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A "Simplified" PC-Based Thermo Analysis of Iron During Combustion[2]

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ABSTRACT: NASA Chemical Equilibrium software and JANAF data are used to generate detailed thermodynamic curves for iron and its oxides over a wide range of conditions of interest to oxygen safety. Key issues as to whether and when iron can burn as a liquid or vapor are explored as well as when iron slag inflation by combustion vapors may be possible. Perspectives and terminology for describing metal combustion are stressed such as "batch combustion", "transient/incremental/ partitioned (TIP) combustion", "pass-through heat", "equivalent heat of combustion", and "*in situ* heat of combustion" to make metal combustion more easily understood and analyzed. Apparently flawed existing analyses in the literature and apparent quirks found in the NASA software are examined that raise questions about its proper use, and its results including the results in this paper will require validation and verification in that context also.

KEY WORDS: CEA software, Gordon, McBride, JANAF, iron, combustion, batch combustion, transient/incremental/partitioned (TIP) combustion, equivalent heat of combustion, *in situ* heat of combustion, pass-through heat, excess oxygen, wustite, magnetite, hematite.

The thermodynamics and phase-change[3] behavior of metals are critical to the ways these metals burn and the hazards these metals can represent in oxidant systems. However, these behaviors during combustion are complex subjects that may be well appreciated by only a few, if any (and the writer is not among them). They are a source of much unreconciled debate and argument. Simple answers do not appear to be available to the wide assortment of Oxidant Safety Practitioners (OSPs) who might not be thermodynamicists nor metallurgists but who seek to provide safety to oxidant handling systems and need to know how metals burn. As the quest to determine these answers becomes ever more complex and obscure to all but a cadre of highly trained specialists, there is a need to simplify the thinking, if possible. This is one such effort to simplify at the risk of error that seeks to avoid as much abstract math as possible by employing far more analysis and words and more numerous figures than would tend to be or could usually be employed in a typical technical journal. Time will judge the extent to which it accomplishes this.

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[3]The precise meanings of words often used loosely in this field have been the source of much controversy. Phase-change behavior herein is taken to include all of the mechanisms of materials by which liquids and solids convert into other than liquid and gaseous states, including combustion, evaporation, boiling, dissociation, decomposition, sublimation and perhaps others.

OSPs have been long interested in the phase of burning metals. Those bulk metals believed to burn principally as liquids or solids have tended to burn more slowly and less destructively (less explosively) than those that are believed to burn principally as vapor. Vapor burners are therefore often viewed as categorically more dangerous to use for the construction of oxygen handling systems. There are, of course, materials that are even more dangerous than vapor-burning metals. However, this perspective presumes the oxidant is not uniformly incorporated in the material as is the case with the most aggressive of explosives (e.g. nitroglycerin and mixtures of fines or liquids of fuel/oxidant), but these materials are seldom used for construction. Similarly, it also presumes a separate oxidant is needed for a reaction unlike materials that can experience explosive decompositions (e,g. nitrous oxide or acetylene) that are also seldom used for materials of construction. While some metals may burn in more than one way simultaneously, thermodynamic analysis has been long and to some extent controversially used to assess any tendency for structural metals to resist combustion or to burn principally as liquids or vapors.

In many cases, those seeking to achieve combustion, specifically rapid combustions as for boosted explosives and rocket engine use have sought to predict vapor phase combustion, perhaps with a tad too much zeal. The prediction of combustion is very challenging to even the best and brightest. Nonetheless their efforts to analyze have been useful and are valuable.

More importantly, for metals, low combustion heat, in combination with high latent and sensible heat capacity or other unique properties, such analysis has also been used to *exclude* the prospect of rapid vapor-phase combustion and on occasion to even exclude the prospect of a liquid-phase combustion. This use is somewhat less controversial, though the actual analysis may sometimes be flawed. Uses of these properties in this way have been taken as rather good indicators of when either combustion category can *not* occur and that is very useful information to the OSP. However such analysis is much less able to infer when vapor-phase or liquid-phase combustion *will* occur because many parameters dictate when combustion of any kind is ensured. And the fact is that when any kind of combustion can not be excluded, it does not mean that that combustion will ever occur. OSPs sometimes use materials on the basis that possible fires will not occur, as well.

Iron is a metal that is used very widely in oxygen service, often in circumstances in which combustion could occur but probably will not, but it is typically considered to be combustible only in the liquid phase. This is based upon low heat of combustion, high heat capacity and several specific natures of iron that are interpreted as tending to prevent any vaporization. In addition, when experimental test-rods are viewed during combustion, they simply appear to be burning as a liquid. A droplet forms and grows and there is very little (but not zero) oxide dust cloud formed and no obvious flame. Finally, incidents involving iron have usually if not always been limited in scale. However, prudence demands caution, lest there be some specific scenario in which a rapid vapor-phase regime might lead to an unexpectedly severe event. This paper will highlight thermo data that suggest any degree of iron vapor-phase combustion is possible in any scenarios.

The topic of liquid-versus-vapor burning appears often in the metal-combustion literature. There has been substantial controversy about its significance and the precise ways to analyze such behavior. Some have attempted to predict maximum combustion temperatures and compare them to the metal “boiling point” (but should have been more cautious to stress

the precise vaporization tendencies) of the metals. Other have compared the heats evolved to the heats needed to vaporize the metals. These methods have also been disputed.

The need of a material to heat itself as a condition of combustion traces to the beginnings of modern combustion science and the work of Humphry Davy in 1817 [*1*][4]. It became of renewed importance to OSPs in the 1970s when Southern Research Insitute (SRI) formulated related "burn ratios". However, the value of these ratios (both the numerical "value" and the practical "value") has been disputed.

It is not merely the potential amount of heat evolved that drives combustion. Materials that have sufficient heat to vaporize themselves if completely combusted do not always completely combust, and the degree to which the combustion is incomplete is often described using the complex concept of entropy. Therefore the ability to burn (either as a vapor or even a liquid or solid) is driven by the "available" portion of the heat of combustion. But the lack of potential heat is a still more nearly robust (but not perfect) criterion on which to rule out combustion than is a lack of available heat.

Entropy is also the key concept that allows for the calculation of chemical equilibria of systems including systems undergoing combustion. The mathematics of chemical equilibrium calculations is daunting for many (including the writer) but fortunately there is modern software available that allows for such calculation and a number of papers published within the ASTM G-4 collegium and elsewhere have employed such software [*2-8*].

Gordon and McBride code {also variously referred to as McBride and Gordon code, Coefficients and Properties (CAP) and most recently Chemical Equilibrium for Applications (CEA)} is one of the first and most widely cited software packages. Leading commentators on combustion endorse its use [*4,9*], and it is employed in this paper on that basis with no intent to appraise its validity. It is currently freely available from NASA but it is based on ideal gas theory which is flawed at high temperatures or at temperatures too near the saturation condition and for some metal combustion, including iron combustion, the adiabatic flame temperature is indeed near the saturation condition. So there may be flaws. Caution! This software has exhibited numerous quirks that appear to have led to errors in past publications and which might plague this paper also. Therefore verification and validation of these results is needed. Nonetheless, use of this code will allow the avoidance of much math and any flaws will be left for others to assess. This effort will explore the implications of this code taking it as accurate. The software and its context are elaborated upon in Appendix A.

Finally, starting in 1992 [*2*], the phenomenon of massive excess oxygen (oxygen greater than that amount necessary to form the most stable oxides) in the molten slags of burning iron was first reported. A series of subsequent papers elaborated on this mechanism in substantial and complex detail, ultimately asserting and treating its validity as proven, and also often examining the thermodynamics using the CEA/precursor software.

The writer "ignited" a related thermodynamics controversy in the later 1990's when challenging the massive excess oxygen hypothesis. In a brief series of tests [*10*], he observed what appeared to him to be behavior that disputed the possibility of the large amounts of excess oxygen (beyond that known to be present in the eutectic point for wustite) that were being measured by others. Instead, he suggested it might be explained by less exotic mechanisms such as the simple inflation of the slag with a gas, possibly including gas in the form of vaporized iron (whether boiled or otherwise congruently or incongruently produced). However, a substantial group (substantial in size and qualifications) that had investigated ex-

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

cess oxygen was so confident of their hypotheses' validities, that some of their number strenuously opposed publication of the paper and largely dismissed its analysis and data. That opposition effectively grid locked the ASTM peer review process and ultimately prevented (censored in a practical sense) its inclusion in ASTM STP 1319. The paper was self-published in 1998 and has been cited in only one paper to the writer's knowledge, since. This paper will highlight data that bear on the massive-excess-oxygen controversy and more detailed background is included as Appendix B.

A later paper [*11*] provided compelling reason why inflation of steel (as opposed to pure iron) slag was not only possible but probable, but also presented strong thermo-based argument as to why iron would not develop vapors capable of inflating slag. These arguments against iron vapor formation are overviewed in Appendix C, and this paper will highlight results that argue inflation of pure-iron slag may be possible.

While this paper will employ the CEA software along with data from the JANAF tables to explore the thermodynamics of iron in combustion, it will also specifically focus on new ways (or at least ways that do not appear to have been previously published or found visibility in the literature) on whether it can burn as a liquid or gas, and whether enough of any gases that might form would enable inflation of the slag. Hopefully this will provide one of the more thorough and detailed and therefore simplified descriptions of iron combustion thermodynamics that has been published. A few cases of controversy and flawed or incomplete analysis will also be examined. The writer is not aware of any similar treatment in the oxygen safety literature and he wishes such a overview had been available to him three decades ago, providing of course that this very thorough perspective does not prove fatally flawed and is not validly opposed nor dismissed.

"Congruent" Terminology

Among the various controversies surrounding this topic is the liberty taken with words. This effort will doubtless take it own liberties, but several past problems warrant introduction here and more detailed follow-ups in the later sections.

"Boiling" has been a problem word in the past, not only within G-4 but in the combustion community at large. For many, boiling has come to exclusively mean the forced addition of heat to liquid causing its vapor pressure to exceed the ambient and leading to its rapid conversion into a "congruent" gas (a gas chemically identical to the liquid) and producing entrained gas bubbles in the liquid. However one dictionary definition of "boil" [*12*] is "to generate bubbles of vapor when heated" such bubbles of which might be "congruent" in the first sense, but it does not constrain them to congruence and in a second sense which is more liberal and broad merely cites: "a swirling upheaval".

This has lead to exchanges [*3-5*] as to whether metal behavior during combustion is really "boiling" (meaning in the first sense) when in fact it might be decomposing into different gases upon heating (in the second sense) even if the two senses are visually identical. This can be important because such a latter endothermic decomposition mechanism may or may not produce the latent heat character usually associated with boiling and instead may even lead to a sensible warming of the products.

Loose terminology is not uncommon in the field. The writer himself has similarly and recently observed [*13*] that whereas industry has identified a fire hazard commonly

known as a BLEVE (a boiling liquid expanding vapor explosion) in which the liquid involved is not boiling in the first sense of the word but is instead flashing (a process in which reduced pressure changes the thermodynamic state of matter and causes it to vaporize without the addition of forced heating, in fact to vaporize while it is cooling yet having the appearance of "boiling" in the first sense). Indeed, in modern air conditioning systems compressed and liquefied working fluid is sprayed into a low pressure system to yield "a swirling upheaval" but which is not being force heated, instead it is flashing, and it is congruently vaporizing under reduced pressure to actually produce reduced temperatures.

The writer has sought a concise term similar to "flash" that can reflect the more narrow meaning of "boiling" in the most common congruent sense but has not been successful.

Further, the writer has experience in industrial laboratory study of decomposing ammonium nitrate under forced heating to produce nitrous oxide for the medical industry. In this case, it achieves a temperature at which it is in "swirling upheaval" that looks like boiling but does not produce congruent ammonium nitrate gas, instead resolving completely into nitrous oxide and water. And yet this is also commonly referred to as "boiling" and he recalls it was fairly latent in its behavior.

The mechanism by which metals convert to vapor during burning is significant in determining whether and to what extent the phase change will limit temperature, and potentially hazard, *or not*. Indeed, for several metals the fact that they decompose upon vaporization (do not exist as a gas) has been taken to mean that they can not produce temperatures above the decomposition temperature (a.k.a "boiling point" in the loose sense) just as congruent boiling limits temperatures. Instead, it is taken that the heat of decomposition would reabsorb the heat of combustion much as latent heat of boiling would. This paper will explore the extent to which the NASA CEA program interprets these phenomena.

However, the means by which the literature determines some metal oxides do not exist as a congruent vapor are not clear. Heating (call it boiling if you wish) ammonium nitrate produces gases that can be analyzed and they do not contain ammonium nitrate. So one might conclude it does not exist as a vapor. It does not however decompose to its elements but instead forms two distinct individually chemically complex compounds. How do we know that Al_2O_3 does not exist as a congruent vapor? What forces it to self-destruct? And most importantly to this paper, what are the vapors of iron oxides, if any, and how do we know that? This is an important aspect which this writer is not presently equipped to explore. Therefore this paper will not seek to answer these key questions but will instead detail the respected analysis embodied in the CEA software results.

The Thermodynamics of Iron

Thermodynamic data that are available for iron and its oxides are not as robust as one might hope for. Data are scattered and the collection methods and resources are not always clear. And Iron and its oxides are difficult to test. Data are often taken from the JANAF tables but the gases included in them are treated as ideal and the rule of thumb is not to assume ideality when one is near a phase transition condition or at very high temperature. Iron combustion is near a phase transition for the oxide and the iron, also.

Nonetheless, Figure 1 exhibits available data for one g-mol of iron that has been extracted from JANAF Tables and CEA (using the HP mode) where the writer was adequately

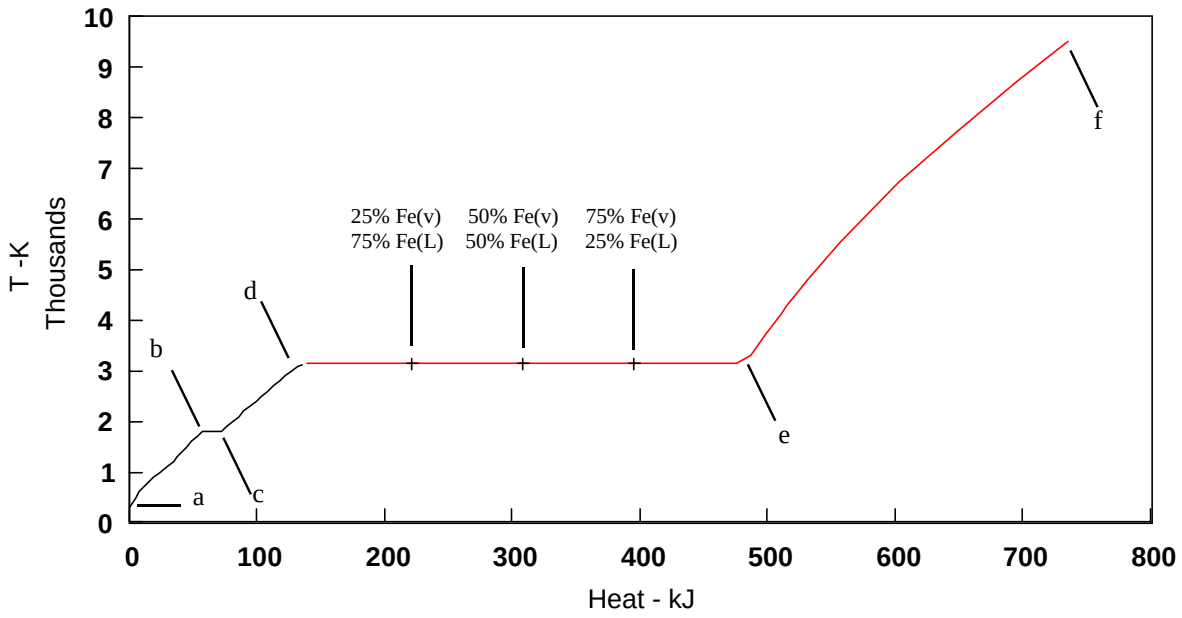

FIG. 1—*Thermodynamics of one g-mol of iron. From 298 K to 9500 K.*

skillful to tease the desired data from CEA and for heating up to about 9500 K. JANAF data in black depict sensible heating of the solid as shown from the room temperature point “a” to the melting point (1809 K) at point “b”, the latent heat of melting of 13.807 kJ is shown from point “b” to point “c” and then sensible heating of the liquid is shown from point “c” to the congruent boiling point at 3133 K per JANAF and 3138 K per CEA at point “d”. Point “d” is the lowest point at which the writer was able to extract thermo data from CEA. At temperatures above point “d” all of the data in red are from CEA software.

As the liquid is heated, its vaporization is latent and congruent (it produces a vapor of the same chemistry as the liquid), and when the latent heat of 349.6 kJ (per JANAF) has been added at point “e” it is completely Fe vapor. Flags indicate the vaporization predicted by the CEA software is linear in added heat, as expected. At temperatures above point “e”, the iron is entirely gas and its heating is wholly sensible. At some point ionization is yet another heat sink but that is not being addressed here.

The Thermodynamics of Oxygen

The thermo data for oxygen were all successfully extracted from CEA software, perhaps because oxygen is a gas over the entire temperature range of interest starting at 298.15 K. Figure 2 exhibits these data for five different quantities of oxygen that relate to the gram-mole of iron shown in Fig 1. The left most curve is for 0.42 g-mol of diatomic oxygen gas, the amount that would be present if the iron of Fig 1 reacted with it to convert 80 percent of the gram-mole of iron into wustite with 20 percent of the iron unreacted. The second curve is for the amount of oxygen, 0.528 gram moles of diatomic oxygen, that would be stoichiometric to the formation of wustite ($Fe_{0.947}O$) containing one gram-mole of iron (that is, one gram-mole of $FeO_{1.056}$). The third curve is for 0.666 gram-moles of diatomic oxygen that would react with one gram mole of iron to form magnetite (Fe_3O_4). The fourth curve is for

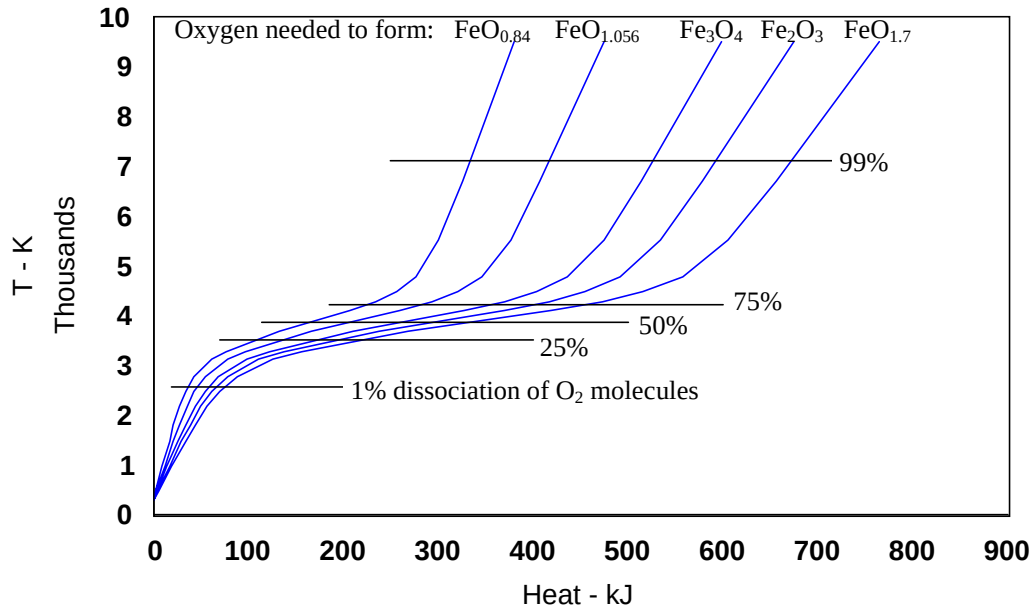

FIG. 2—*Thermodynamics of oxygen for five reactions with one g-mol iron. From 298 to 9500 K.*

0.75 gram-moles of diatomic oxygen that would react with one gram mole of iron to form hematite (Fe_2O_3). The fifth curve is for 0.85 gram-moles of diatomic oxygen that would react with one gram mole of iron to form the lower level of reaction reported by excess oxygen proponents ($FeO_{1.7}$) as reviewed in Appendix B . All five are shown for sensible heating to about 9500 K. The five curves are simply horizontal multiples of each other with constant factors.

