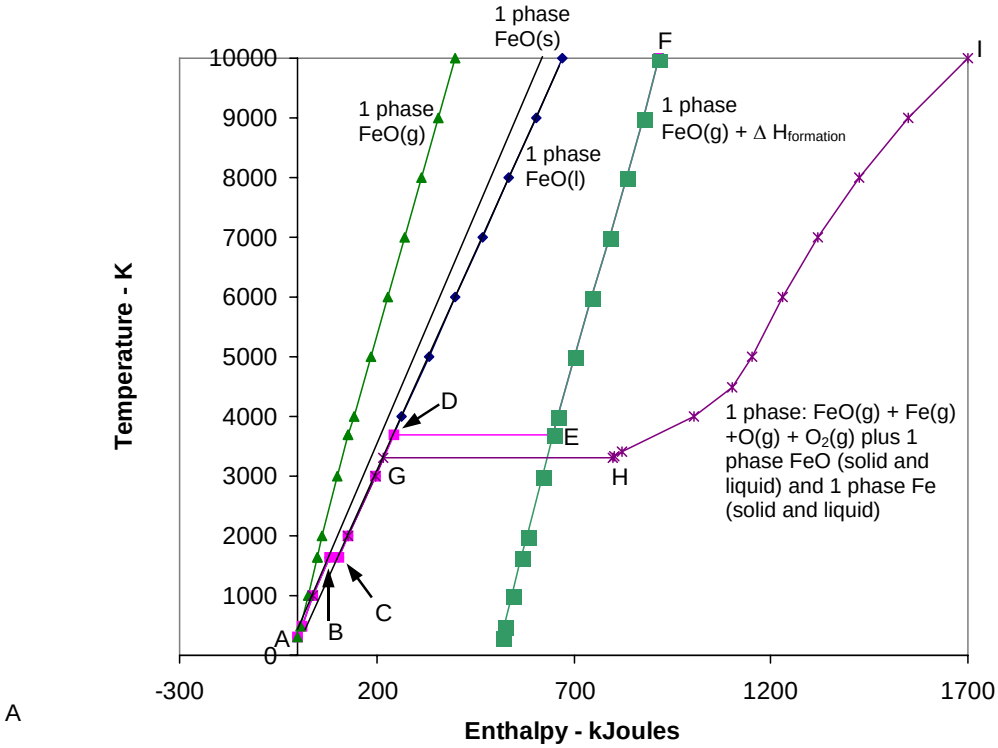
hibits in part A the one and two phase heating of iron and the heating of single phase oxygen. The sum of the separate heats to warm 1.0 mole of solid iron and 0.5 mole of gaseous diatomic oxygen (stoichiometric to Fe_1O_1) separately to 10,000K is shown in part B for both the expected heating of real two phase and hypothetical one phase Fe. This is what this worker has attempted to do in less astute earlier efforts and yet this presumably improved version is remarkably similar.

Iron Oxide Properties

Recall from the earlier section on Phase Malise, there are three iron oxides: wustite (Fe_xO where $0.92<x<0.99$, but apparently tends to a 0.947 value), magnetite (Fe_3O_4), and hematite (Fe_2O_3)]. Heats of formation at ambient temperature (aka standard heats of combustion to form the pure oxides) vary in the same sequence Fe_xO, Fe_3O_4, Fe_2O_3 and this has caused some consternation historically as to whether iron that burns to form higher oxides might be more prone to fires and less acceptable of use than if it can somehow be limited to form only the lower less energetic oxides. And even more curiously, if quench speed is one known critical factor, are there other factors based on free energy? Most importantly, why would iron burn to form one oxide preferentially over either of the other cases? Thermochemical profiles from HSC will help give a very plausible (even if imperfect) perspective to this old issue. So next we examine how HSC assesses the similar heating of the iron oxides: ~FeO, Fe_3O_4 and Fe_2O_3.

Heating ~FeO (Wustite)

Figure 6 exhibits HSC results for the heating of $Fe_{1.0}O$ to 10,000K. If HSC is listed on the input form with two phases: FeO (solid and liquid) and FeO(g) (gas) one obtains the curve ABCDEF very much like that for the water of Fig. 1. However, room-temperature



A

Fig. 6—*Heating of FeO to high temperatures.*

wustite is not in thermodynamic equilibrium, it is apparently in what is called a "frozen equilibrium" consistent with being quenched from a high temperature[15] as this worker has replicated [***17***]. The multi-phase curve ABCGHI was generated as specified by HSC instructions with a first gas phase listing containing the gases: diatomic oxygen, monatomic oxygen, FeO gas, Fe gas (and a trace of argon gas to ensure a gas phase calculation can be performed). Two more separate phases listed were FeO (solid/liquid) and Fe (solid liquid)[16].

Basically, at point A, HSC indicates, in this case, the scenario is entirely room-temperature frozen-equilibrium FeO. If devoid of extra oxygen and since higher oxide phases are not available to the algorithm, it warms until it achieves its melting point temperature about ~1650K, point B, at which it is still FeO. It then undergoes a latent heating while it converts into liquid FeO at point C. The liquid FeO heats until it achieves another roughly latent transition point G at about 3110K. This point is often loosely reported as and referred to as a "boiling point". However as Steinberg et. al.[***1***] advise it is not just changing FeO(l) into FeO(g). In the case of the HSC algorithm, it is also changing (dissociating)

[15] A "frozen equilibrium" is where a material appears stable because its chemical reaction has been cooled and slowed to where its rate of conversion to its ultimate thermal equilibrium appears nonexistent. Wustite (~FeO) can be heated in oxygen, ignited, and burned as it cools to produce Fe_2O_3 its ultimate cold equilibrium.