Since the oxygen is a gas at these temperatures, its molecules and their collisions produce a distribution of velocities within it. Some are much higher than the average and when heated sufficiently, some of the fastest molecules achieve energy levels great enough for them to dissociate (to break apart) into atomic oxygen (from O_2 into 2O). CEA predicts the equilibrium that develops between the monatomic and diatomic oxygen and five lines through the five curves indicate the temperatures where CEA software predicts the dissociation of the diatomic oxygen is at the 1%, 25%, 50%, 75% and 99% levels (again ignoring ionization).

The dissociation occurs at rather high temperatures, largely above 2500 K, because diatomic oxygen is held together quite tenaciously. Indeed, the energy released when monatomic oxygen is reacted (combusted) with itself to form diatomic oxygen is significant compared to that released when it is reacted (combusted) with iron! It is this large decomposition energy that creates the “S” shaped nature to the curves of Fig. 2, in which the curve initially heats quickly to about 2500 K, then takes on a dramatically lower heating rate to about 4500 K in decomposing the oxygen entirely from diatomic to monatomic forms, then reverts back to a faster heating rate at higher temperatures. Again, these data are theoretical and apply to ideal gases and might change significantly if real-gas data were employed.

Indeed, even the most conservatively calculated burn ratios in the past that included the heating of the stoichiometric oxygen apparently employed ideal diatomic oxygen in the

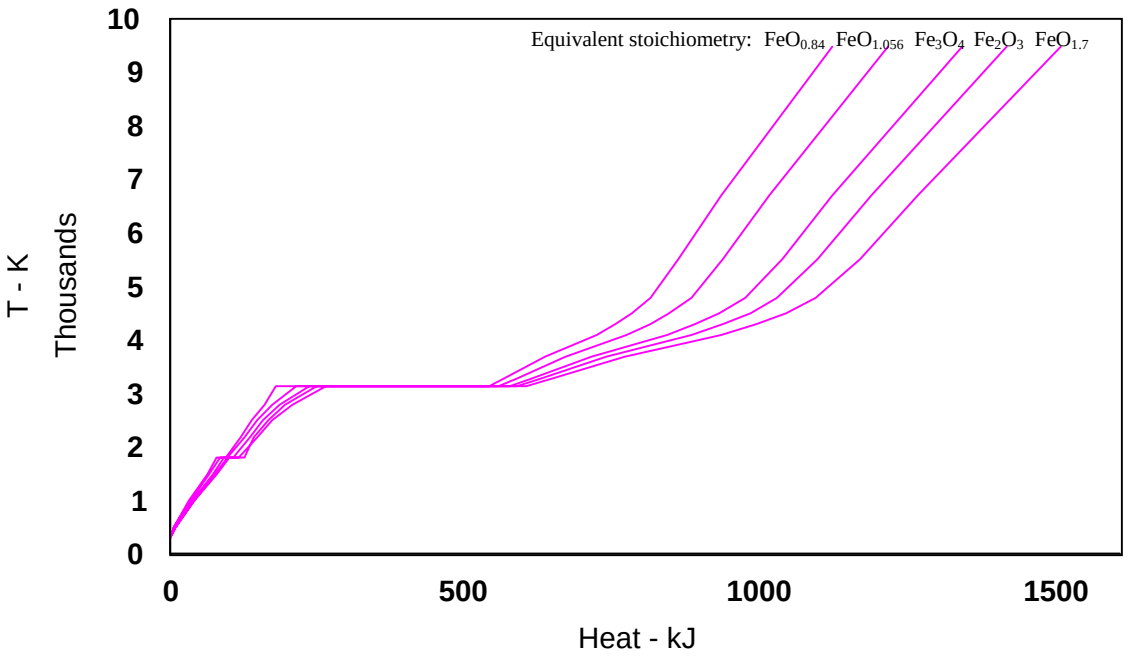

FIG. 3—*Thermodynamics of unmixed iron and oxygen.*
Various equivalent stoichiometries from 298 K to 9500 K .

sensible heating and may have error, not so great for the melting point burn ratio calculations but perhaps significant errors for the boiling point burn-ratio calculations.

The Thermodynamics of Unmixed Iron and Oxygen

Figure 3 combines the data of Figures 1 and 2 to exhibit the heating that would be required to heat unmixed iron and oxygen to corresponding elevated temperatures.

The Thermodynamics of Wustite, $Fe_{0.947}O$ (also $FeO_{1.056}$)

Figure 4 exhibits thermo data for wustite that contains 1 g-mol of iron under forced sensible and latent heating up to 9500 K. JANAF data in black depict heating of the solid as shown from point “f” to the melting point (1650 K) at point “g”, the latent heat of melting of 31.338 kJ is shown from point “g” to point “h”. JANAF data were not found for Wustite above the melting point (although data for liquid FeO are available) and so sensible heating of the liquid is shown from point “h” to merge with data from the CEA software at a temperature of about 2600 K, the lowest point at which the writer was able to extract thermo data from CEA. At temperatures above roughly 2600 K all of the data in red are calculations from CEA software.

The blue symbols were generated using the HP mode of CEA for the heating of wustite. The red curve was generated using the combustion HP mode of CEA for a mixture of one mole of iron with 0.528 mole of diatomic oxygen. The two sets of data reflected similar equilibria throughout, and so the “combustion” data are being shown to reflect the thermo properties.

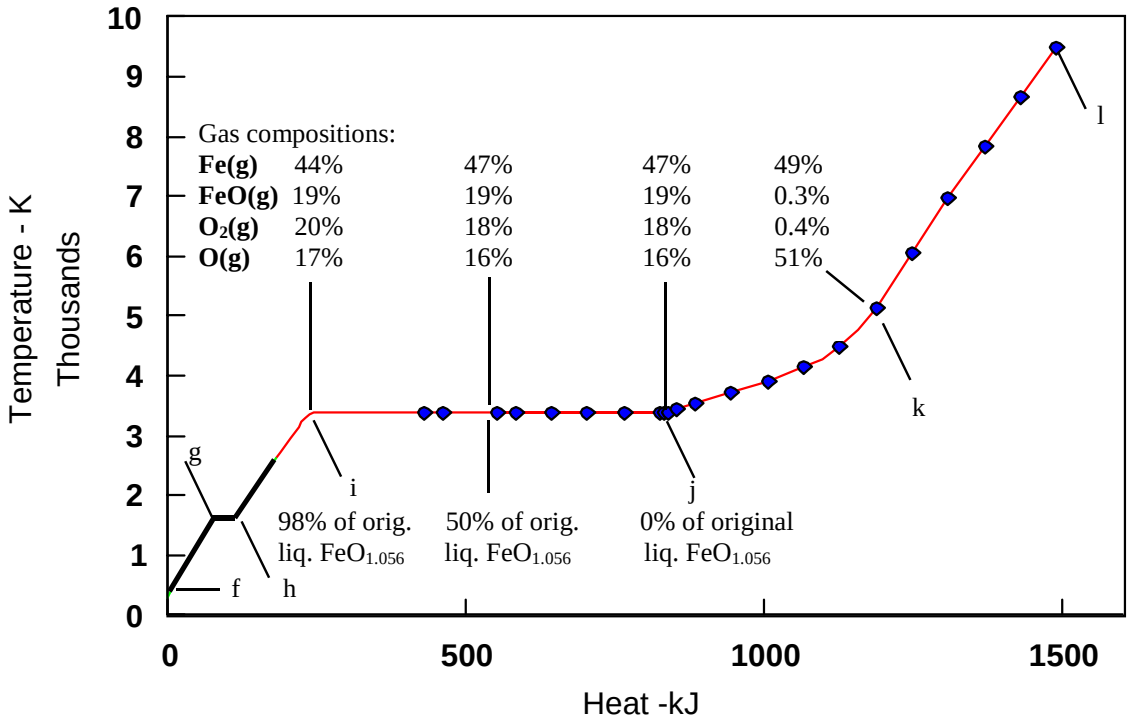

FIG. 4—*Thermodynamics of wustite ($Fe_{0.947}O$ or $FeO_{1.056}$). The curve is for 1.056gram-mole wustite that contains one gram-mol of iron (one gram mol of wustite itself contains only 0.947 gram-mol of iron).*

CEA predicts that as the liquid wustite gets hotter, its composition changes and ultimately gases begin to evolve at approximately point "i" at approximately 3390 K. At this point about 98% of the original wustite liquid is still present and the vapors formed include gaseous FeO and are approximately 44% Fe gas, 19% FeO gas, 20% diatomic oxygen and 17% monatomic oxygen. A temperature-controlling latent (insensible) heating region begins at point "i". Under further heating to approximately point "j", the temperature does not rise significantly. Furthermore the composition of the gases evolved changes only slightly, if at all. At point "j" the temperature is still about 3390 K, there is no liquid wustite remaining, and the vapors are about 47% Fe gas, 19% FeO gas, 18% diatomic oxygen and 16% monatomic oxygen. At the mid-point of the latent plateau, there is about 50% of the original liquid wustite present and the evolved gas composition is about 46% Fe gas, 19% FeO gas, 18% diatomic oxygen gas, and 16% monatomic oxygen gas.

At point "j", all of the liquid wustite is vaporized/decomposed, but nearly 30% of the original gram-mole of iron is still present as either real or apparent congruently vaporized FeO gas, and there is a similar amount (in moles) of diatomic oxygen present. Beyond "j", sensible heating again obtains and its slope then goes through two successive increasing natures.

Above the point "j" up to point "k" at a temperature of about 5000 K, there is approximately linear sensible heating and decomposition of both the FeO and O_2 gases. At point "k" there are predominantly monatomic gases remaining and only vestiges of the diatomic gases (less than one percent each). Above point "k", further heating is sensible and at a greater rate (lower effective heat capacity) because there is no endothermic decomposition taking place, and

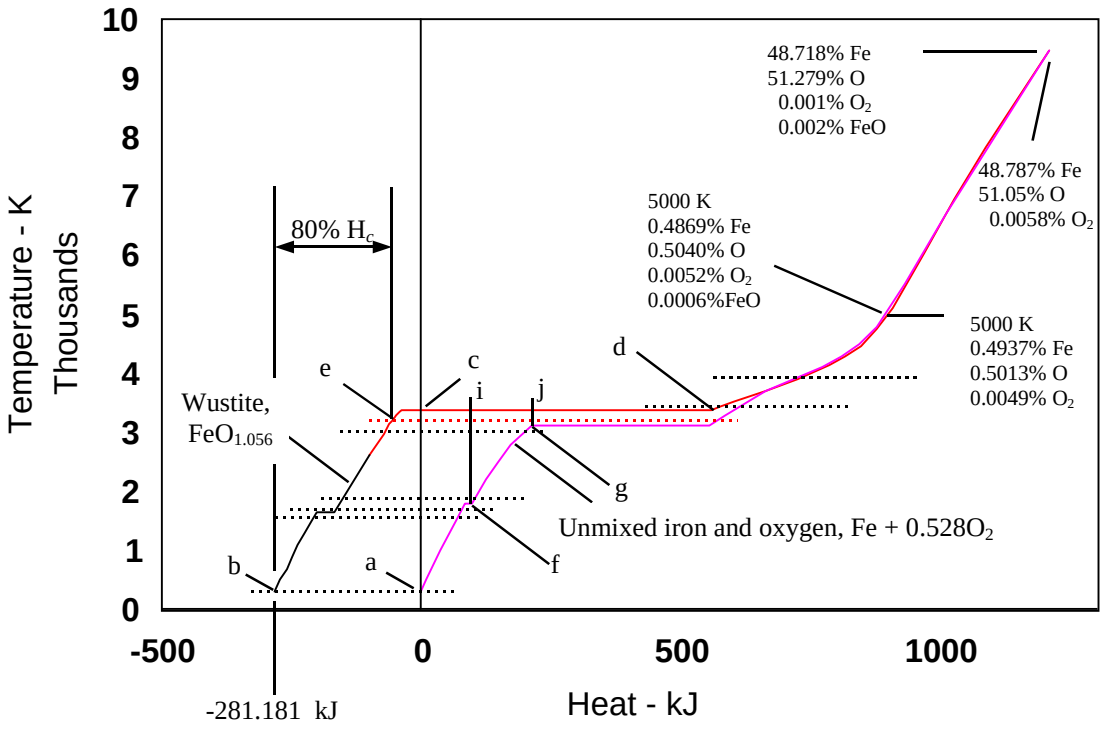

FIG. 5—*The combustion of one gram-mol of iron to wustite. From ambient to 9500 K.*

all heating is going into low-heat-capacity monatomic gases.

These data may suggest the decomposition of FeO gas is *not* a latent insensible process (however as a liquid it may behave differently). However, it also again begs the question: Is there a gaseous form of FeO as the software predicts?

The Combustion of Iron

Figure 5 combines selected data from Figures 3 and 4. In this case, the lower unmixed iron/oxygen curve of Figure 5 is shown again from Fig. 3 for the heating of unmixed stoichiometric constituents of wustite at a starting point of about 298.15 K and at a zero added-heat starting point. However, in addition, the data of Figure 4 are added as the heating data for wustite.

The starting point for wustite, itself, is shown translated in a manner taught to the writer by Michael Lanyi but which he did not use in a paper he himself was preparing at the time [*11*]. The starting point is plotted at -281.181 kJ which is the standard heat of formation, heat of reaction and standard heat of combustion for wustite containing one mole of iron based on the JANAF tables. If one starts with iron and oxygen shown at point “a” and burns it to completion, constraining it to form wustite upon cooling, and then cools it back to ambient, the heat release will be the –281.181 kJ separation as shown. The writer has not seen iron data plotted in this way before. Related plots are shown in both the Glassman [*14*] and Kuo [*9*] texts but they choose to plot the products to the right of the reactants.

This Figure 5 has some interesting properties. If one draws a horizontal line (like the

lower dotted line in black though the starting points for the curves at 298.15 K, then the length of the line between the curves is the standard heat of combustion. If one draws a horizontal line anywhere above these starting points then the length of the line from the point where it intersects the constituents curve and the wustite curve is the heat of reaction for those starting conditions, and for these particular reactants, it is also the heat of formation *for those equal starting and finishing conditions*. And if this reaction to exclusively produce wustite were possible to achieve through combustion (and the writer has achieved it at atmospheric pressure) then this would also be a "nonstandard" *in-situ* heat of combustion ($_{is}H_c$), that is to say a heat of combustion with nonstandard but equal starting and finishing temperatures. Indeed, any line drawn in this way would be an $_{is}H_c$, and in fact, the length of any segment that was a projection from any starting point on the unmixed iron-plus-oxygen curve for Fe + $0.528O_2$ to the projection of any point on the wustite curve would be the $_{is}H_c$ for those particular differing starting and finishing conditions.

This last observation begs for a simplified computer program similar to that previously proposed to ASTM Committee G-4 by the writer for the simplified analysis of adiabatic compression in real gases [*13*]. And such a draft program is in preparation for consideration and will be available. The writer hopes that G-4 will find it of sufficient merit to warrant adoption of something like it and expansion of it as an "as is", "use at your own risk" adjunct to one of its standards, perhaps G 94 on *Evaluating Metals for Oxygen Service*.

One can see how significantly the predictions of the CEA software vary for differing conditions. Note especially that at the highest temperature presented of roughly 9500 K the wustite and unmixed iron-and-oxygen curves are very close (they are basically the same compositions of Fe gas and O gas, and would differ only by an expected small energy of mixing and the formation of trace amounts of FeO and O_2), hence they lay virtually on top of each other. At this temperature, the heated wustite has virtually fully decomposed and dissociated to form a gaseous mixture of Fe and monatomic O atoms as is the exact same case for the unmixed gaseous iron and diatomic oxygen constituents (the diatomic oxygen of which has essentially fully dissociated into monatomic oxygen at that temperature). In other words, at this temperature there is no heat of combustion, no $_{is}H_c$, and the unmixed iron plus oxygen is not flammable relative to the same final temperature state. Combustion is excluded through lack of reaction heat.

Notice very significantly that the two curves also are still approximately equal at 5000 K, at which there is only a small amount (0.0006%) of FeO gas formed and on that curve and the corresponding reactants curve there are small yet much larger amounts of diatomic oxygen formed (0.0052% and 0.0059%, respectively). The oxygen is more difficult to break apart. This indicates that the heat of combustion of iron with oxygen is not too greatly different than the heat of combustion of monatomic oxygen with itself.

The numeric value of the $_{is}H_c$ goes through a maximum near the red dotted horizontal line located between the boiling point of Fe and the latent "boiling/decomposition" point of wustite, where Fe gas is reacting with oxygen, and it is much larger than the standard heat of combustion of iron to form wustite at room temperature. Figure 6 exhibits very approximate *in-situ* heat of combustion as a function of equal starting/ending temperatures. These data relate to the combustion of iron in an ambient at elevated temperature. This curve starts out with the standard heat of combustion of iron to form wustite, and exhibits numerous abrupt changes in value at phase-change points.

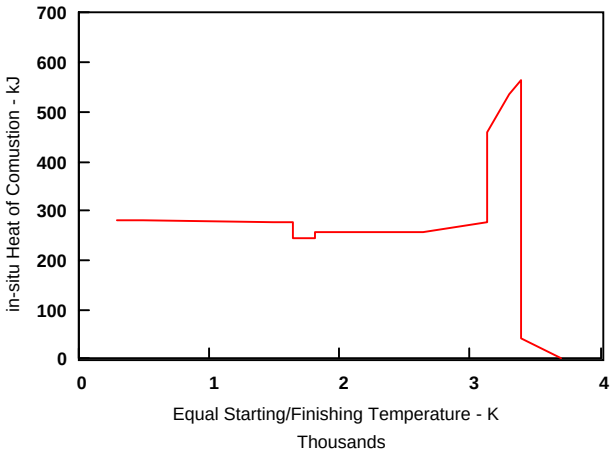

FIG. 6—*Nonstandard (in-situ) heats of combustion of one gram-mole iron to wustite versus temperature. Relative to Fig. 5.*

Adiabatic "Flame" Temperature and Vapor Fractions

The maximum uniform temperature that a burning metal, including iron, can produce is referred to as its "adiabatic flame temperature". For iron, for which so many definitional problems have been asserted, even this appellation is troublesome. There are numerous subtleties that accompany attempts to measure properties of combustion and many other parameters. At present many experts agree that iron does only and can only burn as a liquid, which if true implies it is without a flame (without a "glowing gaseous part of a fire") and, if this is the case, then it could have no meaningful "temperature of its nonexistent flame" but that does not prevent calculation of a maximum adiabatic temperature that can be produced in the liquid during combustion using the same approach as if it did have a flame and referring to it as the misnomer "flame temperature".

To calculate "adiabatic flame temperatures" [*14*] the traditional approach is to treat combustion as a series of snapshots. In the present case for "simple iron", at moment one, snapshot one, you have iron and oxygen. At moment two, snapshot two, after ignition the combustion has ceased, you have hot products. And these products then cool back to the starting temperature at moment three, snapshot three, to provide the heat transfer between point "a" to point "b" of Figure 5. During the cooling step, further reactions may occur. It is very difficult to imagine the bulk uniform conditions at the precise adiabatic moment two, right after initial reaction ceases, and the transient, perhaps rapid or perhaps slow, perhaps nonuniform, perhaps incremental route the combustion takes as it passes through the metal to get from moment one to moment two. However, it is often, but maybe not always, valid for one to take the products of combustion ($FeO_{1.056}$/$Fe_{0.947}O$ in this constrained case), and deduce a transfer back into them of the entire heat of combustion (standard or *in-situ* as applies), which is also the heat of formation and heat of reaction as the case may be, that is recovered from the cooled burned iron (-281.181 kJ in the standard combustion case) to find out where moment two might have been located on the thermodynamic curve for wustite $FeO_{1.056}$ (that is, $Fe_{0.947}O$ with one mole of iron). To be valid, this demands that there are no irreversible reactions involved.

As will be reviewed later, this is much different than transferring the heat of combustion

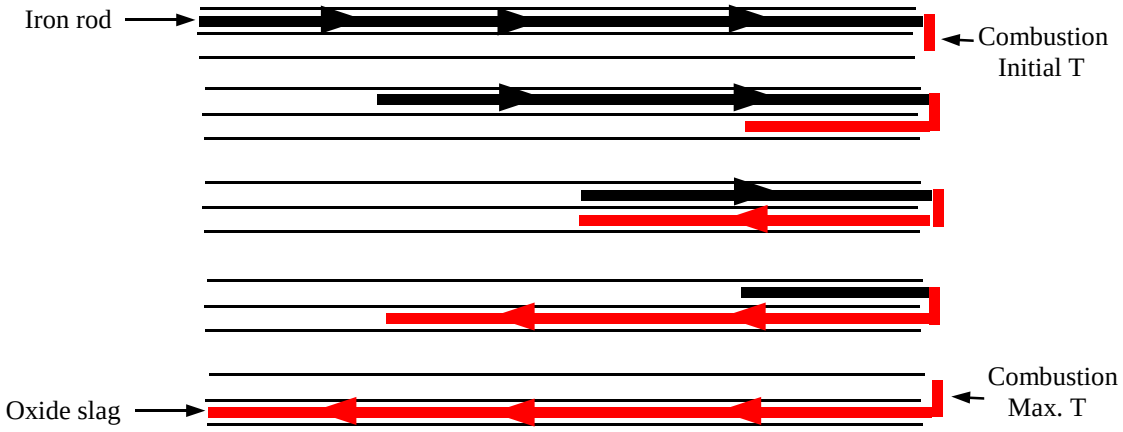

FIG. 7—*Schematic counter-current heat exchange for burning iron rod*.

into the unreacted iron as occurs during transient incremental nonuniform combustion and as is done in calculating burn ratios as has been lamented variously [*3*]. This is more like Lanyi [*11*] was doing as reviewed in Appendix C. To put any heat from a batch combustion step *into* any unreacted iron, it must be transferred *out* of previously reacted iron. For a discrete batch, or sub-batch, incremental transfer, the combined materials would ultimately equilibrate at an intermediate temperature possibly but not always well below the adiabatic flame temperature that would result from a uniform batch combustion of an entire specimen. There would be some optimum fraction of iron combustion that would yield the maximum combined average batch temperature. In order to heat unreacted iron and stoichiometric oxygen to higher temperatures would require partitioning perhaps as in a sophisticated counter-current heat exchanger.

Counter-current heat exchange, Figure 7, is one of the more efficient kinds of heat exchange. However, with it only the latter transient combustion of the last portion, the last increment of the iron would achieve the highest temperature (but possibly as high or higher than the batch adiabatic flame temperature from which this fraction may go on to combust to even higher temperatures or greater vapor-combustion fractions) but these highest nonuniform temperatures would be a transient effect (or transient/incremental/partitioned (TIP) combustion). Nonetheless, in real incident scenarios heat may incrementally transfer from burned fractions of the iron back into unburned fractions and yet it may not provide heat capacity that limits the ultimate temperature (which will be examined in more detail later), but when “normal” equilibrated batch combustion is complete, at moment/snapshot two, all of the heating is taken as uniform throughout all of the products.

Graphically, in Figure 5, one can draw a vertical line through point “a” which is 281.181 kJ from the room-temperature point “b” for the moment/snapshot three $FeO_{1.056}$. This point happens to be at the origin. As the product $FeO_{1.056}$ is warmed from point “b”, it will ultimately intersect this vertical line when the full standard heat of combustion has been transferred uniformly to it. The intersection occurs at a point “c” at which CEA software predicts both dis-

sociation and evaporation of the $FeO_{1.056}$ would yield at least a fractionally vaporized FeO/iron/O_2/O gas fraction at one atmosphere. Indeed, at point "c", about 6.8% of the original $FeO_{1.056}$ has vaporized and for a liquid-to-gas volume change ratio of 100-800, this would be sufficient to inflate the slag significantly. This is taken as "batch" moment two (whereat initial combustion would cease), the point at which the adiabatic flame temperature is manifest, and since there is elemental iron and oxygen present, the CEA prediction is that the iron is not completely converted to iron oxide at this point. It must be cooled somewhat before any final reaction can occur. However, the decomposition of $FeO_{1.056}$ and even more importantly, its partial vaporization (including any congruent boiling fraction) to FeO do indeed limit the "batch" combustion temperature to about 3389 K, the latent plateau temperature.

One can similarly draw vertical lines through any point on the Fe-plus-oxygen curve through the $FeO_{1.056}$ thermo curve to identify the "moment one to moment two" batch adiabatic flame temperature for any preheated starting condition relative to a corresponding final temperature condition. This is equivalent to back-heating $FeO_{1.056}$ that is at the same starting condition temperature with its respective ${}_{is}H_c$. Note that any preheating of the reactants will place the vertical line to the right of the room temperature starting point and therefore it will intersect the $FeO_{1.056}$ curve to the right of the standard location at "c". Since there is a latent heating plateau in the $FeO_{1.056}$ heating curve to point "d", the final temperature will not change for substantial preheats but the amount of vaporized species in each will be greater.

The writer asserts that this adiabatic result, namely the presence of Fe vapor at point "c" implies there is sufficient heat of combustion in iron to allow for partial vapor-phase combustion, even during a uniform batch combustion, but to a much greater extent for transient/incremental/partitioned (TIP) combustion. On the one hand, this fractional amount of vapor-phase combustion might not greatly accelerate the combustion and hazard, but on the other hand, it would be more than sufficient in volume to inflate a slag bubble.

In this case, the traditional view that the gaseous reactants condense into liquid oxide during combustion would not fully apply. Since CEA predicts a presence of gaseous: Fe, O, O_2, and very importantly FeO gas, one could foresee Fe and oxygen partially forming gaseous FeO (with back radiation to the surface) and/or condensation of Fe and oxygen into liquid $FeO_{1.056}$ aerosol (and back radiation), as well as direct condensation of gaseous FeO into the bulk liquid $FeO_{1.056}$.

Therefore at least partial vapor-phase combustion cannot be entirely ruled out thermodynamically. However, Lanyi [*11*] (Appendix C) has prudently warned that real-world combustion is not nearly adiabatic and if his estimate of 20% loss were applied, then back-heating of the $FeO_{1.056}$ with 80% of the standard heat of combustion would occur at point "e" at which CEA software predicts an equilibrium composition in which 99.9679% of the oxide is liquid and the remainder has formed equilibrium vapors in the amounts 6.88% Fe(g), 7.80% FeO(g), 17.89% O(g), and 67.43% O_2(g). Due to the decomposition, the gas contains more molecules and therefore has more volume than would a purely congruently boiled vapor. For a liquid-to-gas conversion rate of 100-800, this would provide a total vapor cloud of only 3.5-25% of the volume of the liquid. It would pretty nigh rule out vapor phase combustion and significant bubble inflation. *Or would it*?

In Lanyi's warning, the lost batch heat is transferred to an external system. However, the kinetics of even a closed system may exhibit a similar transient effect resulting from partitioned temperatures during the transition from moment one to moment two. When there is a collection of reactants, the way in which the combustion proceeds can appear to provide transient heat

losses from the atoms that react earlier to the atoms that react later. If a pair of atoms combine, the pair heats but will transfer much heat to the remaining bulk — therefore only the final partitioned stages may exhibit any vapor phase character (if it is going to, the slag may abruptly inflate). Excess iron (iron beyond that necessary for stoichiometric reaction) can also be a heat sink.

However, just as Lanyi cautions us about external heat losses, and as we have been sensitive even to transient internal heat loses between one region of a specimen to another, we must also be sensitive to heat gains, even transient internal heat gains between one region and another. In the oxygen furnaces that Lanyi recounts, the iron is first melted by external means. In some cases torches or electric arcs are used. In other cases, oxygen is blown in to burn carbon and to bring the iron to a fully melted state, and in fact in preparing steel Lanyi has thoroughly described how carbon in the furnace is not only protective against reaction of the iron but actually forces any oxide present to shed its oxygen (reducing it to pure iron) until the carbon is reduced to a low level, and in fact the goal (for which there is a potent economic incentive) is to stop an oxygen blow when the carbon level achieves the desired level for a particular specification of steel.

However, depending upon the amount of preheating from torches or electric arcs or carbon combustion, the analysis Lanyi provides does not precisely apply to the blast furnace. His analysis applies more nearly for the usual laboratory test configuration (that starts near standard temperature conditions with a small localized ignition energy on the specimen tip) and not the scenario in a blast furnace (with bulk preheating of the entire iron batch). In a blast furnace, the iron is already molten when any oxygen combustion would obtain. It may be just-molten or it may be heated well above the molten point. The starting point for this combustion would lie on the segment “f” to “g” of Fig 5. The actual combustion (moment/snapshot 2) would therefore lie between the points “i” and “j” shown on Figure 5. As a result much greater heat losses can be endured with there still being a sufficient heat left over to promote at least a partial vapor phase presence.

CEA software also predicts the presence of a substantial amount of inert FeO vapor. Inert gases in a vapor phase combustion zone are well-known to often thwart rapid gas phase reaction, and perhaps this is also a reason for the lesser severity incident scenarios that have been seen with iron combustion. Indeed, in the many severe aluminum combustion incidents, many analyses have determined that the apparent lack of non-reactive gas dilution in the flame zone has been a key factor. However, there has been analysis that appears to argue that aluminum combustion vapors do contain numerous less reactive vapors than has been assumed in the past and that perhaps the batch or transient/incremental/partitioned adiabatic flame temperature of aluminum is not a constant that is fixed by a latent heat sink. This argues an analysis similar to this one would be of great interest for aluminum, if such an analysis is possible. The writer hopes to attempt such an analysis.

However this present analysis not only provides support for the prospect of iron vapor, but in addition oxygen vapor and FeO vapor, being present in sufficient amounts to provide a significant degree of vapor phase combustion and to even more convincingly inflate the slag that forms, especially if it were configured as is present on the bottom of a standard laboratory test rod during combustion. To inflate a slag droplet to 2.5 times its liquid size would require vaporization of gases equal to 1.5 times the volume of the droplet. And since most liquid-to-gas volume conversion rates run in the range of 100 to 1000, this would suggest only 0.15% to

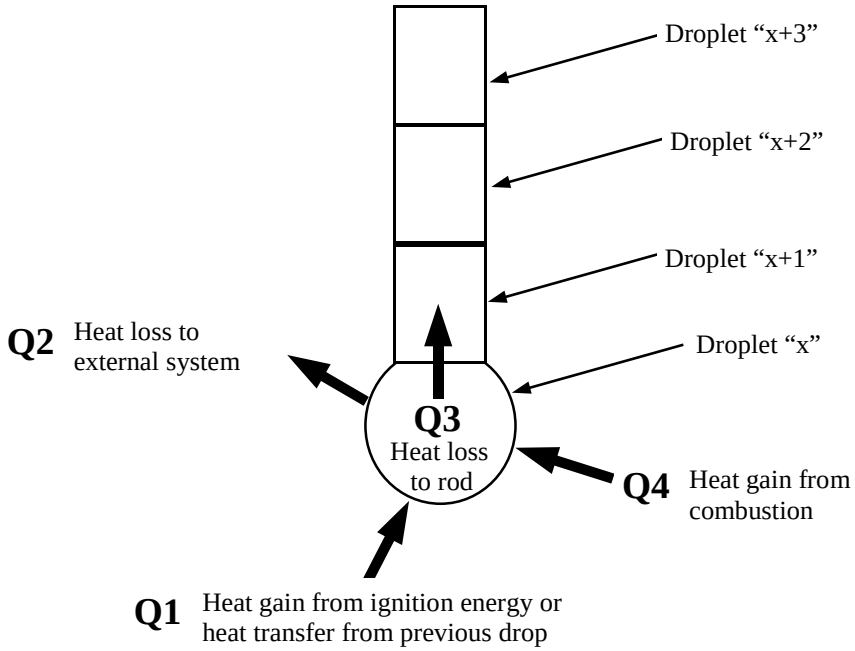

FIG. 8—*Heat losses/gains in rod tests*.

1.5% of the liquid would need to be present as vapor. The CEA software predictions are far above this level for slag at point "c" and all higher heat inputs. However, even more significant is that the CEA software not only predicts a presence of Fe vapor, but the presence of O_2, O and FeO vapor as well, so its conversion rates may be higher than usual.

Partitioned Combustion

The writer participated in speculation in earlier publications [*7*,*8*] that considered hypothetical "partitioned" heterogeneous combustion (combustion that occurs by more than one characteristic mechanism such as liquid burning combined with vapor burning, burning in several liquid or solid phases, etc.). This earlier speculation calculated burn ratios and proposed derivative parameters in calculating partitioned burn ratios (albeit for two partitioned "sub-batch" combustions). Burn ratios are frequently cited in inferring the exclusion of some combustion mechanisms where the thermodynamics do not seem to provide an adequate heat accounting.

There is experimental support for this prospect. Indeed with regard to magnesium combustion, there are published photos [*5*] that exhibit burning magnesium producing a cloud of apparently vapor combustion products but also resulting in a solid structure much like the initial magnesium specimen that may have reacted even as a liquid or a solid.

This earlier analysis has examined some of the shortcomings of burn-ratio analysis but the concept of partitioned combustion is still of interest. Partitioned combustion presumed that part of a specimen burns in one way at one temperature maximum (or perhaps heat input) and part of the specimen burns in another way to another different temperature maximum (or perhaps heat input). Is this possible to achieve short of using a counter-current heat exchanger?

Consider the standard bottom-ignition rod burning test of Figure 8. In the beginning, the

rod tip is externally preheated (much as is the iron in a blast furnace) and an ignition energy is introduced which in the case of iron typically melts it and perhaps heats it above the melting point. The tip continues to burn proving that the preheat is at least to the ignition level, growing a molten slag droplet on the end until the droplet becomes too large to support with surface tension, and it falls off. The entire rod is slowly going through a batch moment-one-to-moment-two transition, however between those moments, each droplet that forms on the tip of the rod is going through its own more rapid localized moment-one-to-moment-two fractional sub-batch transition in sequence.

After each droplet falls, some molten material remains behind and a new droplet soon grows and falls off also. This leads to succeeding droplet formation.

Consider the rod broken into sections that produce each of these droplets. Fig 8 exhibits a single droplet and the regions of the rod above that will become succeeding droplets. Initially, an ignition energy, Q1, heats the first segment. This is a heat gain. By the time the first segment ignites, a fraction of the heat energy will have transferred to segment two, Q3, possibly some even into segment three. This is a heat loss to the first drop, but it is a gain for the next drop. As the segment ignites and burns, some of its heat is lost to the next segment two and perhaps even the segment beyond. As the droplet burns, its transfers heat, Q4, to the droplet due to combustion, another heat gain, and if the entire specimen combustion were not adiabatic some of the heat would transfer externally, Q2, as an external loss.

After the initial droplet falls, we know for a fact through observation that the Q3 heat losses from the previous droplet were heat gains for the succeeding droplet. We know it because the tip of the rod is visibly hot and partially molten. Furthermore we know the heat loss/ gain was equal to or greater than the ignition energy for the next segment of the rod (or else combustion would stop).

Ultimately (for a long specimen) a stable interim pattern emerges before all of the rod is converted into a single moment-two batch-slag pile formed from the accumulation of all the sub-batch droplets. When a droplet detaches, it takes away heat and this is a heat loss. But before that has happened, even in an overall adiabatic system, it has also lost heat through conduction and convection and radiation to the next segment—to the rod above. As the next segment begins to burn, some of the heat losses of the prior segments are heat “gains” for it. It has been preheated and this preheating or “pass-through heat” acts very much like additional heat of combustion. Even though the original ignition energy may have been small compared to the heat of combustion of the entire rod, it may be substantial compared to the heat of combustion of a single droplet. The pass-through heat may also be substantial.

During combustion, each droplet is transferring heat into the section of rod above it, preheating it, thereby significantly increasing its apparent *in-situ* heat of combustion (moving the moment one starting point up the iron thermo curve relative to the original standard finishing point. Ultimately a stable condition is expected in which the amount of heat gain which preheats each section of rod will equal the amount of heat lost that preheats the section of rod further above. This is a “pass-through” heat and can be significant in comparison to the heat of combustion and even any external heat loss.

However, we have seen how to analyze extreme-case preheated iron. Figure 9 shows four hypothetical levels of average preheating that might obtain due to assumed pass-through heat. One is at the melting point of iron, point “f”, one level is near a high tip temperature that might exist half way between the melting point and boiling point, point “g”, one is arbitrarily

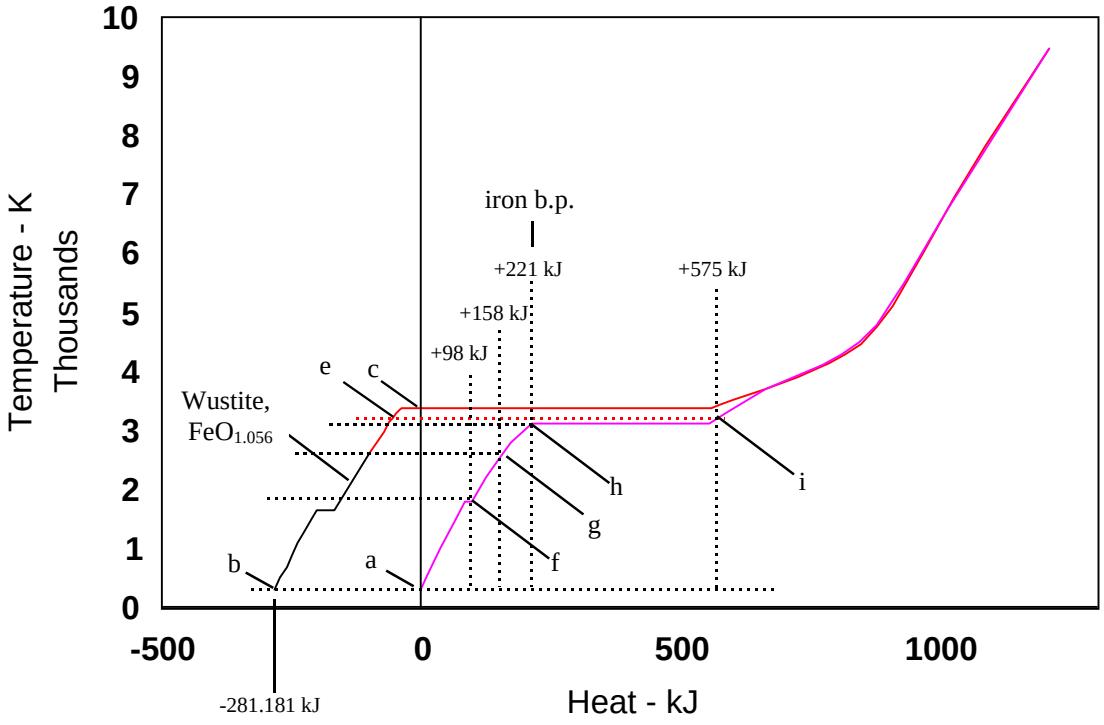

FIG. 9—*Preheating by pass-through or ignition heat. For wustite of Fig. 5.*

selected at the onset of boiling, point "h", and one is at the point where complete vaporization occurs, point "i". Indeed, *this range covers combustion scenarios that may prevail with iron combustion, even in blast furnaces, and the point "i" has been almost preheated to the standard batch adiabatic combustion temperature.*

For each of the example preheats, new dotted horizontal baseline and vertical lines are drawn. For each scenario there is a different ${}_{is}H_c$ that applies. These vertical lines are significantly to the right of the origin line through point "c" that applies for standard batch combustion.