[16] Previous efforts to generate the iron thermal profile have been much less cautious (nay clueless) in considering phase effects and may still need revision and more context than applied herein. Nonetheless many plausible, approximate and possibly even apparently and approximately correct, curves were produced.

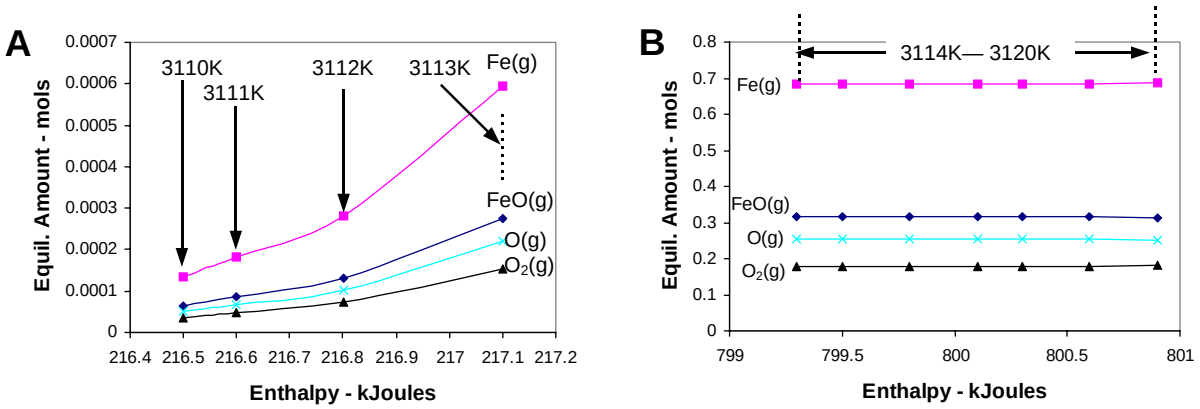


Fig. 7—Latent phase transition of FeO(l).

roughly twice as much FeO(l) into Fe(g) and O(g) the latter of which is released and is reverting (reacting/combusting) into O_2(g).

Figure 7 magnifies how this HSC scenario predicts the latent transition should occur. In part A, at 3010K virtually all of the FeO is liquid but it is starting to split into four gases. As the temperature rises in one degree increments to about 3013K, the four gases grow, mostly being Fe(g) but with about half as much FeO(g) and much smaller amounts of O(g) and O_2(g) shed from the FeO(l) dissociation and vaporization to Fe(g). By the time temperature has reached 3014K, part B, virtually all of the liquid FeO is gone, all four gases have increased in amounts and in the same order and roughly the same proportions.

Part B on Figure 7 corresponds to point H on Figure 6, roughly where all the liquid FeO is gone and all the remaining constituents are gaseous, hence the tail of an "S-shaped" curve typical of one-phase behavior begins in which the gases are heated and further dissociated until at a point between H and I virtually all of the original FeO has been converted into Fe gas and all diatomic oxygen produced is converted into monatomic oxygen gas that is then heated further to 10,000K. Further mechanisms like ionization that can absorb heat are not addressed.

Figure 8 presents what happens if the software use instructions are disobeyed and only one phase is declared so that all the previous phases are "combined" (which contains the integrated solid/liquid data for FeO and Fe), a very similar curve results except the flat latent portion of the FeO two-phase vaporization, DE, changes into an "S-shaped" nature of a one phase conversion, CHF. This could introduce likely error that might be important if it were valid in any scenario. However, the formation of homogeneous liquids and gases is again worth noting *not* recognized at present. If these disobedient software calculations have any merit even though the materials are not existent, then at point C, the liquid FeO would start breaking up into the liquid and gaseous derivatives as indicated happens for oxygen in Figure 3 and would rejoin the prior curve at point F.

For purposes of understanding, recall that FeO is a frozen equilibrium. It appears like a stable material and its properties can be measured: density, specific heat, melting point,

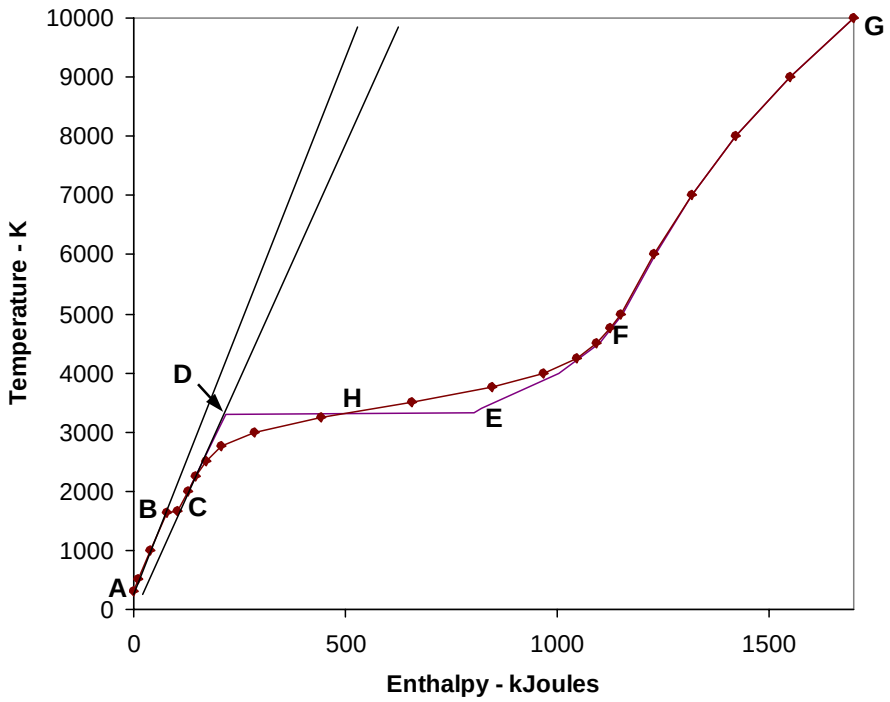


Fig. 8— *Heating single-phase FeO liquid-to-gas phase transition.*

and even what might physically appear like an apparent “boiling point” (that actually combines boiling and dissociating processes). However if one adds both an Fe_3O_4 solid/liquid data option (no gas form has been observed) and an Fe_2O_3 option (solid only, no liquid or gas forms have been observed) as separate phases in HSC, then HSC estimates the curve of Figure 9.