Consider the preheating to point "f". This preheating is about 35% of the standard heat of combustion (about 98kJ). The *in-situ* heat of combustion based on the elevated temperature starting point and the room temperature finishing point at "b" is about 379 kJ. The *in-situ* heat of combustion based on equal starting and finishing temperature is about 251 kJ. However, the adiabatic flame temperature that results from back-heating point "b" with 379 kJ is the same as that from back-heating the point above that is defined by the intersection of the dotted horizontal line through "f" with 251 kJ. That adiabatic flame temperature is on the latent plateau and is the same 3389 K as for point "c". In this case, although the temperature is the same, the equilibrium vaporization is different and the amount of the original liquid oxide that has vaporized has increased from 6.8% at "c", to 22.5% at +98 kJ, to 32.2% at +158 kJ, to 42.6% at +221 kJ.

With similar analyses, the preheating of points "g", "h', and 'i' corresponding to additional apparent heats of combustion of 56%, 79%, and 205%, respectively, more heating than the standard for back-heating of point "b". Table 1 shows more details comparing the standard combustion scheme with these four preheat levels. All of these preheating levels are large and

TABLE 1 — *Back-heating of $Fe_{1.056}O$ to Predict Combustion Properties of Preheated 1.0Fe Plus 0.528O_2 per Fig 9.*

	Point "a"	Point "f"	Point "g"	Point "h"	Point 'i'
AFT - K	3389.73	3389.80	3389.81	3389.81	3442.53
Residual Liq $Fe_{1.056}O$	93.2%	77.5%	67.8%	57.4%	0%
Fraction converted to gas	6.8%	22.5%	32.2%	42.6%	100%
% gas as Fe(g)	46.55%	47.32%	47.42%	47.46%	48.2%
% gas as FeO(g)	18.94%	18.96%	18.96%	18.96%	17.1%
% gas as O	15.93%	15.70%	15.67%	15.65%	17.6%
% gas as O_2	18.58%	18.03%	17.95%	17.91%	17.1%

tend to rule out the prospect of external heat loss precluding either vapor phase combustion (even if slow) or inflation of the slag.

This illustrates the second cutting edge of heat loss during droplet detachment. Indeed, *these very simple laboratory testing methods are in fact a vary sophisticated mechanism for partitioning the combustion* so as to make (at least fractional) vapor phase combustion thermodynamically viable, even if that does not magnify the hazard. The lower segments of the rod that produce the initial droplets, burn by one scenario at one temperature, and the later segments that produce the later droplets can burn by a different scenario at a different temperature. When a slag droplet falls, it has helped to preheat the material above, then removes part of combustion products (and seriously complicating matters, perhaps some molten iron also) so that they are no longer a heat sink to further combustion. And combustion propagation may depend on whether each droplet transfers a larger or smaller heat gain than the previous droplet. There is a need in the future to consider the presence of surface-tension modifying materials that might alter the ratio of products-to-molten-iron that form in each droplet.

In performing a laboratory rod combustion test, this transient heat sink effect is present but is overcome. First the rod tip is preheated from an external source until combustion begins. Fig 8, Q_1. As the slag droplet grows it is transferring heat into the rod section above it through convection currents, radiation and conduction. It is very difficult to predict the thermal profile that would develop and the writer does not recall any attempts to measure it to date. However when the slag droplet falls, we do know that there is molten slag and metal residual that clings to the rod, and that the rod above the droplet is preheated to some extent. The added heat in this condition is in addition to that which will subsequently evolve during further combustion. Hence the apparent ${}_{is}H_c$ for each droplet is not the standard heat of combustion, nor would one add the ${}_{is}H_c$ back into standard temperature iron oxide to predict the droplet's adiabatic temperature. Hence the oxide temperature in any inflated droplet's annulus might well fall in the range of those that would be present for bulk molten iron in a blast furnace during an oxygen blow. To prevent the presence of gaseous iron, FeO and both atomic and molecular oxygen

would require much greater heat loses than Lanyi has estimated, possibly more than would be conceivable for droplets that are known with fair certainty to be molten.

Still More Definition Angst

This paper has struggled to provide a consistent, detailed, improved and simple perspective on iron thermodynamics as it affects combustion by trying to construct "the big picture", and describe it with additional terms that may help, and there is more to follow. However such analyses are often done in a somewhat approximate fashion that is often reasonable and acceptable, but sometimes breaks down. The writer is not a novice student of this topic, but yet has often found difficulty reconciling the various publications. Hopefully this approach simplifies the thermo analysis of iron in combustion to the point where such break downs can be anticipated and avoided, because analysts will have a better gut feel for what the answers should be. A few examples from the oxygen safety literature may seem to be in conflict with this perspective and are noteworthy and in the writer's surmise are instances of apparent potential breakdowns. They warrant an attempt at reconciliation or at least elaboration.

As noted in the Appendices, early writers cited the relationships between combustion temperatures and the thermodynamics and boiling/decomposition tendencies of metal oxides. These writings asserted that some oxides do not exist as a vapor and hence if they were to vaporize, they would have to decompose and therefore absorb significant amounts of the heat of combustion. So either they would burn to form liquids (the gases would condense into liquid oxide) or they would not burn at all. Hence in some very important cases the combustion temperatures would therefore be limited to those at which the oxide vaporized, because at higher temperatures, the vaporization would result in decomposition.

As reviewed earlier and in Appendix B, in the early 1990s, a previously mentioned challenge to these methods of predicting combustion temperatures and phases [*3*] was published by some who were also Excess Oxygen Proponents (EOPs). Definition of what it meant "to boil" was a central issue. And there were several rebuttals to it [*4,5*]. Among the definitional issues raised were the precise ways in which the still-decades-earlier commentators were using definitions that were not precise. "Boiling" is often taken to mean a phase transition in which a latent (insensible) heat is transferred that is quite powerful in its ability to limit the temperature of the phase-change process to a rather precise value.

However, these EOPs focused on the many cases in which the oxides of interest decompose upon vaporization. And in this case, the heat absorption might not be latent and might not precisely limit temperature. They examined aluminum as a metal often cited as an example of this effect, and it is variously noted that Al_2O_3 oxide does not exist as a vapor, but the critics cited that its decomposition at high temperature would not necessary mean reversion of the oxide all the way back into aluminum and oxygen, there being numerous other intermediate compounds that might form that might, indeed, exist as vapors. The critics employed the use of Gordon-McBride code (CEA/precursor) in this and several subsequent papers.

A strong rebuttal to this critical paper by Glassman [*4*] cited fairly constant adiabatic flame temperature calculations by the same Gordon and McBride code for a range of aluminum/oxygen mixtures as aluminum is heated through its decomposition/adiabatic flame temperature, and it mentioned in passing but did not concentrate on the specific critique of decomposition to intermediate gaseous species. Instead, it concentrated in depth on what it asserted was an apparent definitional error in the critic's own interpretation of the applicable heat bal-

ance. Whereas the EOPs asserted "...complete decomposition would produce elements, and the enthalpy of dissociation would be the negative of the enthalpy of combustion (i.e., formation) never greater than it", Glassman's rebuttal stressed that it is not the standard heat of combustion that would be absorbed by a metal like aluminum vaporizing at its apparent high temperature limit, but rather the heat of formation ...*at the vaporization temperature*". This is called the ${}_{is}H_c$ here.

*Glass*man's rebuttal appeared to downplay the concern over whether decomposition might not always yield a latent heat transfer, and indeed, the data he presented suggest it does not in every instance even in the case of aluminum. However, it continued to cite the temperature limiting effect as a boiling (actually pseudo-boiling) mechanism indeed apparently implying and in fact illustrating a latent heat characteristic.

To some extent, the rebuttal proved the critic's point, in that it demonstrated in a figure (Glassman's Figure 3) that although the flame temperature is constant, *is latent*, for a range of heat input, that ultimately it *does* rise with heating specifically for aluminum oxide. Furthermore the rise happens after all liquid aluminum oxide has vaporized, which is when the Al_2O_3 oxide is largely decomposed, but it is *before* other aluminum oxides (specifically AlO) have decomposed back to the constituents. He cites this as demonstrating a boiling-point-like effect *which it is* while there is vaporizing and decomposing liquid present, but which *it is not* when the liquid is gone but the decomposition is continuing, and the latter more nearly fits the critic's concern.

A rebuttal to the Glassman rebuttal from the EOPs [*5*], appeared to again focus on the latent (or not) nature of any decomposition process. In this case, the rebuttals' rebuttal, refocused on the latency aspect but did not appear to embrace the rebuttal's definition issue regarding the heat of formation *at the vaporization temperature*.

The writer believes both sides of the analysis have merit and flaws. And both arguments appear to be supported also and even more impressively in this present case of iron.

On the first hand, we have seen with iron combustion that the CEA code predicts there *is* both a latent region (from point "e" to point "d" of Fig. 5) in the decomposition of force-heated liquid $FeO_{1.056}$ oxide that is a strict temperature delimiting effect in which part of the vaporized oxide is congruent and part is decomposed, but there is also a sensible region (beginning at point "d") in which the further addition of heat forces decomposition of the congruent oxide vapor and does absorb heat but does *not* rigidly limit temperature. The iron oxide is not completely decomposed until it has been heated from point "d" all the way to about 5000 K. Score one for the EOPs.

Therefore, for iron oxide, there is both "boiling" in the narrow sense and decomposition occurring. But when the latent temperature limiting region is passed, there is still decomposition occurring. The exact mechanism for this apparent "congruent" boiling is not clear. Does the liquid oxide normally boil to congruent vapor and then partially decompose into constituents? Does the oxide decompose into constituents which then congruently vaporize and partially recombust into oxide? Thermodynamically the two or any combination are equivalent.

However, the writer also believes the specific analysis of these effects by the original critics were flawed, and that Glassman's rebuttal was correct in its own definition issue, therefore several analysis by the EOPs were not what they may have been intended to be because of this definitional aspect. The writer believes, the critics were indeed employing an inappropriate heat of formation. Score this one for Glassman. Furthermore, this writer wishes to question whether additional flaws may have been present in the EOP's analysis.

For example, a paper [*6*] several years later with several of the EOPs in common with the rebuttals' rebuttal, again applied the Gordon and McBride code (the earlier command line version of the CEA code) this time to predicting iron combustion properties in order to exhibit the effect of pressure on combustion. And in it, its Table 3 apparently sought to employ the Gordon-McBride code's HP mode to predicting both the adiabatic flame/decomposition temperature of $FeO_{1.056}$ oxide (to answer their question two on their page 241) and also the equilibrium composition at that point (as cited in their question three on their page 241) both by (1) a calculation of the direct combustion of the reactants and also by (2) showing dissociation by transferring into liquid FeO oxide products, the standard heat of combustion stating: "the thermal energy input is the negative of the enthalpy of formation". The calculations will be reconstructed in detail here, however, in the intervening decade the thermodynamic data in the NASA tables have been tweaked, so small differences must be expected.

The analysis that the writer is "assuming" they employed, perhaps somewhat riskily, is the same one he himself attempted to use numerous times when first deploying the CEA software in preparing this paper but was thwarted by the CEA quirkiness. Fortunately he benefited from the recent GUI interface that at least facilitates large volumes of calculations and gave context.

The CEA software allows for the specification of a mode of calculation (HP or enthalpy and pressure in this case) and reactants (at temperatures and by amounts) for which it calculates the adiabatic flame temperature and equilibrium compositions during combustion. Alternatively, one can "name" a species (in this case an oxide and a temperature, 298 K, in this case) and specify an enthalpy (in interesting units of g-mol K/(gram of mixture) to in effect heat a species. Unfortunately, the writer could easily "heat" either the oxide or combustion products a lot (could enter large values for heat input) but it was much more difficult to "heat" them a little (to enter small heat values). At low levels of enthalpy specification the software often would not converge. This is not uncommon and is why reversion to JANAF tables was resorted to by the writer several times when the writer was insufficiently "astute" to tease low-heat data from the software. This is some kind of quirk!

This led the writer to err in his early results, and fortunately he could not generate a reasonable complete thermodynamic curve. He suspects the EOP critics may have had one or more of the same difficulties and in the process become overly wary. That apparent error is to assume, quite reasonably one hopes, that when one uses CEA software to heat a candidate *that the starting point for the candidate is the temperature the user has specified*. This does not appear to be the case. It is instead equivalent to this case when the named material is not a product (is an inert or element) and when the specified conditions are at room temperature. However, when one specifies an oxide (like $Fe_{0.947}O$) the starting point for the calculation appears to be the combustion condition at which the oxide was formed from its constituents *at the specified room temperature*, which is already at a rather high temperature. In other words, apparently when one specifies $Fe_{0.947}O$ at 298 K and "adds" heat to it, one is actually adding heat to $Fe_{0.947}O$ that has just formed from the combustion of room temperature 0.947Fe plus $0.528O_2$, which is already hot, indeed is already at the adiabatic flame temperature of its constituents. To obtain a result for lightly heated oxide, the writer had to actually enter negative heats (one must enter the heat to be added, a positive number, plus the heat of combustion, a large negative number), and the CEA software is least accommodating with these data and most often fails to converge, leading one to instead examine only the higher heating levels, and perhaps falling back to the JANAF tables for the rest.

TABLE 2—*Reconciliation of the EOP Results* [*6*] *in the Lower Part of Their Table 3 Relative to Figure 10* . **Note! Data are fractions of total system liquids plus gases.**

	EOPs Page244, lower[a]	Fig. 10 Point "c"[b]	Fig. 10 Point "c′"[c]
T- K	3400	3389.73	3389.81
Fe(v)	0.29	0.04660	0.28487
FeO(v)	0.11	0.01896	0.11336
O(g)	0.09	0.01595	0.09321
O2(g)	0.10	0.01860	0.10631
FeO(l)	0.41	0.89990	0.40225

[a]These data are taken from the lower half of the EOPs Table 3 [*6*].
[b]These data apply to the point "c" of figure 10.
cThese data apply to the point "c′" of figure 10.

The EOPs sensed difficulties and took precautions but never seemed quite confident of their results—with good reason.

In one of the EOPs calculations (lower part of their Table 3) they used the software's HP mode, and they added the "negative of the enthalpy of formation" to FeO liquid at 298 K. This is the appropriate way we have seen that one can estimate the equilibrium adiabatic "batch" conditions during combustion. The writer is assuming the EOPs intended wustite (either $Fe_{0.947}O$ or $FeO_{1.056}$) when they reported these calculations because they do say in their text: "wustite ($Fe_{0.95}O$) will be treated as FeO". And their result is a (perhaps rounded) atmospheric-pressure final temperature of 3400 K, and the composition they obtain is cited in Table 2 of this paper as column 2 (titled "EOPs Page 244, lower").

Their Q_{input} is cited as 249.5 kJ/mol and is of particular interest. The JANAF tables (p. 1237) cite the heat of formation of liquid iron oxide (FeO) as

$$\Delta_f H = -249.532 \text{ kJ/mol},$$

and the writer suspects this is the basis of the heat input used in their Table 3. However, this is also the standard heat of combustion at 298 K for the oxide product. It should also be noted however that this JANAF datum is a theoretical standard heat of formation/combustion result because the oxide FeO(l) does not exist at 298 K as a liquid, and the JANAF tables do not provide theoretical data for the comparable molecule $FeO_{1.056}$ as a low temperature liquid. However, the two should not be greatly different. Indeed, the CEA software (a version a decade newer than that used for their Table 3) does not appear to allow one to specify $Fe_{0.947}O$ (and therefore $FeO_{1.056}$) as a liquid below 1650K (its melting point).

Figure 10 again replicates data from Figure 5 which applies more precisely to $FeO_{1.056}$ and attempts to reconcile these data. Keep in mind that the earlier review in the present paper generated these curves using the HP mode of CEA for direct combustion and then found them to be identical with data for heating of $FeO_{1.056}$ oxide but only after working around the quirk

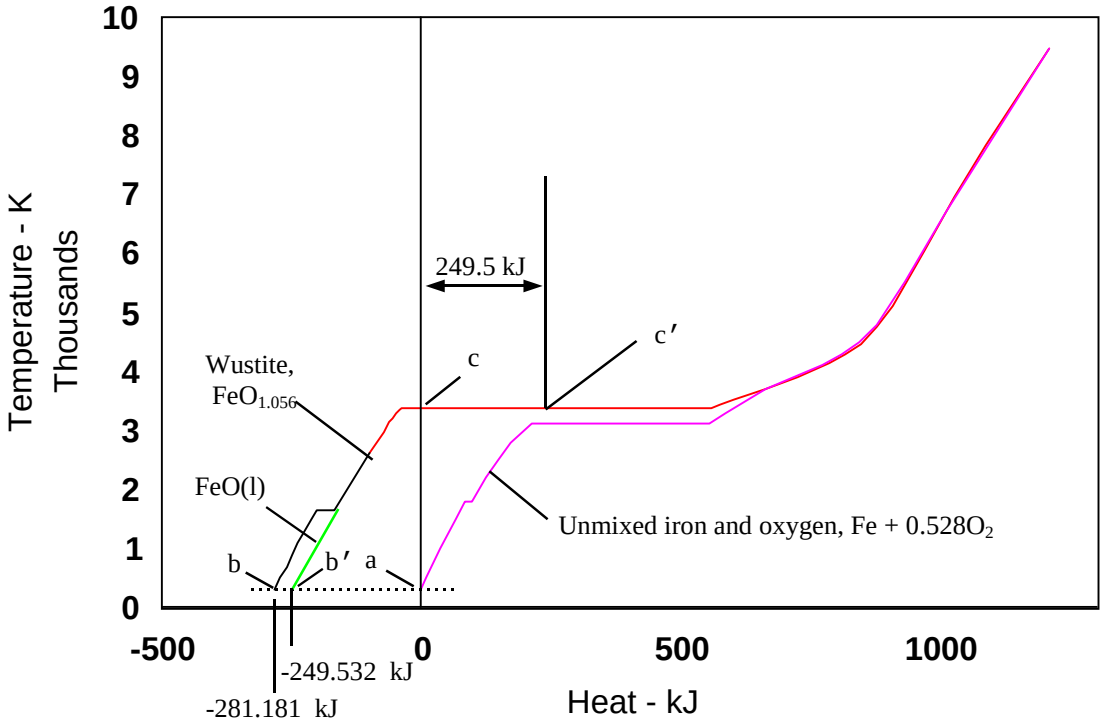

FIG. 10—*First reconciliation of EOPs 1997 data* [*6*].

identified above.

The heat of formation (also combustion) of liquid FeO cited in the JANAF Tables is shown at point "b′" and is appropriate to this plot for FeO containing one mole of iron. They would differ slightly from the data for wustite containing one mole of iron ($FeO_{1.056}$) due to the several percent of additional oxygen in $FeO_{1.056}$. Ignoring that difference, point "b′" is blended into the $FeO_{1.056}$ curve as a green line.

If one has combusted solid iron to yield solid $FeO_{1.056}$, then one starts at point "b" and follows the black and then red heating curve until it intersects the vertical line positioned to the right by the amount of the heat of combustion (-281.181 kJ) which is at the origin, in this case to get to point "c" as establishing the adiabatic flame temperature and composition. If one has combusted solid iron to yield cooled *liquid* FeO, then one starts at the point "b′" and follows its green heating curve, which merges with the previous black curve, until it intersects the vertical line positioned to the right by the amount of the heat of combustion (-249.532 kJ) which is, *again*, at the origin, in this case, to *again*, get to the same point "c" as establishing the same adiabatic flame temperature. This latter "calculation" is what the writer assumes the EOPs were pursuing with the second calculation in the lower half of their Table 3. This calculation of temperature at point "c" is at 3389.81 K per the writer's efforts.

However, although the AFT established by the EOPs of 3400 K is about the same (within the margin of potential error for thermo table changes in the software and possible rounding), the compositions the EOPs report in column two of Table 2 are not close to those for the point "c" on Figure 10 given as column three (heading: Figure 10, Point "c") in Table 2. In-

Table 3—*Reconciliation of EOP Results* [*6*] *in the Upper Part of Their Table 3 Relative to Figure 11.* **Note! Data are fractions of total system liquids plus gases.**

	EOP's Fe(v) + .5O2 At 0.1 MPa[a]	**FIG. 11, Point "c′" Plus 420.59 kJ**	**FIG. 11 Point "g"[b]**
T- K	3400	3389.62	3389.81
Fe(v)	0.41	0.40932	0.43177
FeO(v)	0.15	0.15753	0.17214
O(g)	0.13	0.12502	0.14181
O2(g)	0.14	0.13790	0.16202
FeO(l)	0.17	0.17025	0.09227

[a]These data are taken from the upper half of the EOP's Table 3 [*6*].
[b]This point is equivalent to point "c′"plus ~483 kJ.

deed, the compositions reported in column two of Table 2 are more nearly found on the upper curve of Figure 10 at point "c′" which are listed as column four (heading: Figure 10, Point "c′") in Table 2. This is neither the point at which the adiabatic flame temperature is established (though it is the same numeric value) nor is it at the point where full dissociation would occur. This is at a point which is about 249.5 kJ heating units from the origin and is the likely point the EOPs inadvertently calculated when trying to heat the oxide, perhaps unaware they were actually starting at point "c". This is why it appears the software quirk was operative. This error was likely present in earlier EOP papers also, however those papers only reported the temperature which is constant throughout the latent plateau.

In the second analysis the EOPs also employed Gordon-McBride code this time again using HP mode for direct burning. They report iron combustion at 0.1 MPa (and higher) and warily specify the iron reactant as a vapor at 3133 K (its boiling point) with oxygen stoichiometric to FeO at 298 K. This is apparently because they warily note "the code is limited for application to iron burning because it does not handle multiphase systems well" and they presumably did not want to risk its results for burning solid iron.

Table 3, column 2 (heading:"EOP's Fe(v) + $0.5O_2$ at 0.1MPa"), exhibits the direct-combustion adiabatic flame temperature and composition results they reported. Figure 11 again exhibits writer-generated data of Figure 5 but also shows points extracted for stoichiometry consistent with FeO rather than $FeO_{1.056}$. Data points for unmixed iron and oxygen are shown as circles. Data points for the combustion products are shown as "+" signs. At lower temperatures there is negligible differences between the FeO and $FeO_{1.056}$, but at the higher temperatures, the

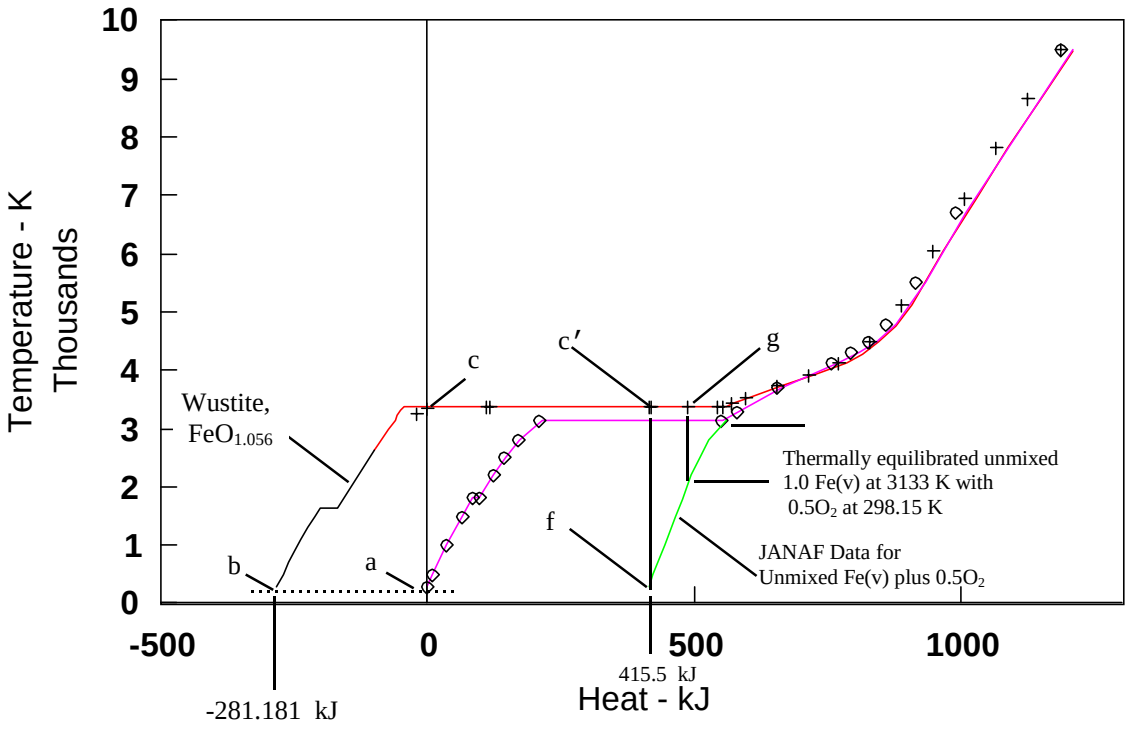

FIG. 11—*Second reconciliation of EOPs 1997 data* [*6*].

curve for FeO products and reactants are located slightly to the left (lower heat due to lesser mass) of the FeO curves. These are data the writer submits are applicable to the EOP's calculation. Keep in mind that the earlier review in this present paper generated its data using the HP mode of CEA for direct combustion and then found them to be identical with heating of related oxide but only after working around the quirk identified above.

To avoid software problems, the EOPs took the precaution to specify iron vapor at its boiling point (so that the calculation would apply to a fully gaseous system which they asserted it is most suited to). But the oxygen was at 298.15 K, room temperature. Was this step necessary? What would have been the result if the EOPs had specified equal iron and oxygen temperatures based on an equilibration, even though that would mean a mixed phase system would be present in the CEA calculation? The writer is not able to accomplish this calculation with his current CEA software (which allows specification of gaseous iron but does not appear to actually perform that calculation—another quirk). However, it appears the earlier EOP software was able to do this calculation, *but only in part*, absent one quirk but still subject to the other. The writer will nonetheless try to reconcile the results indirectly.

Although the point corresponding to hot iron gas and cool oxygen gas cannot be depicted on Figure 11, the data the EOPs reported (Table 3, column two of this paper), can be duplicated by specifying direct combustion of room-temperature oxygen and iron and adding 429.59 kJ of heat, a number found through trial and error. This is shown as column three of Table 3 (heading: Fig. 11, Point "c" plus 420.59 kJ") and as point "c′" on Figure 11.

Figure 11 also shows JANAF data in green for one mole of unmixed iron gas plus stoichiometric oxygen between 298.15 K and 3133 K, and its starting point "f" is 415.5 kJ

above that for point “a” for unmixed solid Fe plus oxygen gas. These are theoretical data because iron is not a gas below the boiling point. A vertical line is drawn through the 298.15 K point “f” of this gas curve and, very significantly, it roughly intersects the point “c′”. Although the writer was not able to coax his copy of CEA to actually perform this calculation for gaseous iron directly, the analysis methodology reviewed here, suggests that the data reported by the EOPs for the combustion of hot iron vapor and cool oxygen gas were reconciled by this writer with the data that should result from direct combustion of *room-temperature iron gas and room-temperature oxygen gas*. It again appears that quirks in the software produced a result different than the user was apparently trying to specify.

If one were to heat iron gas from 298.15 K to the boiling point, the JANAF data (their page 1226) would require transfer of 67.518 kJ of heat to it. This is the same heat that would be added to the unmixed room-temperature iron vapor plus oxygen to address an equilibrated combination for direct combustion. This point is shown to the right of point “f” and a vertical line drawn through it intersects the $FeO_{1.056}$ curve at point “g”, the composition and temperature data of which are shown as column 4 (heading; Fig. 11, Point “g”) in Table 3. The writer believes this is the point the EOPs were attempting to specify.

Here again it appears a reasonably close adiabatic flame temperature result, due to the long latent heating plateau, was obtained for a point that was apparently far from the point being sought. However, the composition appears to be different from that reported. It also appears, *a fully vaporized system was not crucial to obtaining the desired results*.

As a final note, please observe on Figure 11, that the heat of formation/combustion is appropriate for adding to the oxide at point “b” to establish the adiabatic flame temperature at point “c”. However it is inappropriate for adding to the oxide even for a starting point at the beginning of the latent plateau temperature as a heat of decomposition. Indeed, the heat of decomposition that Fig 11 would imply is appropriate is more complex than is a typical latent heat of boiling. Whereas numerous experts have cited that one should add the “heat of formation” (which is called the *in-situ* heat of combustion in this work) to achieve complete dissociation, we have seen on Fig 5 that full decomposition occurs at about 5000 K at which point all of the liquid at the start of the latent plateau is vaporized but in addition, all of the gaseous FeO *and* O_2 have also decomposed back into their constituents. Therefore the starting point and finishing points for establishing the heat addition that will fully decompose the liquid oxide (the heat of decomposition) is between unequal temperature points, 3389 K and about 5000 K, a much more complex concept to specify. This may explain why so little data are present in the literature for decomposition heats.

As powerful and useful as the CEA software appears to be, if this analysis is correct, then it is quirky and involves a steep learning curve and would benefit from a number of simplifications and much more detailed and elementary documentation. And there may be bugs or misuses that lead to the apparent problems encountered by the writer and apparently numerous others as well. The source of CEA will be contacted to suggest modifications. If this surmise proves correct, and if the data reported herein are correct, it is a potent reason for ASTM G4 to deploy a simplified computer program for its adherents to use with these vital data, scrupulously based on data from CEA or similar software but tailored to its oxygen safety audience, because these data are tractable even though many in that audience are not thermodynamicists or metallurgists.

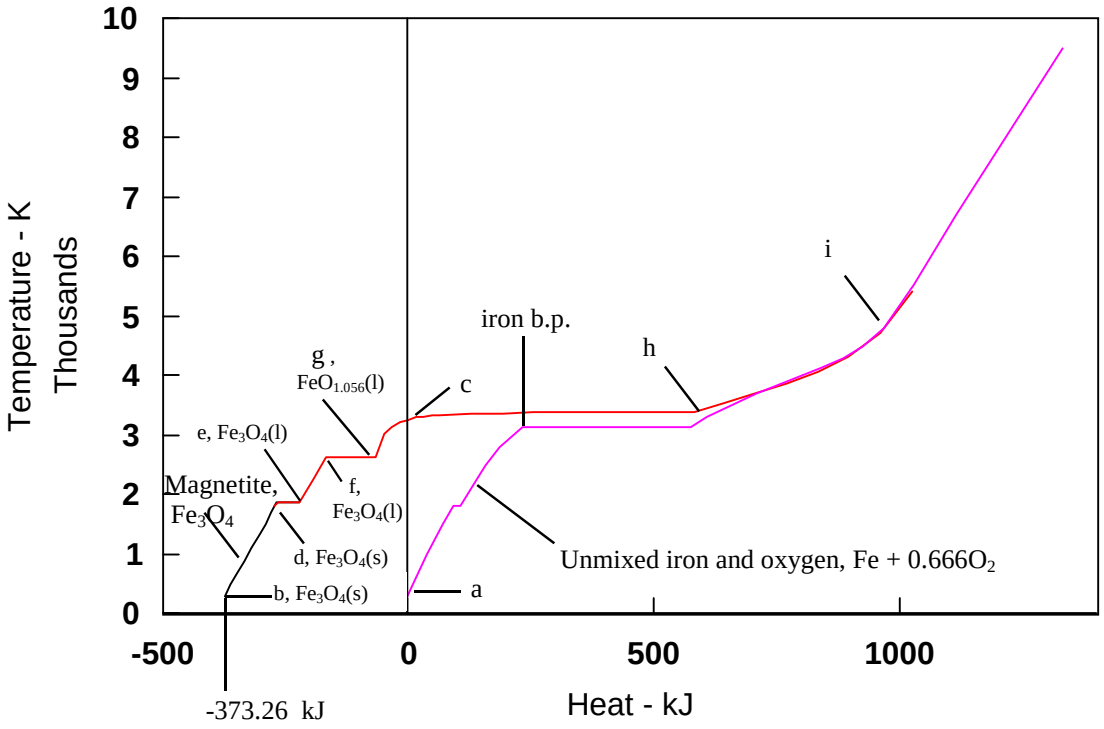

FIG. 12—*The combustion of one gram-mol of iron to magnetite (Fe_3O_4).*

Role of the Higher Oxides

Although the writer has burned iron (more precisely low-carbon steel) [*10*] in a fashion in which virtually only $Fe_{0.947}O$ formed during combustion, he has also burned it in ways in which the slag contained regions of unburned iron, and he and others have burned it in ways in which the ultimate combustion products were scant of $Fe_{0.947}O$ and instead contained mixtures of the higher oxides: Fe_3O_4 and Fe_2O_3 which both result in higher heats of standard formation/ combustion/reaction than does $Fe_{0.947}O$. This latter result is rather more common and so this section will examine these alternative products, starting with individual combustion scenarios that assume exclusive production of one or the other oxides – scenarios which may be fictitious.

Fe_3O_4:

High-powered specialists in thermodynamics teach us that if a mole of iron could be reacted with oxygen to exclusively produce a cooled Fe_3O_4 slag, the heat release (from JANAF tables), would be about –373.26 kJ (or –1120.89 kJ/mol Fe_3O_4 per JANAF Tables page 1250). Thermodynamic data for pure Fe_3O_4 are shown in Figure 12, taken from both JANAF Tables and CEA software, and it is similar in appearance to Figure 5. Points “a”, “b”, and “c” have the same physical significance as in earlier analysis. In this case point “a” is the 298.15 K starting point for unmixed iron and oxygen gas stoichiometric to the production of Fe_3O_4. This is the middle curve from Figure 3, and it exhibits sensible heating to the iron melting point, a latent

heat of transition followed by sensible heating to 9500 K during which the diatomic oxygen gas is dissociating due to temperature.

Point "b" is solid magnetite at 298.15 K. As was done for wustite, the normal heating curve is translated so that the point is displayed to the left of the starting point for the constituents by the amount of the heat of combustion/reaction/formation of the material that contains one gram-mole of iron. In this case the JANAF tabular data in black are plotted up to the melting point "d" of Fe_3O_4 at 1870 K and through the latent heat of transition to point "e".

Data from CEA begin just before the melting point "d" and are used up to the 9500 K end point. Between the melting point "e" and point "f" at approximately 2626.8 K the heating is again sensible, and at point "f" decomposition of pure liquid Fe_3O_4 into liquid $FeO_{1.056}$ is beginning and gaseous diatomic oxygen is released. The decomposition proceeds to point "g" at which the liquid is pure $FeO_{1.056}$ and the gas is nearly pure diatomic oxygen. Thereafter heating of the liquid wustite is initially sensible again but is shifting as it approaches the standard combustion point "c" to evolve small amounts of FeO(v), Fe(v), O_2(g) and O(g). Further heating leads to a progressively more latent character to the temperature effect as more and more $FeO_{1.056}$ is converted into gases, until at point "h" all of the liquid is vaporized/decomposed.

In this case, the greater amount of gaseous oxygen that is present compared to decomposing wustite acts (by LeChatelier's Principle) to suppress the amount of gaseous Fe(v) that is present. At the end of the near-latent plateau, the temperature CEA predicts is approximately the same as it predicts throughout the latent plateau for wustite, 3387.48 K versus 3389.81 K.

Beyond point "h", decomposition of the diatomic FeO(g) and O_2(g) occurs. At point "i", for the most part only monatomic gases are present and the heating thereafter is sensible and the slope of the heating curve increases as a result.

Notice that for standard combustion, the vertical line drawn from the reactants starting point which intersects the heated oxide curve at the adiabatic flame temperature, is virtually identical to that for Wustite (Figure 5), the latter shifted only slightly due to the extra oxygen that must be heated to form magnetite.

Fe_2O_3:

We can take the same approach used for $FeO_{1.056}$ and Fe_3O_4 to analyze Fe_2O_3. If one mole of iron is reacted with oxygen to exclusively produce a cooled Fe_2O_3 slag, the thermodynamicists teach us the heat release would be about –412.25 kJ (or –825.50 kJ/mol Fe_2O_3 per JANAF Tables page 1248). Thermodynamic data for pure Fe_2O_3 are shown in Figure 13, taken from both JANAF Tables and CEA software, and it is similar in appearance to Figures 5 and 12. Points "a", "b", and "c" have the same physical significance as in earlier analysis. In this case, point "a" is the 298.15 K starting point for unmixed iron and oxygen gas stoichiometric to the production of Fe_2O_3. This is the fourth curve shown on Figure 3, and it exhibits sensible heating to the iron melting point, a latent heat of transition followed by sensible heating to 9500 K during which the diatomic oxygen gas is dissociating due to temperature.

Point "b" is solid hematite, Fe_2O_3, at 298.15 K. As was done for wustite and magnetite, the normal heating curve is translated so that the starting point is displayed to the left of

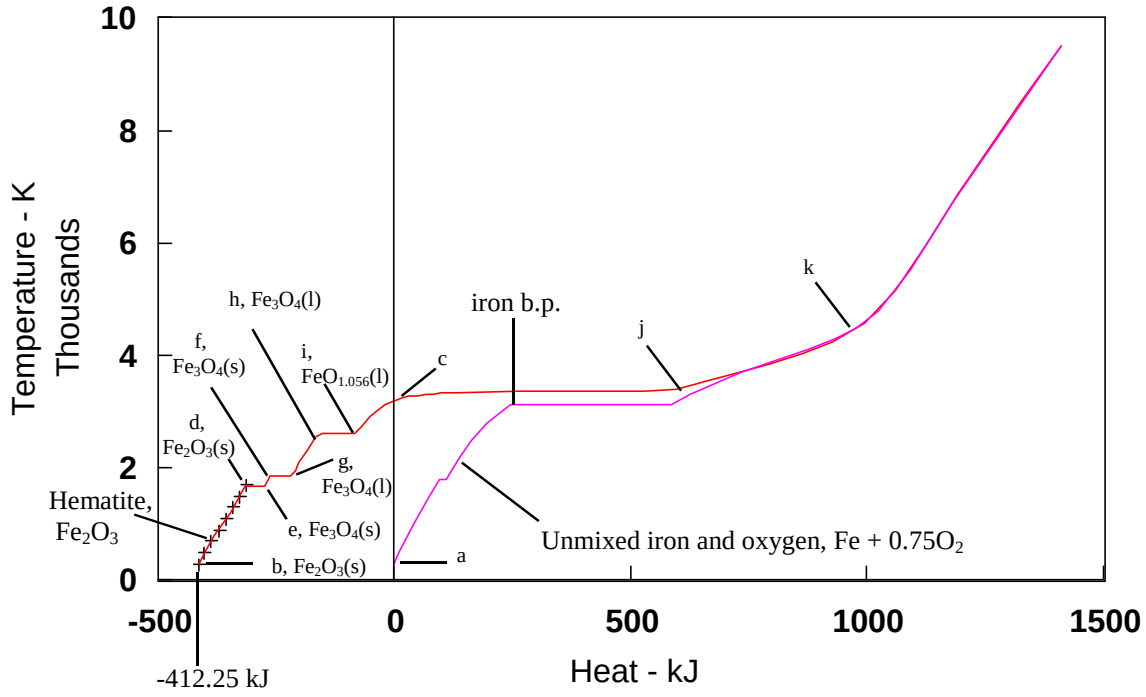

FIG. 13—*The combustion of one gram-mol of iron to hematite (Fe_2O_3).*

the starting point for the constituents by the amount of the heat of combustion/reaction/ formation of the material that contains one gram-mole of iron. In this case the CEA results were extracted all the way down to 298.15 K, but JANAF tabular data in black "+" symbols are plotted up to the decomposition point "d" of Fe_2O_3 at about 1681.96 K and through the latent heat of transition to point "e".