In Figure 9 points A to B again illustrates a portion of the heating curve for 1.0 kmole of solid frozen-equilibrium FeO as was shown in Figure 8 between its points A and B. When the separate phase options for Fe_3O_4 and Fe_2O_3 are included in the HSC calculation the ultimate room-temperature equilibrium is estimated at point E at -12.24 kJoules and comprises just two solid phases: 0.25 moles of Fe and 0.25 moles of Fe_3O_4.

Heating these two phases in equilibrium produces the curve from point E through D to point C. Adding further heat results in a latent (constant temperature) transition to point B akin to melting or boiling but both points are solids. The solid Fe_3O_4 phase is dissociating into solid FeO and releasing oxygen that is reacting with the solid Fe phase to produce more solid FeO and so at point B the local equilibrium is solid FeO. However, if the solid FeO at point A were “solid-combustible” (capable of rapid change in a spontaneous reaction like thermite), then its combustion would result in an abrupt vertical jump to point D where the formation of Fe_3O_4 would take oxygen from some FeO leaving some pure Fe behind. It would then cool to point E and release the 12.2 kJoules heat of combustion/formation.

So if one were to heat to the equilibrium situation at point E, ala Glassman’s teachings, to determine its adiabatic combustion temperature we would find its adiabatic self

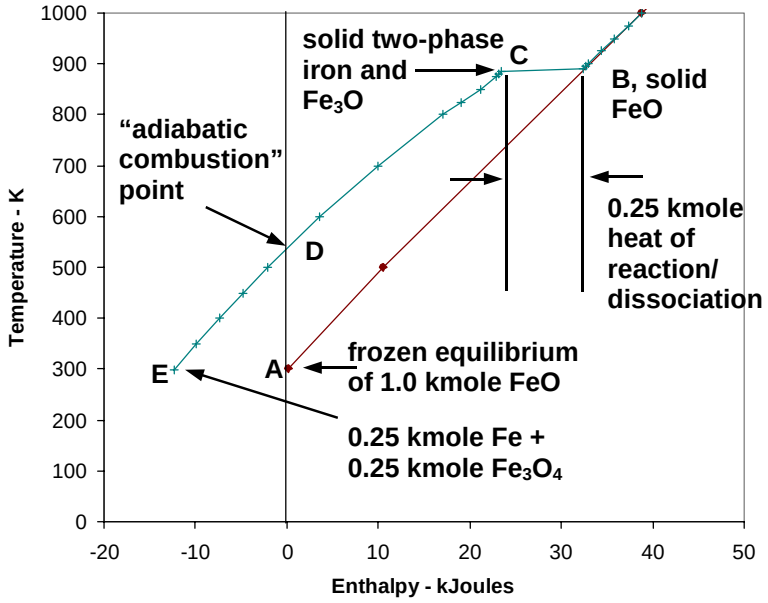


Fig. 9—*FeO combustion.*

combustion temperature to be about 540K.

Heating Fe_3O_4 (Magnetite)

The Fe_3O_4 story is partially similar to the FeO story. Like FeO, Fe_3O_4 is a frozen equilibrium, but it is apparently more durable at room temperature.[17] Figure 10 Part A exhibits HSC estimates for the heating of 0.333 moles of magnetite oxide (Fe_3O_4, having one mole equivalent of iron). This used the same phase setup in HSC as for FeO.

Basically, at point A it is entirely room-temperature Fe_3O_4. It warms until it achieves its melting point temperature ~1869K at point B, at which point it is still Fe_3O_4. It then undergoes a latent heating while it converts into liquid Fe_3O_4 at point C. With subsequent heating the liquid Fe_3O_4 warms to point D at ~3060K. Still further heating and the liquid Fe_3O_4 goes through a latent transition into liquid FeO and released gaseous oxygen. at point E at ~3065K. Further heating produces both a temperature rise and dissociation of the liquid FeO into gaseous Fe with lesser amounts of Gaseous FeO, O_2 and O_1 until the temperature merges with the dissociation/vaporization curve of FeO (absent extra gaseous oxygen) at ~3114K. The latent transition is complete at point F which is a slightly greater heating level than was the case for FeO due to the additional oxygen released from the Fe_3O_4 that is being heated in this example. Thereafter further heating beyond point F is ex-

[17] Fe_2O_3 is commonly cited as the most stable iron oxide, (because if you heat Fe_3O_4 or FeO sufficiently and slowly cool them, they will tend to produce Fe_2O_3. However, either can be quenched to form a frozen equilibrium that will persist for long periods of time.