Between the decomposition point "d" and "e" solid Fe_2O_3 is changing into solid Fe_3O_4 and the conversion is linear in added heat. At and beyond point "e", the curve is nearly the same as for the Fe_3O_4 curve of Figure 12 but with some additional oxygen that would upset the composition data slightly (via LeChatelier's Principle). At point "f", the solid Fe_3O_4 begins melting at 2626.80 K, then point "g" is where the melting is complete, and after some sensible heating, at point "h" latent decomposition into $FeO_{1.056}$ is beginning along with the release of more gaseous diatomic oxygen.

At point "i", decomposition into $FeO_{1.056}$ is essentially complete. At this point the atmosphere is nearly pure diatomic oxygen. Beyond point "i", further heating of the liquid $FeO_{1.056}$ is initially sensible again but is shifting as it approaches the standard combustion point "c" to evolve small amounts of FeO(v), Fe(v), O_2(g) and O(g). Further heating leads to a progressively more latent character to the temperature effect as more and more $FeO_{1.056}$ is converted into gases (through both apparent boiling and decomposition), until at point "j" all of the liquid is vaporized/decomposed.

In this case, the still greater amount of gaseous oxygen that is present compared to decomposing solid $FeO_{1.056}$ acts to (by LeChatelier's Principle) suppress the amount of gaseous Fe(v) that is present. At the end of the near-latent plateau, the temperature CEA predicts is approximately the same as it predicts throughout the latent plateau for wustite, 3384.58 K versus

3389.81 K.

Beyond point "j" decomposition of the diatomic FeO(g) and O_2(g) occurs. At point "k", for the most part only monatomic gases are present and the heating thereafter is sensible and the slope of the heating curve increases as a result.

Notice that again for standard combustion, the vertical line drawn from the reactants starting point which intersects the heated oxide curve at the adiabatic flame temperature, is virtually identical to that for wustite (Figure 5) and magnetite (Figure 12), shifted only slightly due to the still extra oxygen that that must be heated to form hematite.

Real World Combustion

We have seen that regardless of whether one burns Fe to yield any of its oxides, back heating the cooled products with the respective *is*H_c yields very nearly the same "moment 2" condition at point "c". Real world combustion may produce $FeO_{1.056}$ (or its equivalent $Fe_{0.947}O$) or any of a range of mixtures of Fe_3O_4 and Fe_2O_3. However, without delving into elaborate proofs, regardless of the mixture of oxides that forms, back-heating of any cooled slag would yield very nearly the same moment 2 condition at point "c", as it must because the starting conditions and effective heats balance are about the same for all such contingencies.

Note that the same analysis scheme is applicable for considering the combustion of wustite to yield the higher oxides or any mixture of them as well. Each has an $_{is}H_c$ that can be graphically back-heated into the products. Two extreme scenarios more nearly like real world combustion will be reviewed in this section: combustion richer (higher in iron) that that which would produce $Fe_{0.947}O$, and combustion leaner (higher in oxygen than that which would produce Fe_2O_3.

Rich combustion

The writer has burned low-carbon-steel rods in oxygen and rapid-quenched the droplets that fell. They exhibited entrained iron embedded in a matrix of largely wustite ($Fe_{0.947}O$). This was real world iron-rich combustion. The exact amount of unreacted iron was not quantified, but for the sake of this analysis it will be estimated as an overall $1.0Fe + 0.4224O_2$ formula. This is iron with enough oxygen to convert 80% of itself into wustite. In other words, for one total gram-mole of iron, it is equivalent to

$$0.8(1.0Fe + 0.528O2) + 0.2\ Fe \rightarrow 0.8FeO_{1.056} + 0.2Fe$$

Where the 0.2 Fe is the excess iron.

Figure 14 exhibits the CEA result for combustion of this combination in the style of Figures 5, 12 and 13. We again take the same approach as before. If 80% of one mole of iron is reacted with oxygen to exclusively produce a cooled $FeO_{1.056}$ slag, the thermodynamicists teach us the heat release would be about 80% of that shown in Figure 5 or –224.95 kJ (-281.101x 0.8). Thermodynamic data are shown in Figure 14, taken from both JANAF Tables and CEA software.

Points "a", "b", and "c" have the same physical significance as in earlier analysis. In this case point "a" is the 298.15 K starting point for unmixed iron and oxygen gas stoichiometric to the production of $0.8FeO_{1.056} + 0.2Fe$. This is the first (left) curve from Figure 3, and it exhibits

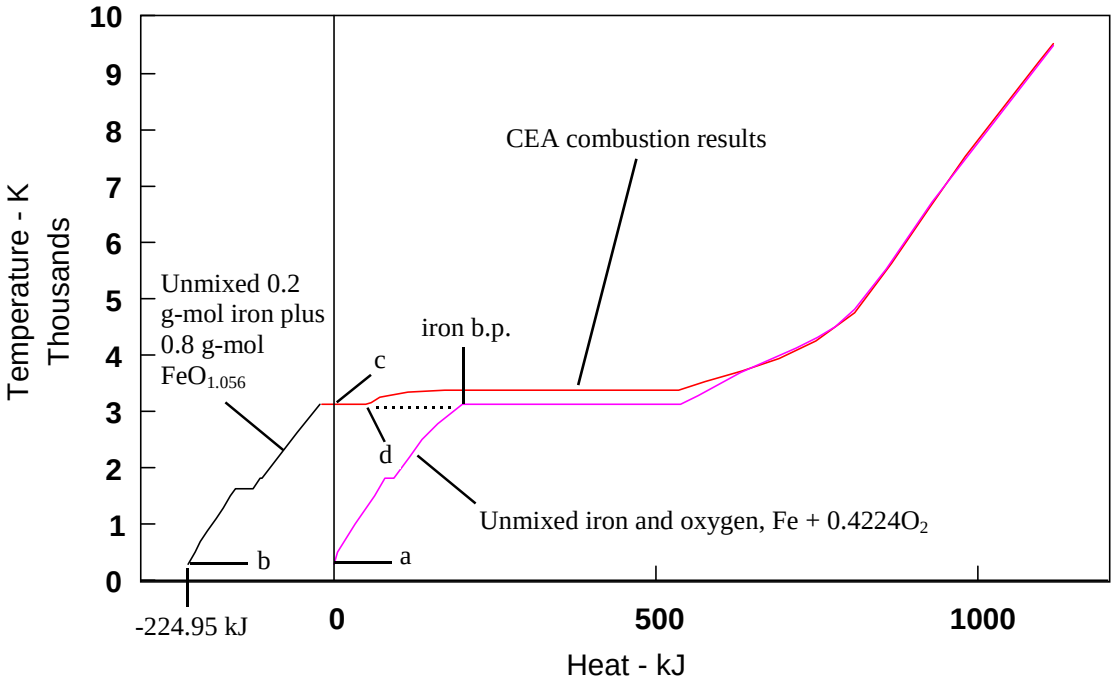

FIG. 14—*CEA data for combustion of 1.0 g-mol of Fe with 0.4224 g-mol O_2 to yield 0.8 g-mol Wustite ($FeO_{1.056}$.) containing 0.8 gram-mole iron plus 0.2 gram mole of excess iron.*

sensible heating to the iron melting point, a latent heat of transition followed by sensible heating to 9500 K during which the diatomic oxygen gas is dissociating due to temperature.

Point “b” is a summation of thermo data for wustite containing 0.8 g-mol $FeO_{1.056}$ and 0.2 g-mol pure iron. The normal heating curve is translated so that the starting point is displayed to the left of the starting point for the constituents by the amount of the heat of combustion/reaction/formation of the material that contains a total one gram-mol of iron. In this case, the data are shown in black but were extracted both from JANAF and earlier CEA results. This curve warms to the melting point for wustite at 1650 k, then exhibits a latent heat input, warms to the melting point of iron at 1809 K and goes through a barely discernable latent heat input then warms to the boiling point of iron at 3133 K. These data nicely seem to merge with the lowest data the writer was able to coax from CEA software for direct combustion.

Data from CEA for combustion (red curve) begin just to the left of the origin at the approximate boiling point of iron (the software reports 3121.91 K) and there is a small latent plateau present. As heating level increases the fraction of the material that is liquid iron is decreasing (boiling) until point “d” is reached at which the liquid iron is gone. The length of the short latent plateau is about 115 kJ, and this is somewhat more than the heat needed to boil 0.2 g-mol of iron (about 70 kJ) the difference apparently resulting from simultaneous decomposition/ evaporation of $FeO_{1.056}$ into several gases.

Upon still further heating beginning at point “d”, a transition to a nearly latent plateau that has been exhibited by liquid $FeO_{1.056}$ occurs. At the end of the near-latent plateau, the temperature CEA predicts is approximately the same as it predicts throughout the latent plateau for wustite, 3387.61 K versus 3389.81 K. Beyond the plateau, there is a range of decomposition of the diatomic FeO(g) and O_2(g) occurring. Finally, for the most part only monatomic gases are present and the heating thereafter is sensible and the slope of the heating curve increases as a

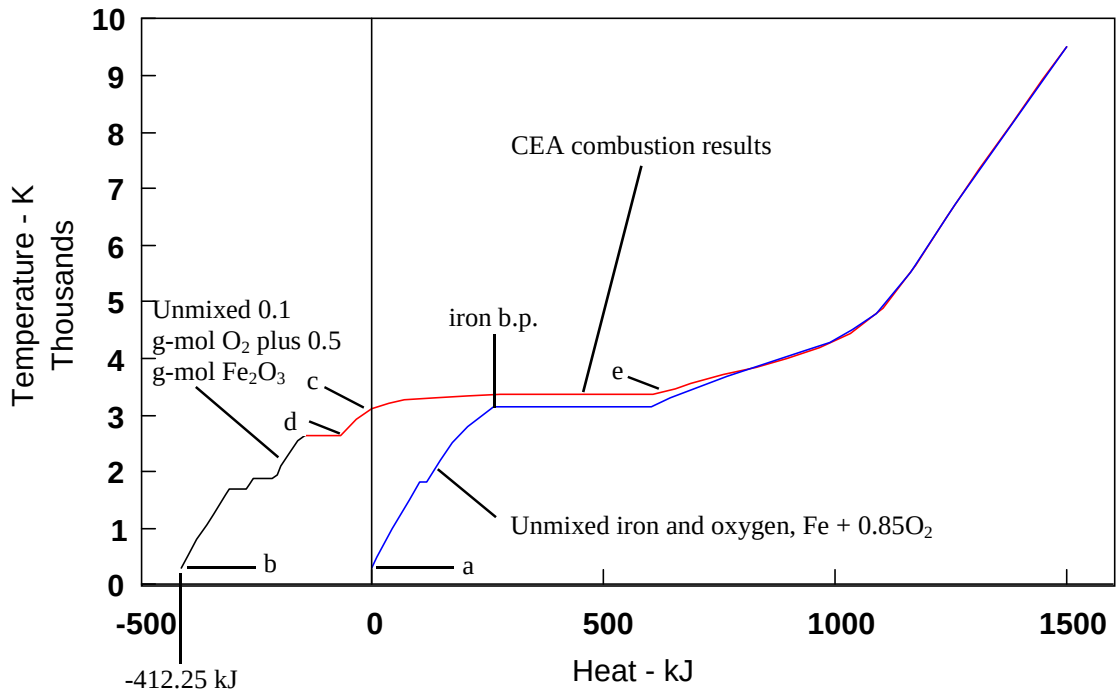

FIG. 15—*CEA data for combustion of 1.0 g-mol of Fe with 0.85 g-mol O_2 to yield 0.5 g-mol hematite (Fe_2O_3.) containing 1.0 gram-mole iron plus 0.1 gram mole of excess diatomic oxygen.*

result.

Notice that again for standard combustion, the vertical line drawn from the reactants starting point which intersects the heated oxide curve at the adiabatic flame temperature, is determined the same as for pure wustite (Figure 5) and magnetite (Figure 12), but is a significantly lower temperature (the boiling point of iron), due to the excess iron that is present.

Lean Combustion

Proponents of excess oxygen theory have reported the burning of high purity iron rods and have interpreted the composition of the slag droplets that fell. They have concluded the slag is a mixture of $Fe_{0.947}O$ along with high order ions of this or other oxides chemically bonded to surplus oxygen [*6*]. The exact amount of additional oxygen was reported to be at least equivalent to a mixture of $1.0Fe + 0.85O_2$ (this is about 10-15% excess oxygen in comparison to that needed to form hematite.

Figure 15 exhibits CEA data the writer was able to extract for the direct combustion of this combination in the style of Figures 5, 12, 13, and 14. In addition, data are shown for the thermodynamics of the unreacted constituents. At heat levels below those that were calculated with CEA, data for a linear combination of Fe_2O_3 data from Figure 13, are combined with oxygen data in correct proportion from Figure 2. This is because the excess oxygen should shift the oxide upon cooling to the most stable oxide and the leftover would then be a heat sink. These latter data in black fit very nicely with the CEA data in red, but may not be precise.

We again take the same approach as before. If one mole of iron is reacted with oxygen to exclusively produce a cooled Fe_2O_3 slag, the thermodynamicists teach us the heat release

would be about the same as that shown in Figure 15 or –412.25 kJ.

The CEA software does not contain thermodynamic data for high ferrite ions, nor apparently do such data exist, and so the CEA software can not provide equilibrium data for these species, *if they are in fact present to any significant degree*. However if they are not, then the results of this figure would likely be the theoretical equilibria.

Points "a", "b", and "c" have the same physical significance as in earlier analysis. In this case point "a" is the 298.15 K starting point for unmixed iron and oxygen gas stoichiometric to the production of $1.0Fe_2O_3 + 0.1O_2$. This is the last (right-most) curve from Figure 3, and it exhibits sensible heating to the iron melting point, a latent heat of transition followed by sensible heating to 9500 K during which the diatomic oxygen gas is dissociating due to temperature.

Point "b" is the beginning of the summation of thermo data for hematite containing 1.0 g-mol iron linearly combined with 0.1 g-mol pure diatomic oxygen. The normal heating curve is translated so that the starting point is displayed to the left of the starting point for the constituents by the amount of the heat of combustion/reaction/formation of the material that contains a total one gram-mol of iron. In this case, the data are shown in black but were extracted both from JANAF and earlier CEA results. This curve warms to the decomposition point for hematite to solid magnetite at 1681.96 K, then exhibits a latent plateau, the resulting solid magnetite plus oxygen warms to the melting point of magnetite at 1870 K and goes through a latent heat input to become liquid magnetite, then the liquid sensibly warms to the decomposition temperature of magnetite at 2626.80 K. These data nicely seem to merge with the lowest data the writer was able to coax from CEA software for direct combustion.

These CEA data (in red) begin with the decomposition of the liquid magnetite (Fe_3O_4) into liquid wustite ($FeO_{1.056}$) with the release of further oxygen and the conversion to wustite is largely complete at point "d". At point "d", a long curved transition to a nearly latent plateau that has been exhibited by liquid $FeO_{1.056}$ occurs finishing at point "e" at a temperature of 3380.11 K (versus 3389.81 K that was exhibited in Figure 5).

Beyond the near-plateau, there is a range of decomposition of the diatomic FeO(g) and O_2(g) occurring. Finally, only monatomic gases are present and the heating thereafter is sensible and the slope of the heating curve increases as a result.

Notice that again for standard combustion, the vertical line drawn from the reactants starting point which intersects the heated oxide curve at the adiabatic flame temperature, is determined the same as for pure wustite (Figure 5), but is somewhat lower in temperature (3109.97 K) versus 3389.91K, and it falls short of the latent plateau, yet about 3% of the original liquid is Fe(v) or FeO(v).

A composite perspective

So far, five equivalence ratios (ratios of iron to oxygen) have been examined and they are similar. Figure 16 exhibits them together and shows the gross similarities and differences. Regardless of the "moment one" starting materials, the "moment two" adiabatic flame temperatures are similar and are established over a significant range by the respective latent or near-latent characteristics of decomposing liquid wustite ($FeO_{1.056}$) or, in one case, boiling iron. Beyond the latent plateaus, the higher flame temperature would prevail but the *in-situ* heats of combustion are much smaller. Therefore any temperature "bump" upon combustion is much smaller relative to the same final temperature.

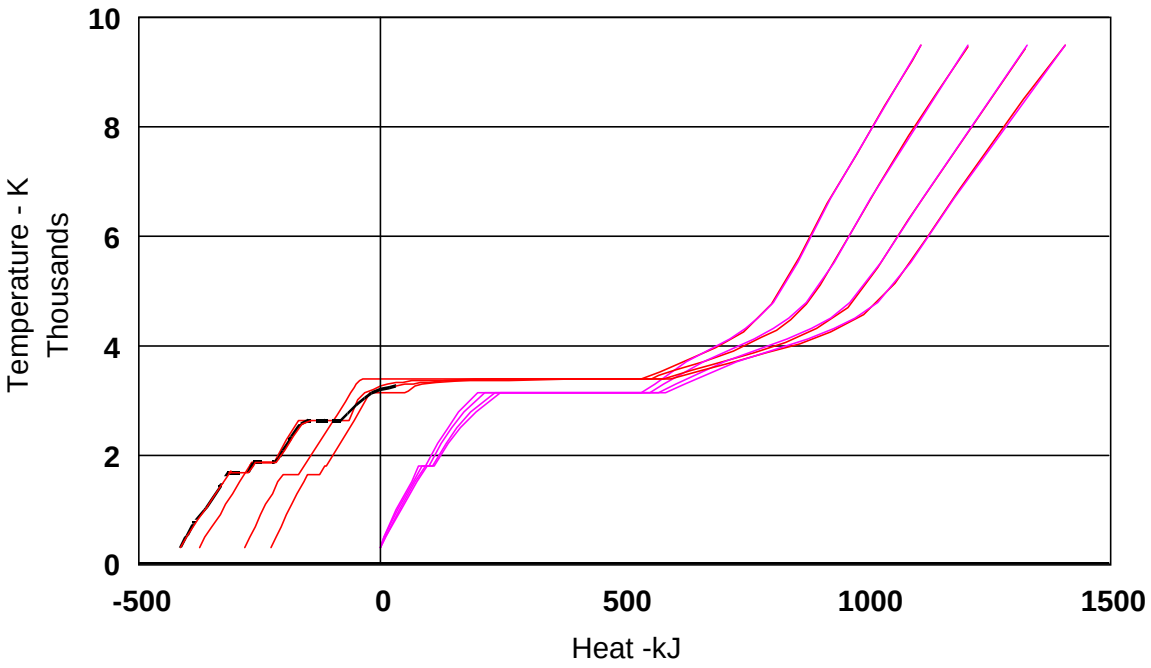

FIG. 16—*Composite thermodynamics of five combustion scenarios. From Figs. 5, 12, 13, 14, 15.*

Table 4 exhibits the standard adiabatic combustion characteristics, the conditions at the respective AFT points (usually points "c"), that would be expected, and the conditions where the iron fraction of the reactants is at its boiling point.

Role of the Pressure

Finally, pressure is commonly elevated in oxygen systems and it is a major influence in the hazards of most systems. Does pressure change the analysis presented here to any great extent? Should it change the combustion modes or alter the excess oxygen prospects or even just the abilities to inflate slag balloons?

CEA code includes the facility (again affected as it is by ideal gas or other factors) to predict equilibria at elevated pressure. This facility has been used in prior publications [*4,6*].

Figure 17 depicts data for iron/FeO at the most commonly tested pressure of 6.9 MPa (6.9 Mpa, ~1000 psig) in comparison to the corresponding atmospheric pressure data from Fig. 5. Unfortunately there are no well defined data for the sensible energies of these materials at elevated pressure in the JANAF tables.

Figure 17 depicts such data for a constant-pressure system (and this already large analysis will not address the different case of a constant volume system even though some of the metals flammability testing that has been performed has been accomplished in a fixed, albeit fairly large, volume system).

Figure 17 deals with the combustion that yields stoichiometric wustite ($FeO_{1.056}$) and again predicts that there are both decomposition and latent evaporation mechanisms operating. Again, at elevated heat inputs the curves for FeO and iron-plus-oxygen converge. It appears very likely that the high pressure, high temperature, curves would merge with the low pressure

Table 4—*Combustion properties of six scenarios in this paper.*

		Fe + 0.4224O_2	Fe + 0.528O_2	Fe + 0.666O_2	Fe + 0.75O_2	Fe + 0.85O_2	Fe + 0.528O_2
	Starting Reactants	0.8$FeO_{1.056}$ plus 0.2Fe	$FeO_{1.056}$ (wustite)	Fe_3O_4 (magnetite)	Fe_2O_3 (hematite)	Fe_2O_3 plus 0.1O_2	6.9 MPa 1000 psig
AFT in K	At 298 K[a]	3121.91	3389.73	3264.78	3190.18	3109.97	3990.71
	At iron B.P.[b]	3374.45	3389.81	3379.91	3369.97	3356.90	4868.11
Fe in Liq. Fraction(s)	At 298 K[a]	~93.63%	~93.21%	~95.29%	~96.14%	~97.00%	~99.99%
	At iron B.P.[b]	~57.78%	~57.4%	~59.06%	~59.27%	~59.47%	~51.78%
Fe in gas fraction(s)	At 298 K[a]	~6.37%	~6.79%	~4.71%	~3.86%	~3.00%	~0.01%
	At iron B.P.[b]	~42.22%	~42.6%	~40.94%	~40.73%	~40.53%	~48.22%
% gas as Fe(g)	At 298 K[a]	93.16%	46.54%	11.38%	6.22%	3.27%	0.56%
	At iron B.P.[b]	62.53	47.46%	35.58%	30.77%	26.38%	45.64%
% gas as FeO(g)	At 298 K[a]	6.02%	18.94%	10.45%	7.25%	4.80%	2.23%
	At iron B.P.[b]	18.07%	18.96%	17.96%	17.12%	16.11%	17.27%
% gas as O	At 298 K[a]	0.67%	15.93%	19.91%	17.38%	14.34%	15.64%
	At iron B.P.[b]	10.55%	15.65%	18.90%	19.89%	20.56%	24.80%
% gas as O_2	At 298 K[a]	0.16%	18.58%	58.26%	69.15%	77.58%	81.56%
	At iron B.P.[b]	8.85%	17.91%	27.56%	32.22%	36.95%	12.29%

[a]These data correspond to the points "c" on Figs. 14, 5, 12, 13, and 15 , respectively and point "c′′" on Fig. 17.

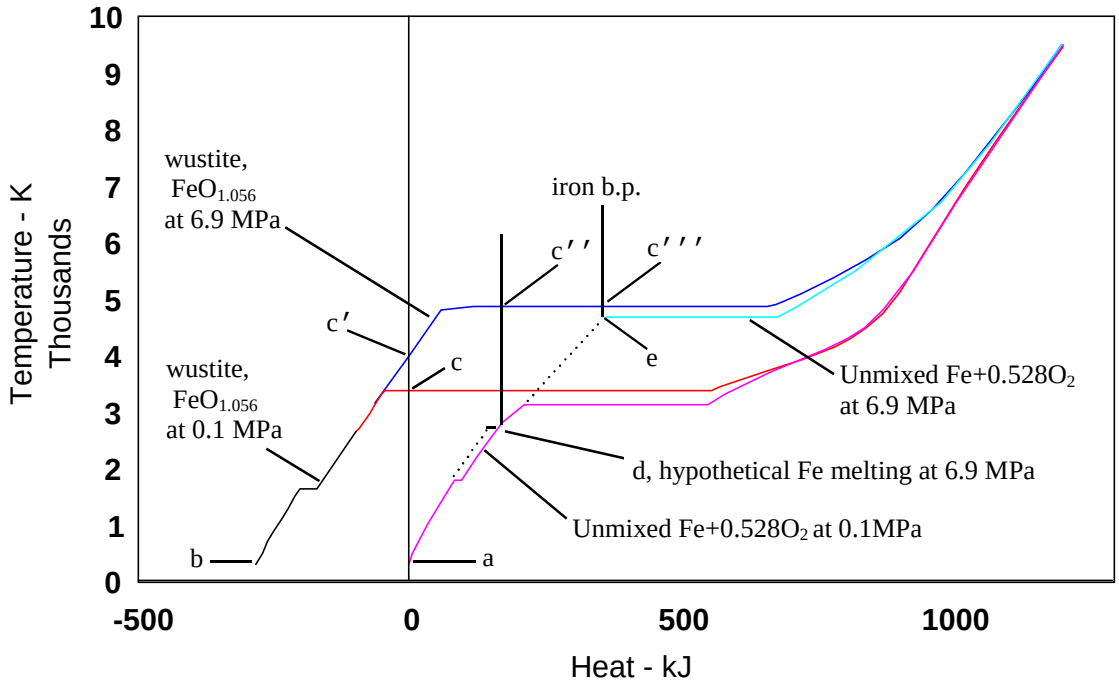

FIG. 17—*Thermodynamics of iron and wustite at 6.9 MPa (1000 psig) . For comparison some data are at 0.1 MPa.*

low temperature curves however, at pressure the melting points and boiling points would be significantly elevated in comparison to those that are depicted.

Very interestingly, this figure suggests that the starting and ending points of combustion at 1000 psig are the same as for combustion at one atmosphere.

Further, the high pressure moment-two condition at point "c′" appears at a location where liquid wustite is being sensibly heated, therefore would have no vapor fraction to allow vapor phase combustion nor to inflate the slag. However, remember that as for lower pressure tests, direct observation of burning droplets indicates that they leave behind a layer of liquid and therefore a significantly preheated specimen tip. And because the melting point is elevated due to pressure, the specimen tip would likely be preheated to significantly higher temperature than at lower pressure. As a result, the "pass-through heat" and "equivalent heat of combustion" are both greater.

Therefore, one would have a condition in which the combustion starting point for each droplet would be on the warming curve of the iron probably between the melting point (shown only as a hypothetical point, "d") and the boiling point "e", representing the equivalence of an elevated *in-situ* heat of combustion/formation. For both of these, the combustion point would be directly above and both of these would yield adiabatic flame temperatures on the latent plateau for the decomposition/evaporation of wustite at a temperature of 4868.11 K.

Note that the boiling point of iron at this pressure, 4674.17 K, is closer to the oxide decomposition temperature, 4868.11 K, than at lower pressure, 3389.81 K versus 3138.45, respectively. The composition of the gas that forms over decomposing wustite in the latent plateau is only slightly different than at atmospheric pressure (Table 4). Fe(v) is about one percentage point lower, FeO(v) is about one percentage point lower, but O_2(g) is about six percentage points lower, while O(g) is about eight percentage points higher. Hence, *fractional vapor combustion and slag inflation are not precluded*.

Discussion/Speculation/Future Work

If this effort to simplify and elaborate on the current understanding of iron combustion finds any acceptance, and is not fraught with error, other metals could be analyzed similarly. Metals that are predominantly liquid-phase burners are perhaps the strongest candidates for meaningful analysis. Predominantly vapor burners and alloys may not be nearly as amenable, but a similar attempt is still desirable, if possible, for a metal like aluminum. Such efforts would be worthwhile and some, perhaps aluminum especially, may be partially within the writer's abilities and interests and available time.

This work on iron might also be expanded to address more elevated pressure scenarios, again depending upon reception and validity of the current effort.

This effort sought to explore and promote the concepts of "batch" and sub-batch combustion in contrast to "transient/incremental/partitioned" (TIP) combustion. The prospect of "pass-through" heat and preheat would seem to be especially important to partitioned combustion and this characteristic has been explored and may help model metal combustion. The text has explored the idea of pass-through heat in real world combustion tests like ASTM G 124 and the way it may act as an increase in the effective heat of TIP combustion. However, where does one find an experimental example of "batch" combustion? Nicely, NASA testing in zero gravity [*15-20*] in which the slag continues to accumulate at a test specimen's tip indefinitely are a sce-

nario in which all of the heat of combustion (save for external losses) would be present in all of the combined products as a “batch” and the effect of any preheat or ignition energy would therefore tend to be less. Therefore, the number of scenarios in which vapor combustion, vapor generation and slag inflation occur may be fewer. However, the present drop-tower and diving-airplane testing could make adequately rapid quenching of droplets a challenge to achieve.

For batch combustion, it is relatively easy to calculate a condition below which sustained combustion would not be possible because the heat of combustion (in combination with any ignition energy) would not be able to sustain a growing liquid slag. But a calculated threshold condition for TIP combustion is much harder to formulate criteria for due to many potential “pass through heating” variables.

Iron that is subcooled or is in heat transfer with a nonreactive [diluent] material would have a more difficult time achieving and sustaining batch or (TIP) combustion because of a more difficult task of melting the product slag mixture. Subcooled specimens would be difficult to test experimentally, and they can only be subcooled to a modest degree (absolute zero being a limit). Therefore, an alternative series of tests might involve standard testing of samll-bore tubular specimens filled with any of the assorted stable oxides of iron. A core of hematite (Fe_2O_3) should produce a higher threshold than magnetite (Fe_3O_4) which should produce a higher threshold than wustite ($FeO_{1.056}$), which should produce a higher threshold than solid iron.

The figures in this report and the careful use of the CEA software begs for many analyses. Indeed, simple graphical software to facilitate reading of the figures would also help with a number of kinds of analysis. That is in the writer’s plans.

ASTM Committee G4 is encouraged to appraise modify and adopt an “as is” and “use at your own risk” PC utility to allow such simplified analysis of iron thermodynamics (once they are validated and verified), and perhaps other, combustion thermodynamics. This would require a consensus on the most appropriate data to comprise the figures that would form its basis.

Iron and steel are such important metals in oxygen service that a thorough understanding of their behavior is crucial. It is often the only economic or practical option and any improved abilities to identify heretofore unrecognized combustion prospects or to upgrade its fire resistance might be among the most important developments possible. This and earlier effort has embroiled itself in the role of specific gases (iron vapors and carbon products) on the burning of iron. Both warrant further experimental work.

Carbon has proven itself to be inhibitive and even protective against iron combustion both theoretically and in practice in both massive ton-scale blast furnaces and in small scale lab tests. The data are compelling in this regard. Whereas most oxygen compatibility data are based on small scale laboratory tests, the role of carbon is buttressed not only by small scale lab tests but mega-scale industrial experience. When massive blows of sonic oxygen are injected in steel making furnaces, the iron is largely prevented from reacting until the carbon is fully consumed.

Since the early 1980s, there have been modern data which suggest the role of carbon even in small amounts may be important. Threshold pressure measurements for combustion of steel that is high in carbon (alloy 440C at about 0.95-1.20%C) have yielded surprisingly high results of about 2500 psig [*21*]. And decarburizing the specimens to 0.2%C produced greatly reduced thresholds of combustion to more commonly observed levels of about 1000 psig in this chromium stainless steel) [*21*]. NASA first shared these data with ASTM G4 in 1983.

In the meanwhile the drastic influence that minor constituents can have has also become manifest in a few other cases. Trace argon in oxygen has shown itself to be a drastic influence on aluminum flammability. These results already suggest that every OSP must be diligent in

any use of aluminum in applications where the oxygen purity may be ultra-high, and in the past decade, or so, commercial grade oxygen has increased significantly in purity. And variations in the composition of Haynes 214 alloy within the specification limits have been shown [*22*] to provide wide variations in its flammability.

Although G4 has often talked of actually inventing alloys of improved compatibility as part of a master plan to expose the recipes for compatible metals, little progress has been reported in more than two decades. And even if new alloys could be discovered, their characterization, production, and manufacture, failure mechanism modes, etc, etc., would be Herculean obstacles against their actual practical deployment. However, steel may be the most thoroughly studied and understood metal for a range of normally used and marketed carbon contents. And yet the role of normal variations in carbon on steel and related alloys (stainless steel) and the exploitation of this variable has been promoted and yet there has been an almost averse reaction to embracing the promise in favor of dismissing it. This, even though carbon is a common constituent, economic, well established in practice, and an easy to deploy constituent that would be relatively easy to adjust and control in oxygen systems The role of carbon warrants study in the field and the development of criteria for its exploitation, but this is unlikely to be a option for the writer. Nonetheless, the earlier discussion suggested testing of tubular iron specimens filled with various oxides, and similar testing with of small-bore tubes with cores of carbon or graphite might also be interesting. And indeed, testing of iron and steel with oxygen and carbon dioxide (perhaps even carbon monoxide) gas mixtures might also be illuminating. Might carbon dioxide or carbon monoxide serve as a potent diluents and/or extinguishants in oxygen?

The writer also asserts and clings to the belief that currently available existing experimental results convincingly disprove the presence of large-scale excess oxygen in burning iron and steel at atmospheric pressure. The presence of large-scale excess oxygen complicates what in the writer's opinion is a more reasonable and consistent way to analyze iron for applications. However, there is a disconnect in these excess-oxygen data. Most past excess-oxygen analysis has focused on combustion in pressurized oxygen as high as 6.9 MPa and on extremely pure iron. The contradicting data focus on atmospheric pressure and steel wire.

The thermo analysis provided here does not in the writer's opinion suggest that combustion at higher pressures should be different regardless of whether there is or is not excess oxygen present in either or both cases. But theory, fact, and opinion do not always square.

Among the lynch pins to the excess oxygen hypothesis, if the theory is appropriate at higher pressures, appears to this commentator, to include the following key observations/ assertions of the Excess Oxygen Proponents:

- Droplets that fall from burning specimens are purely lower-surface-tension liquid iron-oxide draining from retained higher-surface-tension liquid iron, specifically the droplets are hypothesized to be FeO and excess oxygen (present in the slags as exotic high-oxygen ions).
- The surface of fallen slag is highly active as the wustite burns during cooling on the contained excess oxygen to produce the higher oxides and vents any leftover oxygen gas.
- Solidified slag exhibits distorted surfaces, fissures spouts and entrained voids due to the evolution of gases from within and is composed of higher oxides of iron, namely Fe_3O_4 and Fe_2O_3.

These characteristics are plausible and easy to observe and easy to interpret. The presence of excess oxygen at higher pressures has also been directly measured but the experimental approach is complex and even small errors in some of the measured properties by even a few degrees could alternatively explain the measurements and invalidate the conclusions.

However in atmospheric pressure tests with steel wires each of these results did not obtain. Instead droplets did contain entrained iron [*10*], the surface of rapidly quenched or rapidly inerted specimens were calm during cool-down, did not exhibit distortion and few entrained voids (none that had the appearance of gas evolution to the exterior), and the only oxide present was wustite ($Fe_{0.945}O$, $FeO_{1.056}$). And the only voids that were seen on quenched attached droplets were along the previously molten iron-to-oxide interface.

The experimental challenge of dripping, burning molten slag into an argon atmosphere at pressure should not be inordinate, and if such slag proved to be principally wustite, perhaps with a second Fe phase, and if it was also calm-surfaced after solidification (suggesting no venting activity), the result would be a strong contradiction to the existence of large scale excess-oxygen even at pressure. This effort should be relatively easy for numerous active labs, but might even be possible in an abbreviated fashion for the writer, and might be of interest to him.

However, the writer is presently thwarted from performing any examination of ultra high purity iron combustion at any pressure, high or low. Efforts by him to obtain high purity iron several years ago were thwarted by a company that would only sell to companies and universities in what appeared to be an anti terrorism precaution. In the current vogue of going after the rare solitary evil-doer by trampling the rights of everyone else, their precaution has protected the American nation from the thought of what some one with several feet of high purity iron might be capable of doing. Hurray for them!

Finally, these results raise an only loosely related query. Figure 2 indicates how oxygen gas dissociates at temperature. Further, we have seen that monatomic oxygen is highly reactive grabbing hold of oxygen or iron atoms with near equal facility and similar heat release upon cooling. About a year ago the writer published a large tutorial on adiabatic compression of real gases using recent NIST software [*13*]. Apparently neither in that software nor in his recollection of any past analysis of adiabatic compression ignition, has there been a consideration of dissociation of the compressed gas into highly reactive monatomic species. In every case, the diatomic structure of oxygen has been assumed (“apparently”). Do the NIST software equations of state do this? But in fact, in the most hazardous conditions of highest compression, therefore highest dissociation, the step-like transition to highly reactive species may act to absorb heat and lower temperatures, but also to reduce heat capacity and raise temperatures, and enable surface attack of construction materials. A exploration of this mechanism is warranted and is needed. At least a superficial treatment is within the writer’s ability and may be attempted.

Conclusions

- Today yet, the most valuable oxygen safety information about any material is its actual track record in past usage. A long successful history is still the best parameter for designing oxygen systems. For this reason, OSPs have always relied most on judgment in selecting materials for use in oxygen systems, but have tempered that judgment primarily and principally with real world experience but also secondarily with an assortment of theoretical and experimental data that have been hard to apply in any direct fashion. This

approach should continue, but the analysis here, if verified and validated, provides additional perspective to decisions relating to the use of iron especially in new applications outside the experience base.

- NASA CEA software provides a powerful but quirky tool with which to analyze metal flammability. Its power and its free open-source code warrants widespread efforts to exploit the many potential benefits. But simpler software is needed in the OSP community. The apparent conventions used in the software and terse documentation provided (at least on its fundamental operations) can be and have apparently been challenging for even rather advanced analysts to successfully master. Apart from quirks, CEA software is predicated on ideal gas assumptions, and at the high temperatures of metal combustion and close proximity to saturation conditions of both reactants and products, this assumption may be significantly flawed. Validation and comparison of these results with other software is desirable. Further, Kuo [*9*] describes at least one thermo software package that seeks to address nonideality, at high temperature and comparison to results from that package is also desirable.
- CEA software, *if correct*, suggests that any tendency of iron to burn as a vapor will be tempered by a significant volatility of FeO vapor that will tend to dilute, blanket and slow any vaporous combustion process.
- Any presence of even low levels of FeO vapor may be a more important factor to the historically recognized slow liquid phase combustion of iron than its low tendency to vaporize under the influence of its heat of combustion.
- Because of the importance of gaseous FeO species in the vapors of burning iron, it is vital to validate the existence of gaseous FeO, and expert commentators need to weigh in on the subject. If its existence is not known, then experimentation needs to be designed and conducted to verify or disprove this gaseous state of this molecule.
- Because iron is so widely used in oxygen service, further testing to definitively establish its properties and promising chemistries is still warranted. This includes further experimental study of iron and the influence of heat and heat sink.
- Carbon should be considered a crucial constituent of iron and steel alloys and may well be an important factor in their flammability, and its further study is needed.
- Excess oxygen beyond that necessary to form Fe_2O_3 has been largely disproved in steel combustion at atmospheric pressure and is suspect in this commentator's mind with regard to its presence at elevated pressures.
- Regardless of the final slag composition, the temperature and gas-product composition of burning iron should be relatively constant.
- Burn ratios relative to assorted oxides may have little differing predictive value for combustion tendencies, but should be evaluated further for batch versus transient/ incremental/partitioned (TIP) combustion.
- CEA predicts numerous vapor species that would be present during the combustion of iron and steel, including FeO(g), Fe(g), O_2(g) and O(g), and also in the case of steel one would suspect CO_2, and CO, would be present in sufficient volumes to inflate a slag balloon at atmospheric pressure and possibly at pressure to at least 6.9 MPa (1000psig).
- Partitioned (TIP) combustion modes in combination with pass-through heat may yield combustion of steel that behaves as if it has a much greater heat of combustion than it actually does. Further analysis and testing is needed of the way specimens preheat during

combustion to appraise the degree of pass-through heat.