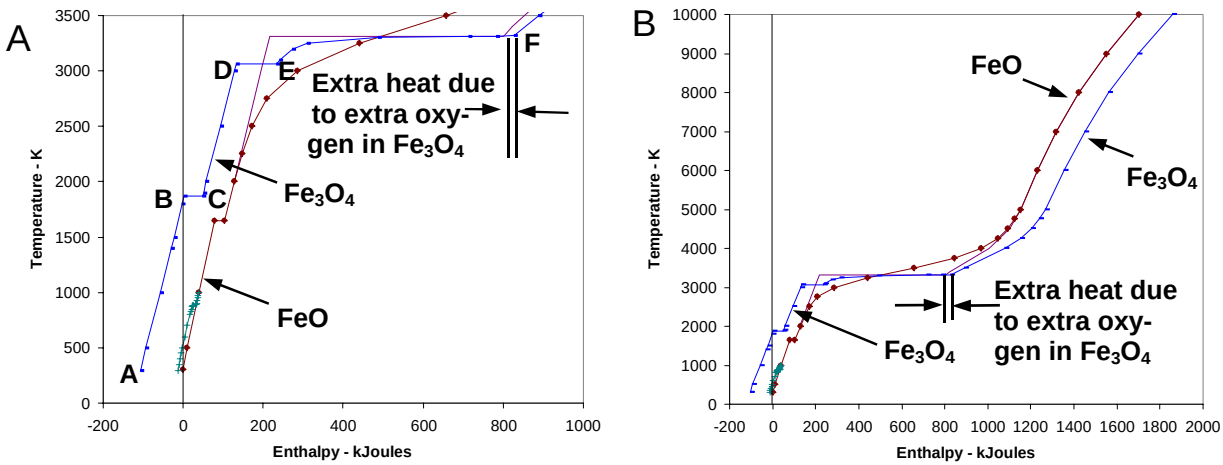


Fig. 10— *Heating Fe_3O_4 to high temperatures.*

hibited in Figure 10, part B, and it replicates the heating curve for FeO gases at high temperatures shifted again to higher enthalpy levels due to the extra oxygen heat capacity produced in the dissociation.

Heating Fe_2O_3 (Hematite)

Figure 11, shown in two scales parts A and B, exhibits HSC estimates for the heating of 0.5 moles of hematite oxide (Fe_2O_3, containing one mole equivalent of iron). Here Fe_2O_3 is not a frozen equilibrium, it is stable.[18]

Basically, at point A it is entirely room-temperature solid Fe_2O_3. It can be warmed until it achieves the dissociation point temperature at ~1659K, at point B, at which it is still solid Fe_2O_3. It then undergoes a latent heating while it converts into solid Fe_3O_4 at point C and releases some oxygen. With further heating the solid Fe_3O_4 then behaves much the same as Fe_3O_4 did but with a small amount of additional oxygen that requires a small amount of additional heat beyond that for plain Fe_3O_4, and that shifts the curve at higher temperatures another small amount to the right (to greater enthalpy levels).

It is not known to this commentator whether the transition from Fe_2O_3 to Fe_3O_4 occurs in only two separate phase regions as this calculation assumed or whether the Fe_2O_3 and Fe_3O_4 can be homogeneous such that a single phase calculation might be appropriate that would produce an "S' shaped rather than the latent transition curve. However for the uses to which these data are put herein, the distinction is not critical to the combustion consequences. Further study by more astute commentators is desirable.

The Grail Finale

Portions of the curves of Figures 4, 6, 9, 10 and 11 are all related and can be shown

[18] See footnote 17. When HSC calculates the equilibrium for Fe_2O_3 it reports Fe_2O_3 .

calculations done with min amount of oxygen as the stoichiometric situation should approach the worst case. However, one is also cognizant of the fact that in many cases off-stoiiometric scenarios are the most explosive or combustible.