- Iron and steel warrant a renewed attention to reconsider its use, its expanded use, it engineering for specific purposes, and the simplified methods to understand and evaluate it relative to geometry and composition of alloy and gas.

Summary

Iron is the most widely used and most important construction material for oxygen systems, but it may also have among the least amount of latitude in use. An improved and thorough understanding of this material might not only improve the ability to understand incidents but might allow for wider, safer use.

This paper has attempted several things. It illustrates a thermo-analysis technique for iron and identifies a PC utility approach to simplify its use. This analysis is based largely upon NASA chemical equilibrium software and may be controversial or contain errors. The software may be flawed for real-world systems. This should be educational and perhaps even spur improved versions, perhaps even corrections, of the thermodynamic maps that are included.

This paper uses the software and data to justify an argument defending fractional, partitioned vapor-phase combustion and inflated structures during simple lab tests of burning iron and steel.

Although the prospects of vapor phase combustion have not suggested severe combustion modes are likely, the potential presence of gaseous materials fires a shot over the bows of excess oxygen proponents, arguing that in the crucial aspects of combustion, the dissolved oxygen may well be modest in comparison to all of the attempted measurements of it so far.

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Appendix A
The CEA Chemical Equilibrium Software

Chemical Equilibrium for Applications (CEA) is a NASA software package written by Sanford Gordon and Bonnie McBride that can be freely downloaded from the Internet. Its roots trace back more than forty years and it is written in Fortran language which employs cumbersome command line input. Recently a graphical user interface (GUI) has been added to simplify its use on modern personal computers. Numerous files are downloaded in compressed formats and must be extracted and initialized. Although the writer avoided this program for a time, wrongly thinking it required a Fortran compiler, in fact the download includes a compiled executable file as well as the source code for those who wish to make modifications with all that that entails. The GUI is a great productivity aid, but in the writer's view the program is not for casual use.

Use of this code is cited in many leading combustion texts [*9,14*], and a recent revision of the Kuo text [*14*] introduces a detailed discussion of it in comparison to numerous other similar products (but not Outukumpu HSC which has also been cited in papers in the ASTM G-4 collegium). Some of the other software is derived from CEA and indeed, CEA may have provided the basis for still others, a testament to the value of open-source freely published software that provides a strong incentive to ASTM Committee G4 to provide derivative and other hopefully simplified software to its audience.

However, CEA is not without its problems. It was apparently developed to address gaseous combustion and the equilibria that form in the gases. It does allow for prediction of whether any condensed phases might form but one paper [*6*] states "it does not handle multiphase systems well."

This writer found the software quirky especially in some modes of use. Often it does not converge to an answer if the temperature is well below the normal adiabatic flame temperature. Some error messages produced are not catalogued. Documentation is not highly detailed. Sometimes it seems to produce results that it refuses to produce at other times, and some of these did not seem plausible to the writer's limited judgment. Often it requires very astute initial guesses to facilitate achievement of the final result, the final products and other parameters. And sometimes it produces apparently valid results different from what the user expects.

It was used exclusively in the HP mode in which the user specifies an enthalpy input (positive or negative) and a pressure, along with reactants or just plain materials. It then calculates a whole range of parameters including the adiabatic temperature that would result and the equilibrium distribution of product materials. It typically starts with an estimate of 3800 K and then does approximations to that number. But in some cases the program does not converge unless a very astute guess is made for the initial estimated temperature (among other parameters). And in some cases the program does not converge even when one estimates the precise temperature that would result if the program did converge. In some cases the program needs a disparate estimate to enable convergence, it needs to start with a wrong estimate to get to a right answer. That is some kind of quirk.

However, when seeking both combustion results and simply heating results, it produced a wide range of plausible reproducible answers consistent with those that others have published

and so this paper was pursued. At low temperature, JANAF [*23*] data were used to complete the curves of interest in a few cases where either the software is not operative or where the writer's inputs were insufficiently astute.

The writer considered comparing the results of CEA with an older version of Outukumpu HSC to which he had access, but the multiplication of effort and expansion in the size of this already large paper were daunting. Perhaps a future effort will be undertaken depending upon the reception to this material.

The writer is also a staunch supporter of the use of PC utilities and their adoption by ASTM Committee G4 (however, G4 at large is not as supportive as it once was) to simplify and upgrade the quality of study and understanding of oxygen hazards. As a result, this paper proposes a method to analyze the apparent thermodynamics of iron, even if these data used are flawed, that could be basis for a simple PC utility similar to one he has proposed for the analysis of adiabatic compression. This approach could employ the "simplified" thermo analysis here and is commended to ASTM G4 for evaluation and potential adoption and expansion to other metals besides iron (if there are any that are amenable).

If the results in this paper prove to be valid (and they may not), they will represent a much more extensive and complete perspective and will allow a much better understanding of iron combustion than the writer has been able to glean from the mainstay oxygen compatibility literature in the past.

Appendix B
The Excess Oxygen Controversy

A 1989 study [*24*] reported that the slag droplets that formed on burning stainless steel at pressure were too big (up to 2.5 times what their apparent volume should be). There appeared to be only one material present that could produce their extra bulk: oxygen, and there would have to be so much present that it would far exceed chemical stoichiometry for any of the common oxides of iron. A little more than five percent excess oxygen is well-known to be present in the cooled slags of the lowest oxide of iron, the eutectic point for wustite ($Fe_{0.9475}O$ or equivalently $FeO_{1.056,}$ and these two designations are used nearly synonymously in this paper) This composition is not in stable equilibrium at atmospheric pressure but is nonetheless commonly present in specimens at atmospheric pressure for periods of time that might fool one into thinking it *is* stable.

However, the first efforts to measure massive excess oxygen in the slag of burning iron were reported in 1992 [*2*] based on a doctoral thesis [*25*] and elaborated upon in numerous following papers [*26,27*]. The initial observations and measurements implied that the amount of oxygen in the slag might be as high as seven times the stoichiometry of Fe_2O_3 (equivalent to Fe_2O_{21+}, or FeO_{10+}). A later paper [*26*] attempted to refine the estimate and bracketed it between an upper limit of seven times and a much lower limit as low as only 1.15 times the oxygen in Fe_2O_3, the latter equivalent to approximately $FeO_{1.7}$. This lower limit for oxygen in a molten slag of $FeO_{1.7}$ would be 12.5 times [(1.7-1)/(1.056-1)] the amount of excess oxygen present in the eutectic $Fe_{0.9475}O$ ($FeO_{1.056}$). However, it would be only 1.3 times [(1+1.7)/(1+1.056)] the number of total atoms. Hence even in a ionized liquid of Fe and O atoms, the lower estimates may be too small to account for the excess slag size. One might not be able to build a liquid droplet 2.5 times as large as expected from the addition of $O_{0.644}$ to $FeO_{1.056}$.

However. today the body of excess oxygen advocacy includes other metals study and this analysis does not seek to consider any other metals at all.

The writer [*10*] examined steel burning in search of the excess oxygen but only at atmospheric pressure in a series of simple tests and surmised that the apparently too-big slag may in fact be caused by bubbles inflating it (possibly even a single slag balloon with only a small mass of gas contained). He photographed burning steel that actually experienced abrupt increases in the slag volume by about the same 2.5 factor [and much larger factors in other scenarios that are even more resemblant of inflation]. In attempting to itemize the gases that might inflate such a slag "balloon", a figure (figure number 4 in the paper) and in related discussion he followed the lead of the earlier experimenters [*6*] and cited gases that might conceivably form: CO, CO_2, O_2, H_2O, H, iron vapor and "others" as potential candidates. He did not cite monatomic oxygen and oxides of iron explicitly, the former an oversight and the latter because he was not sure if any iron oxides existed as vapors. That figure is included here as Figure B1.

The writer worked in an environment rich with steel-working men, all experts in the subject. Strong support was received from among them for the prospect of CO and CO_2 inflating the slag. In 1999, Michael Lanyi [*11*] presented a compelling case for why the apparent slag balloons this writer seemed to observe would exist and be filled with a CO/CO_2 mixture. Curiously, although this paper largely disputes the concept of large-scale excess oxygen, it appears

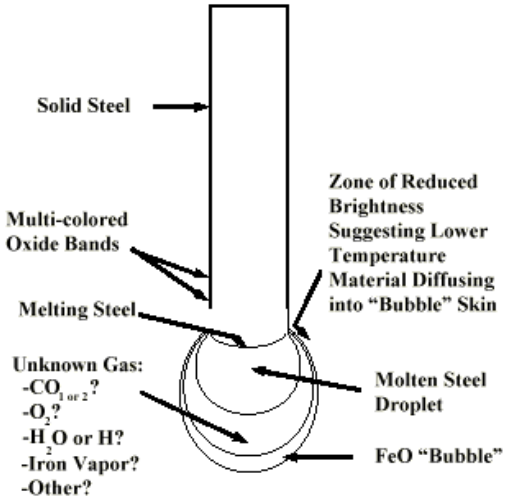

FIG. B1—*Speculation on inflating gases from Werley* [*10*].

to have been cited only once by those who support the excess oxygen model in discussing their analysis but its contradictory aspects were not noted. Indeed, it appeared to be cited as supporting of the excess oxygen model.

The Lanyi analysis is simply compelling in its depth and resource materials and may have the explanation of the writer's experiments on steel exactly right, but in it Lanyi also completely excludes the prospect for iron vapor as a present or possible gas in any annulus. Lanyi bases this upon a thermo analysis and judgment and empirical observations in the steel-making and steel-burning industries.

This leaves the writer with a dilemma. The Lanyi analysis is superb for explaining the combustion of steel and even the likely formation of a CO/CO_2-filled slag balloon. However, the entire large-scale excess oxygen theory began with too-big slag droplets on burning stainless steel (which contains far less carbon with which to make CO/CO_2). Perhaps other constituents in stainless steel can form vapors, and there have also been publications exploring excess oxygen in other metals [*27*]. But very importantly, the original excess oxygen work reported the use of ultra-high purity iron wire with virtually no carbon and virtually nothing else except oxygen present. Slag balloons, if present in the original work are hard to rationalize on the basis of anything but iron or oxygen or their oxides as a slag inflator. Oxygen is a viable prospect, but can the prospect of iron vapor be excluded thermodynamically? The only iron oxide among the three commonly cited that is reported to be present at the temperatures approaching those for the combustion of iron is FeO, and upon heating that is cited as decomposing into Fe (as a liquid or gas) and O or O_2 (as gas or a solute in the liquid). The decomposition of FeO is often taken as a latent phase-change process, but this prospect has been challenged [*3*]. Nonetheless, although the writer has seen little or no discussion of gaseous FeO and no tabulation of measured thermodynamic data for FeO gas in the literature, there is mention of FeO gas in theoretical ideal-gas calculations in the JANAF tables and in several papers based on the CEA/ precursor code. So does FeO vapor exist or not? The writer has no certain answer to this.

Whereas the original insight into the prospect of excess oxygen in iron slag droplets

cited their volume, the original excess-oxygen study (both the publication and the doctoral thesis [*25*] on which it is based) which sought to measure whether oxygen is depleted in the test chamber during combustion did not appear to discuss the volume issue at all, and seems to concentrate on droplet size only in terms of its mass. Indeed the writer found no indication at all as to whether these slag drop volumes were physically small or not, however, the droplet density at detachment was reported to be of 4.61 g/cc (thesis [*25*] Summary page 220) which suggest volumes were measured at least once and one would hope the aizea were not greatly smaller in volume than had been observed in the earlier work, since that would have been highly noteworthy. For comparison, the density of room temperature iron is 7.86 and the density of room temperature FeO is 5.7, Fe_2O_3 is 5.24, and Fe_3O_4 is 5.18. At high temperatures the densities would have been lower and are not greatly larger than that for the droplets, suggesting the droplets should not have been larger. However, any inflation of droplets at high pressure would mean compressed annular gas volumes unless there were another mechanism operating (such as the higher adiabatic flame temperature), to produce similar sized "balloons" at both low and high pressure.

At present, the large-scale excess oxygen proponents (EOPs) have proposed the oxygen is contained in the slag chemically bound as ferrite ions heavy with oxygen up to FeO_7^{-8}. They have cited literature which have identified these ions in slags but they are not discussed widely nor quantitatively. Furthermore there are no data for such ions present in the CEA software and so the software can not factor any such presence into its calculations [*6*].

The writer has no strong attachment to any prospect. Perhaps there are other explanations. Perhaps some equilibrium could be postulated to allow for an oxygen-filled annulus.

The excess oxygen proponents have published with confidence on the topic but to the writers knowledge to date have not acknowledged this challenge therein though they have included statements that may appear to dispute and dismiss it. Curiously, in one paper [*26*] that followed access to the writer's own paper, and that greatly reduces the suspected scale of excess oxygen that is asserted (indeed, reduced it by more than 80%) was added a comment "..It is asserted, the majority of the excess oxygen in the molten drop must be present as higher oxides not as gaseous bubbles".

The writer continues to question the validity of both the earlier and later testing, and is of the opinion that the degree of excess oxygen alleged in these slags is not only challenged at atmospheric pressure by his own work but disproved, and at the higher pressures questions both the larger and the lower estimates as both being too large and the lower estimates as also not resolving all of the issues.

Appendix C
What Excludes Iron Vapor Formation?

Two of the specific arguments that exclude iron vapor formation and therefore both vapor combustion and slag inflation by iron vapor are the following:

- Steel plants do not lose product during oxygen blows.
- Iron does not transfer sufficient heat during combustion to vaporize itself.

The writer does not accept these individually or collectively as clear exclusionary bases for the following reasons.

No Lost Product

Lanyi [*11*] comments that "if the steelmaker (as described in the [his] background section) can inject pure oxygen into an already superheated molten iron on a massive scale and detect no material loses due to vapor phase generation, we can rule out the possibility of producing a vapor phase when combusting ambient temperature iron with ambient temperature oxygen".

This is a powerful argument. However, one must also keep in mind that in the steel making process, one of the purposes of injecting the oxygen is to heat the steel and deplete the carbon to levels that meet specifications. Steel makers are under potent incentives to stop the oxygen injection at that time, while there is still a prescribed carbon presence in the furnace, and that remaining carbon would be protective against iron combustion, as Lanyi describes, and actually acts to reduce any iron oxide present. The writer has read descriptions of the basic oxygen process that point out the importance of interrupting the oxygen blow when the carbon reaches specification, beyond which the consumption of iron accelerates.

This argument would be much stronger if one could cite an instance in which a basic oxygen furnace continued the blow of oxygen for an appreciable time after the carbon had been depleted and in which there was no dust produced. This scenario of burning preheated iron is explored in some detail in the main text here.

Insufficient Heat

Several commentators, including Lanyi [*11*], have estimated the thermodynamics of burning iron. Early efforts back-calculated "burn ratios" in which the heat of combustion of iron to its oxides was added to a corresponding amount of pure iron to see whether it could be vaporized. These burn ratios lacked sophistication but were informative in their time. They have been criticized [*3*] and they are flawed in some cases. Later calculations were more realistic [*3,7,8*] and consider the heat capacity of reacting oxygen but were still flawed.

Lanyi's Figure 3 allows for their analysis. Figure C1 replicates Lanyi's approach. Shown are his thermo curves for both iron and the lowest oxide of iron, FeO, the only oxide that has not decomposed at the temperatures of interest. The enthalpy to fully vaporize solid iron is at point "a" upwards of 115 kcal/g-mol. The heat of combustion of iron to form FeO product is only about 64 kcal/g-mol. Therefore if the entire heat of combustion could be trans-

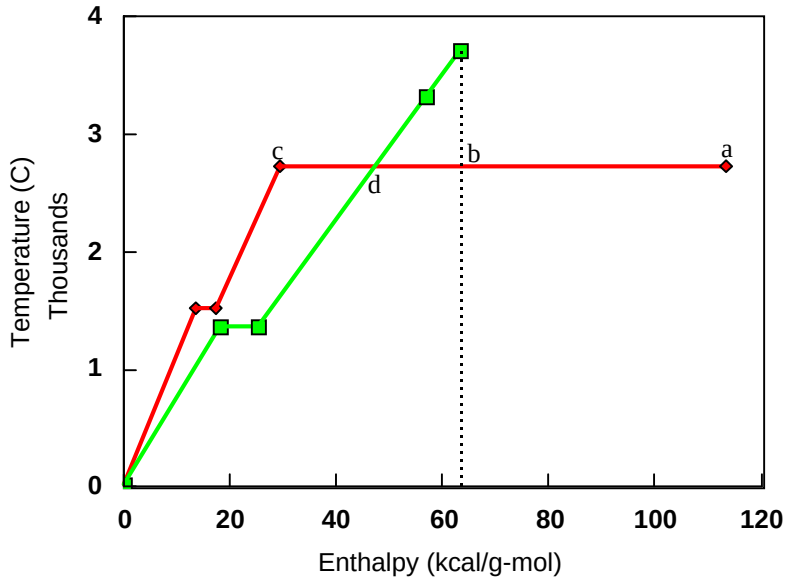

FIG. C1—*Lanyi's heat partitioning* [*11*].

ferred to pure solid iron it would heat it only to point "b", however this point *is nearly half way to complete vaporization* on the latent heat-of-vaporization plateau. So that *nearly fifty per cent of it could be vaporized*. But this is not a realistic scenario in many cases, unless one is dynamically heat exchanging iron oxide against iron in a sophisticated heat exchanger (as reviewed in the text of this paper).

Lanyi notes that any heat from burning any portion (any "batch" or "sub-batch") of an iron specimen must partition itself among heating of the oxide formed, heating of the unburned iron and heat loses to the environment. He then takes the still-conservative approach of apportioning the heat of combustion of an *entire* specimen of iron over his own judgment as to the scale of these three heat sinks, and it then seems obvious that there is not enough heat to get beyond the liquid stage. He could have gone further and noted that, more precisely, if the iron is incompletely reacted, then there is only a fractional portion of the enthalpy of reaction available. And the likelihood of iron vapors would appear to be even less.

However, a further, but still incomplete, analysis can be provided here. Lanyi's curve indicates about 64 kcal of heat results from the complete "batch" combustion of one g-mol of iron. Furthermore, it shows that about 45 kcal of heat are needed to bring one g-mol of FeO oxide to the boiling point of iron. Therefore, there is 19 kcal (64-45=19 kcal) of heat transfer possible at or above the boiling point of iron. His curve shows that complete vaporization of iron requires about 115 kcal per g-mol. Therefore, the excess 19 kcal of heat would be capable in theory of vaporizing an addition 0.165 g-mol of iron (19/115=0.165).

Hence during the combustion of 1.165 g-mol of iron, it would be able to vaporize at most 14% [100x0.165/(1+0.165)] of itself, and this is why a 20% heat loss would preclude even any fractional vapor-phase batch-combustion of iron.

Therefore although these analyses indicate iron does not have sufficient heat of combustion to *fully* vaporize itself, it does not preclude a fractional vapor-phase combustion provided the heat loss rate is below 14%. But this is not the whole story if there is "pass-through heating" and preheating yielding elevated "equivalent heats of combustion" as are reviewed in the text .