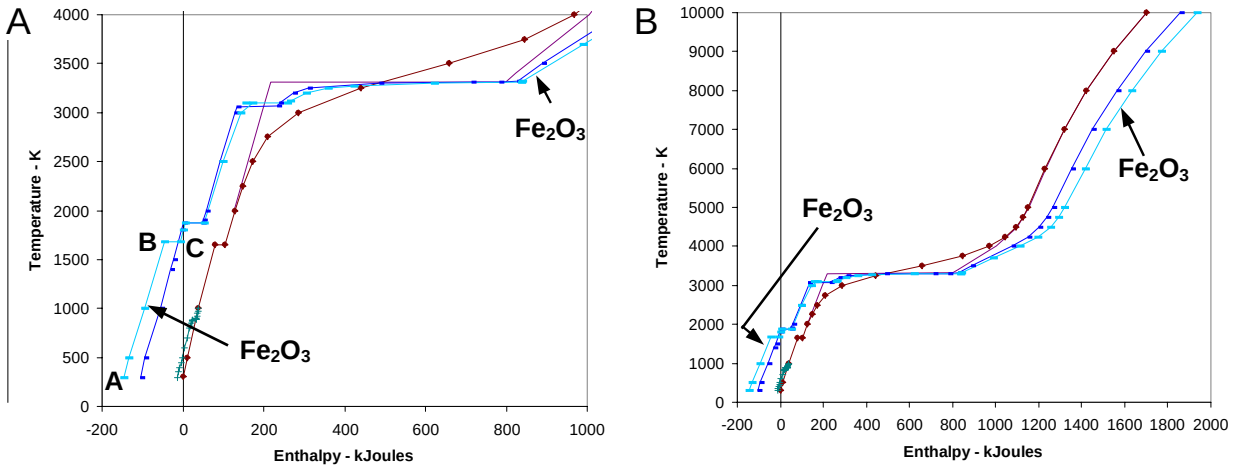


Fig. 11—*Heating of Fe_2O_3 oxide to high temperatures.*

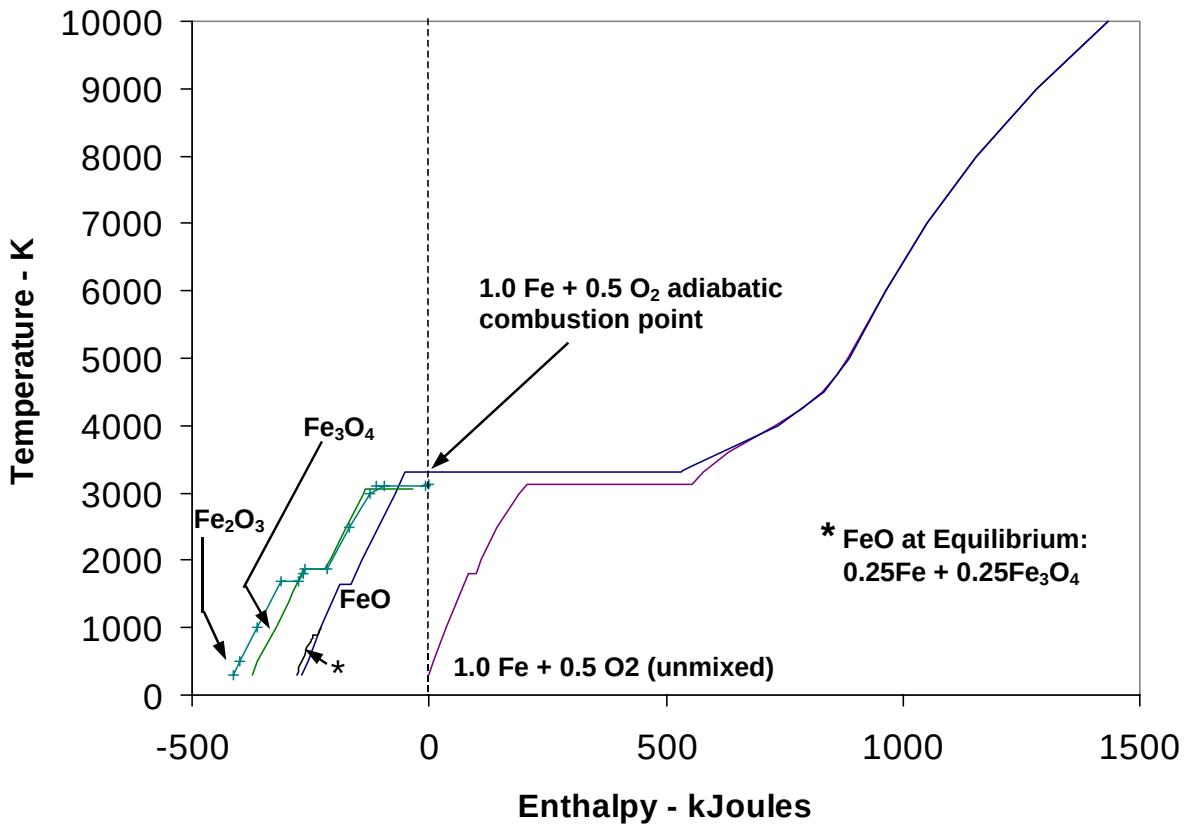


Fig. 12—*Heating/cooling of maximum composite grail results.*

in the composite curve of Figure 12. When reading left to right, one is approximately worst-case heating the maximum sections of the three oxides heating curves (the upper curves) to recreate combustion conditions and then beyond that to 10,000K for FeO. Nestled beneath

them is the summed heating curve for iron and stoichiometric oxygen to produce FeO the two portions of which are heated separately to 10,000K. Fortuitously they essentially join at the common point 10,000K and even below. When reading from right to left one is recreating the after-effects of extreme temperature. With adept quenching, one can theoretically trap specific circumstances (equilibrium in a local or frozen sense if not truly chemical thermodynamic equilibrium) that develop including the formation of the actual oxides.

One must stipulate: the initial suggestion that "this thermodynamically consistent approach be used for discussing combustion of metals and alloys" was prescient for one can employ this format to mighty good advantage. By choosing points and pairs of points this curve allows for the estimation of standard and non-standard adiabatic combustion temperatures (ala Glassman [***11***]), burn ratios and even better rating parameters at the melting point and boiling points and at nonstandard alternative temperatures for elevated temperature applications, and both standard and nonstandard enthalpies of combustion and formation. And it illustrates when burn ratios should be based upon the heats of combustion of the FeO oxide and when larger heats of higher oxides might be important.

Furthermore more sophisticated advanced "burn ratios" can be easily inferred based upon the amount of heat transfer one might estimate [***18***]. For example, one can flip the data about any vertical axis (e.g. zero enthalpy or an alternative) and argue that if the metal combusted to the adiabatic combustion temperature (a worst case condition) and knowing that heat flows from high temperatures to lower temperatures, that the maximum heat transfer possible would be between two specific points on Figure 12. More scholarly effort may identify still other useful parameters and techniques.

The Hits Keep Coming!

Even beyond the uses cited for the Figure 12 curve (or its successors), one can use HSC software (or presumably other software packages) to estimate an even more sophisticated limiting practical combustion thresholds. Consider an iron wire that is burning in a situational equilibrium (meaning its initial ignition energy has decayed into a "pass-through heat") and that each droplet that falls has received the pass-through heat from a previous droplet and transferred the same amount to the next droplet, that all preheat "in" has been matched with a preheat "out". Finally assume the combustion is adiabatic. Hence what is the limiting amount of equilibrium combustion necessary to sustain propagating molten droplet combustion?

This is very much like seeking an even more sophisticated burn ratio in that the original version assumes an amount of iron has combusted and released an amount of heat, then relates that heat to the amount of iron it could melt or boil assuming all the heat is available. The traditional iron burn ratio estimates iron that burns to form FeO oxide will release heat sufficient to melt more than five times as much plain iron. However, if the molten slag from a mass of adiabatically combusted iron were to be placed in contact with a mass of room temperature iron then as it transferred heat into the iron warming it, the temperature of the slag would decay, and heat transfer would cease when the slag and iron

	O2	Enthalpy	Fe	FeO	Fe/FeO
	kmole	kJoules	kMole	kMole	
	0.25	-40.36	0.5	0.5	1
	0.2	-17.79	0.6	0.4	1.5
	0.175	-6.508	0.65	0.35	1.857143
	0.162	-0.6408	0.676	0.324	2.08642
~threshold →	0.161	-0.1894	0.678	0.322	2.10559
	0.1605	0.03623	0.679	0.321	2.115265
	0.16	0.2619	0.68	0.32	2.125
	0.156	2.067	0.688	0.312	2.205128
	0.15	4.775	0.7	0.3	2.333333
	0.125	16.06	0.75	0.25	3

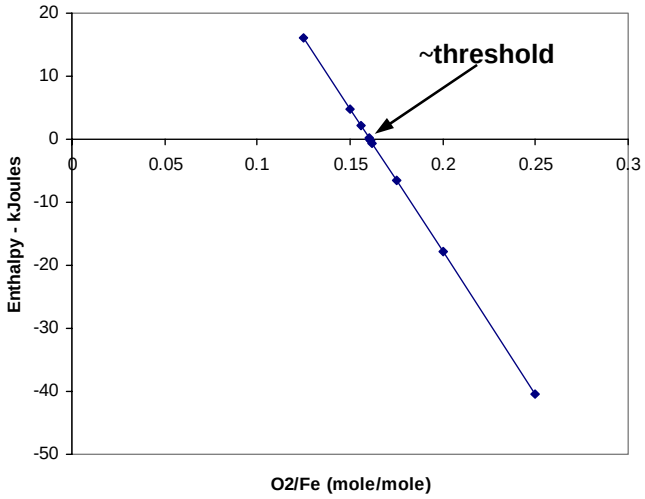


Fig. 13—*HSC calculated burn ratios.*

reached a common temperature. This is the second law of thermodynamics. Hence not all of the heat in the slag would be available to melt iron, and therefore less than five times the amount of iron could be melted meaning iron is less flammable than the original burn ratio suggests. HSC can fine-tune the math so that perhaps a better burn-ratio can be estimated.

Figure 13 shows the result of a series of HSC calculations in which the amount of oxygen reacted with iron was progressively reduced until the resultant temperature with no net heat added or released produces a temperature one degree greater then the iron melting point. The calculation allowed for a full compliment of gaseous species (Fe, FeO, O_2, O, and the obligatory trace Ar), and three phases of solid/liquid species (Fe. FeO, Fe_3O_4, and Fe_2O_3). In each cited data point, only Fe and FeO were produced in significant amounts. In

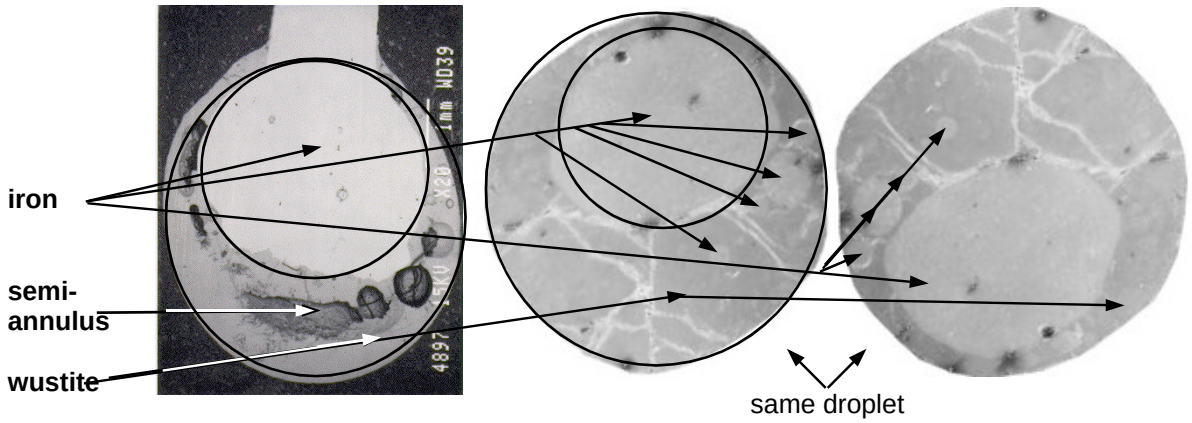


Fig. 14—*Actual quick-frozen iron/steel combustion droplets* [***17***].

every case the input Fe was 1.0 kMole. Input O_2 was varied to find the threshold where enthalpy was neither released (the negative values) nor absorbed (the positive values). The resulting Fe and FeO fractions are listed for each input condition along with the Fe/FeO ratio in the last column. This last column indicates the amount of FeO produced (0.322 kMole) the amount of Fe melted (0.678 kMole) suggests the more precise burn ratio is about 2.1 not the 5.1 value estimated with more primitive means. Of course, this is a worst case estimate since real-incident combustion would experience a number of heat losses.

Indeed early (1995) brief and crude rapid-quench testing of actual combustion droplets that doubtless experienced additional heat losses produced the results of Figure 14. Be advised an attempt to publish the paper with these photos in ASTM STP 1319 was intensely opposed by a contingent of workers led by one editor for the volume that prevented its publication therein, and they are available only because a corporate publication made the paper available [***17***] though it has experienced much disdain ever since. A rough estimate of the amount of oxide to pure iron in the droplet based upon spheres of the relative size as indicated and adjusted for room temperature densities of Fe (7.874 g/cc) and FeO (5.74 g/cc), suggest the attached droplet (left) has a Fe/FeO (burn ratio) of about ~1.33 or greater (voids taken as solid), and the detached droplet on the right has an Fe/FeO ratio of roughly 0.477. The value for the attached droplet would be larger if the void space were subtracted. The value for the detached droplet suggests that not all of the molten iron detached. This writer submits these data offer valuable insights into iron combustion warranting more study and that there is much more to exploit.

Mea Culpa!

In this writer's earlier tyro efforts (his struggle) to generate a composite graph (thermal profile) with both the NASA CEA and HSC software [***10,15,16,18***], little or no astute effort was directed to phase issues and there were doubtless other fledgling bungles. Apologies are offered for that. And yet to a large extent, those fledgling attempts at produc-

ing thermal profiles curves were very similar to these presumably more valid curves herein. A sensitivity to the phase issues to the extent achieved herein is doubtless an improvement over those efforts however both appear to be improvements over the more approximate ways burn ratios and other data have been calculated in the past. Both present data this worker would have relished in his oxygen hazard evaluation days.

Oxygen safety practitioners are cautioned to keep this in mind when considering any of these results that should still be considered preliminary. However hopefully the inherent value of these data when finally vetted and accepted should finally be clear.

What Does All This Mean?

The precise issues with phases in NASA's CEA for Applications software are not well-documented nor easily understood. However as noted the software and others like it are a challenge to use and attempts have produced numerous thankfully nonfatal errors. This exercise argues the results of the CEA efforts are not worthless nor unattainable even though potentially still flawed. However, this argues that HSC and doubtless other software manages phases with more clarity than CEA. To repeat again, the "grail" of Figure 12 can allow at least some phase issues to be easily explored. Figure 12 is presumably now a more sophisticated and reliable indicator of iron combustion even though it bears a remarkable similarity to earlier much less astute efforts to plumb the depths, to climb the learning curve of this theory.

In this analysis the Figures may still be flawed, but certainly can still be improved. They may warrant some perhaps even extensive adjustment when (if) the right sage people finally vet them rather than disdain them. But they may already be quite useful also and warrant exploration by the oxygen safety community. Nonetheless, without a doubt and with concurrence from highly skilled associates, one can assert there is an ultimate curve(s) that *can* be established and that it will almost certainly look very much like Figure 12 and should be something of a grail to this oxygen safety practitioner among others who (for unseemly reasons) may not yet know it. This is the kind of work product that this commentator argues (indeed, refers to its absence as "dereliction") that ASTM G4 should have been seeking to generate and validate, and vet, and autopsy and add to its education program for the past 25 years. Iron, in particular, is the main material in use and one needs a degree of fluency in its understanding. However, aluminum (due to its high risk factor) and copper alloys (at least in part because of unsuspected risk in its alloys with reactive metals most especially aluminum [***18***] should also be studied as a minimum. ***Every*** oxygen practitioner should be familiar with and have access to the corresponding grails for at least these three classes of metals and their behaviors (and have reader utility software for them as well).

Figure 12, ideally with reader software, allows even tyro oxygen safety practitioners to extract non-standard burn ratios (BRs) and understand why the iron BRs should be based upon FeO oxide heats, but it allows estimates of nonstandard traditional burn ratios in terms of starting or ensuing temperatures other than room temperature, and it allows for new and more effective burn ratio formulations that can aid incident investigation and system design that may result in fewer incidents and investigations. It allows extracting the adiabatic com-

bustion temperature. It allows nonstandard heats of combustion and dissociation and their hybrids to be estimated. And more.

Furthermore all of these grails and their estimates can be taught and learned even by rank-and-file (un-lettered) practitioners in the context of a CE course to wit G4's *Fire Hazards in Oxygen*. Similar vital insight is doubtless possible for other non-oxygen oxidants that are much less well-known than oxygen for which the empirical testing bases are scant-to-non-existent. Consequently it is a challenge for this oxygen safety practitioner to respect the lackluster past 25 years of G4's efforts that have appeared to ruminate over angels on a pin, academics and cosmetics and fattening CVs rather than life-saving practicalities. Meanwhile, the writer has been shunned for these same 25 years during which a lack of energy in the committee has been so often lamented. It calls to mind the case of the man who killed his parents then sought pity on the basis of being an orphan.

Is the lackluster because commercial or political interests seek to tilt practices to their will and advantage? Have the self-appointed oxygen safety czars, in some cases academics suffering Dunning-Kruger Effect [***19***] overthrown consensus, "screwed the pooch" and become locked in denial? Has corporate memory loss forgotten or disdained how the G4's greatest hits came about so long ago? Has G4 simply gotten lazy? Or has planned hazzard become a strategy akin to planned obsolescence?

This worker has struggled through out the second half of G4's history to contribute while G4 has reclused and intrigued, ...repeatedly. This worker has freely admitted to being less than well suited to undertake a cause as complex as thermo-chemical equilibrium (TCE). But no one else has stepped up. My early efforts to rescue and resurrect TCE approaches may be a foundering effort shot full of flaws, but even if so, nonetheless point to a far more useful tool than many, perhaps all, of the experimental word-salad, and at times politically biased, papers published in G4's current forum. And if G4 has become this jaded, if G4 is too bored to take its mission seriously, then things need to change, for G4's days are numbered, ...and unless that is a real underlying goal, that may just be another reason for why things are the tragedy they are.

Closure

This latest struggle with thermo-chemistry and software again offers arguments for its exploration and development within industry academia and ASTM Committee G4. It is not as dangerous as some claim artificial intelligence will be.

Hopefully this effort to identify and cope with at least some of the phase issues in a limited perspective suggests that the problems they produce are not intractable. Nor have they totally disqualified early efforts. TCE software provides thermal profiles that may not be precise for every scenario conceivable but, very importantly, they are nonetheless meaningful and in time may be fine-tuned as their complexity becomes more familiar. They in turn allow for the extraction of other parameters (new burn ratio formulations in particular) that are very pertinent to the ranking and therefore selection of materials for oxidant services. These rankings may not be perfect but in time can be as useful as the present formula-

tions that have served so helpfully in the past.

There is a dearth of simplified tutorial on these issues and they need a skillful championing that can talk technical to the lettered among us while talking turkey to the rest of us. ASTM Committee G4 leadership has disdained this pursuit (whether they are daunted or arrogant or otherwise distracted?). To repeat this commentator interprets that as a dereliction of duty.

The speculation herein (called speculation only because the writer's talents are in every case unable to proclaim great certainty, but also out of "an abundance of caution") may provide much needed context to enable and stimulate the oxidant safety community to plumb the potential benefits of this material. This assertion is made from a background of decades of oxygen system design and material selection and incident investigation. This writer would have treasured the ability to tap data from thermo-chemical profiles to supplement other data and experience. The absence of this effort from either reluctant elements of the oxidant safety community or even more conspicuously from the public-service ASTM Committee G4 is beyond tragedy. Oxidant related incidents and deaths continue, and some have been of grand scale, and they raise concern as to whether the right people are doing the right things.

References

[1] Steinberg, T. A., Wilson, D. B., and Benz, F., **"The Combustion Phase of Burning Metals,"** *Combustion and Flame*, Vol. 91, No. 2, 1992, pp. 200-208.

[2] Glassman, I., **"Metal Combustion Processes,"** American Rocket Society, ARS Reprint No. 938-59, New York, 1959, 43 pages.

[3] Benz, F. J., Steinberg, T. A., and Janoff, D., **"Combustion of 316 Stainless Steels in High-Pressure Gaseous Oxygen",** *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Fourth Volume, ASTM STP 1040, Joel M. Stoltzfus, Frank J. Benz, and Jack S. Stradling, Editors., American Society for Testing and Materials, Philadelphia, 1989, pp. 195-211*.

[4] Steinberg, T. A., *Metal Combustion at High Oxygen Pressure in Normal Gravity and Reduced Gravity: Model and Experiment*, Ph.D. Dissertation, New Mexico State University, Las Cruces, New Mexico; University Microfilms, Inc., Ann Arbor, Michigan. 91-01023, 51-08B. Dissertation Abstracts, May 1990.

[5] Steinberg, T. A., Mulholland, G. P., Wilson, D. B., and Benz, F. J., **" The Combustion of Iron in High-Pressure Oxygen,"** *Combustion and Flame*, Vol. 89, 1992, pp. 221-228.

[6] Steinberg, T. A., Wilson, D. B., and Kurtz, J., **"The Solubility of Oxygen in Liquid Iron Oxide During the Combustion of Iron Rods in High Pressure Oxygen,"** *Combustion and Flame*, Vol 113, 1998, pp. 27-37.

[7] Wilson, D. B., Steinberg, T. A., and Stoltzfus, J. M., **"Thermodynamics and Kinetics of Burning Iron,"** *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eighth Volume, ASTM STP 1319*, William T. Royals, Ting C. Chou, and Theodore A. Steinberg, Eds., American Society for Testing and Materials, 1997, pp. 240-257.

[8] Wilson, D. B., Steinberg, T. A., and DeWit, J. R., **"The Presence of Excess Oxygen in Burning Metallic Materials,"** *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Ninth Volume, ASTM STP 1395*, T. A. Steinberg, B. E. Newton, and H. D. Beeson, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2000, pp. 145-162.

[9] Werley, B. L., **"The Great Excess-Oxygen Hornswoggle?"**, Self-published opinion, Public domain 2026, 41 pages.

[10] Werley, B. L., **"A 'Simplified' PC-Based Thermo Analysis of Iron During Combustion",** Personal opinion paper, *BWOpinion*, 2008, 50 pages.
[11] Glassman, I., *Combustion*, 2nd Ed., Academic Press, Orlando, 1987 [and several subsequent editions].
[12] Kuo, K. K., *Principles of Combustion*, 2nd ed., John WIley & Sons, Hoboken, NJ, 2005.
[13] Gordon, S., and McBride, B. J., *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications*, NASA RP 1311, NASA, Washingtopn, DC, October 1994.
[14] Gordon, S., and McBride, B. J., **"Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations."** *NASA SP-273*, National Aeronautics and Space Administrations, Washington, DC, 1973.
[15] Werley, B. L., **"A Comparison of CEA and HSC Software for Oxidant Safety Thermo/ Equilibrium Analysis"**, Self-published opinion, *BWOpinion*, 2010, 31 pages.
[16] Werley, B. L., **"Graphical Interpretations and Parameters for the Thermo-Analysis of Oxidant System Fire Safety"**, Self-published opinion, *BWOpinion*, 2010, 24 pages.
[17] Werley, B. L., **"A Brief Study of Steel Combustion Using Quick-Frozen Test Specimens"**, Presented at the ASTM Committee G-4 Fall 1995 Seminar (14 November 1995, Norfolk VA), Air Products and Chemicals, Inc., Allentown PA, 1998, 27 pages.
[18] Werley, B. L., **"The Aluminum-Bronze Conundrum: Slow-Motion Model Burn Ratios and Their Use"**, Self-Published Opinion, Public Domain 2022, 32 pages.
[19] Werley, B. L., **"Hazards of the ASTM/G4 Deplorable Peer Review Process: Personal Case Studies"**, Personal opinion, Public domain 2026, 27 pages.

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