Barry L. Werley[1]

Graphical Interpretations and Parameters for the Thermo-Analysis of Oxidant System Fire Safety[2]

REFERENCE: Werley, B. L., **"Graphical Interpretations and Parameters for the Thermo-Analysis of Oxidant System Fire Safety"**, Self-published opinion, *BWOpinion* Website, www.enter.net/~bwerley, 2010, 24 pages.

ABSTRACT: Burn ratios and their shortcomings are examined graphically and more sophisticated and powerful alternatives are examined based up thermochemical portraits obtained with the thermochemical software HSC and CEA.

KEY WORDS: burn ratio, chemical equilibrium, thermo portrait, iron, oxygen safety, TIP combustion, batch combustion, oxidant compatibility, oxygen compatibility.

The liturgy of safe oxygen system design includes thermodynamic criteria and parameters including "burn ratios". Burn ratios were formulated in the 1970s and are similar to the ancient (1700s) theory of Sir Humphry Davy [***1***][3]. These parameters compare the amount of heat transfer need to melt or vaporize a metal to the heat of combustion of the metal. And they are very practical and powerful (but imperfect) insights into the hazard of metal combustion.

If the heat of combustion is more than enough to melt all or part of the metal then it may just burn as a liquid (as many metals are known to burn), and if the heat is sufficient to vaporize part or all of the metal then the metal may just burn as a gas (as many other metals are known to burn). However, these parameters are even more powerful when used in the inverse way. If there is not enough heat to vaporize any of the metal, then the "batch" metal is unlikely to burn as a gas and is therefore likely to be restricted to at most slower and less destructive combustion. And if there is not enough heat of combustion to melt any of the metal, then any "batch" combustion will be still much slower and possibly even unlikely to occur at all. Any reaction, such as rusting, that occurs without melting or vaporization of the base metal tends to require either huge ignition energy or to be extremely slow.

In other words, it is one thing to surmise that if a metal's boiling-point burn ratio is greater than one, that it will burn as a vapor, but it is a much more valid and robust to surmise that if a metals burn ratio is less than one that it will *not* burn as a vapor.

Of course, in any precise or borderline situation, a more careful analysis might be needed. But nonetheless those metals with the smallest melting-point burn ratios (gold, silver, platinum) are taken literally as the impractical but gold standards for safety.

[1] Current EMail: bwerley@enter.net (No current mailing address).
[2] This paper was prepared for self-publication on the writers current web site: www.enter.net/~bwerley..
[3] Italic numbers in brackets refer to the reference list at the end of the paper.

In the past, ASTM Committee G4 on Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres has included burn-ratio tutelage in several of its standards and has taught them in its oxygen safety course. However, there has been valid criticism of these parameters [***2***]. G4 has not delved greatly (at least in public) into the related thermochemistry of these materials due at least in part to the complexity of the discipline.

Thermochemical software that is available to assist with this complexity has been used in the G4 collegium to only a small extent, but it has proven quirky and has introduced a range of other issues. The writer has been struggling his way up the learning curve in recent manuscripts [***3,4***] with two software codes (CEA from NASA and HSC 3.0 from Outokumpu Oy). His goal has been to find a practical or at least more simplified way to employ such thermochemical equilibria calculations both to improve on the parameters available to Oxidant Safety Practitioners and to seek new parameters. In these earlier papers, terminology for parameters such as “batch combustion”, “transient/incremental/partitioned (TIP) combustion”, “*in-situ* heat of combustion ($_{is}H_c$)”, “pass-through heat” and “equivalent heat of combustion” were suggested and were illustrated with graphical thermochemistry data generated by the software for iron. This manuscript seeks to examine and elaborate on the burn-ratio concept with the intent to improve, replace or upgrade it in a way more consistent with thermochemical and combustion principles.

As a result, this manuscript will propose, simplify and exhibit a fledgling graphical thermo-equilibria perspective on worst case heat transfer during combustion in search of more precise and more powerful techniques to define where metals may be limited to reduced hazard in practical systems. Since this is new material intended for use not only by chemists and chemical engineers trained in thermochemistry and since it is not proving intuitively obvious, the examples and discussions will be protracted and detailed.

Burn Ratios Defined and Reconciled

Munroe et al. [***5***] proposed the idea of a burn ratio in the Final Report of a U.S. government project to identify safe metals for high pressure centrifugal compressors to be used in synthetic fuels production in the 1970s. He reasoned much as Humphry Davy did for gas fuels two hundred years earlier, that if a metal did not transfer enough heat during combustion to warm itself to a critical level (melting or boiling [or sublimation] point), then it could not sustain combustion. Davy had speculated that gases would need to achieve an ignition condition (in today’s parlance perhaps minimum ignition temperature, minimum ignition energy, or other benchmark). Monroe’s parameters were defined as follows:

$$BR_{mp} = \Delta H_f / (\Delta H_{rt\text{-}mp} + \Delta H_{mp}) \qquad (1)$$

$$BR_{bp} = \Delta H_f / (\Delta H_{rt\text{-}mp} + \Delta H_{mp} + \Delta H_{mp\text{-}bp} + \Delta H_{bp} \qquad (2)$$

Where:

BR_{mp} = Burn ratio at the melting point
BR_{bp} = Burn ratio at the boiling point

ΔH_f = Heat of formation (often taken as heat of combustion) of the metal oxide
$\Delta H_{rt\text{-}mp}$ = Heat to warm metal from room temperature to the melting point
ΔH_{mp} = Latent heat of melting
$\Delta H_{mp\text{-}bp}$ = Heat to warm metal from melting point to boiling point
ΔH_{bp} = Latent heat of vaporization

These parameters do empirically seem to generally divide metals into categories: Those that should not burn as liquids (or gases), those that should not burn as gases.

Burn Ratio Flaws

Both of these burn-ratio parameters have had "issues". Both have suffered the normal birthing pains of new theories. As has been alluded to already in this paper, a metal my not have to *entirely* melt itself to exhibit the increased hazard of liquid combustion. Similarly, a material may not have to entirely boil (or sublimate) itself to exhibit the hazard of gas phase combustion. Indeed, one reference describes simultaneous combustion of magnesium with both liquid and gaseous features [***6***]. And indeed, in the case of carbon, which typically sublimes, rather than boils, the terminology for the boiling-point burn ratio is flawed. Indeed, somewhat more rigorous formulations might be as follows:

$$\Delta H_f / \Delta H_{rt\text{-}mp} \leq BR_{mp} \leq \Delta H_f / (\Delta H_{rt\text{-}mp} + \Delta H_{mp}) \quad (3)$$

$$\Delta H_f / (\Delta H_{rt\text{-}mp} + \Delta H_{mp} + \Delta H_{mp\text{-}vp}) \leq BR_{vp} \leq \Delta H_f / (\Delta H_{rt\text{-}mp} + \Delta H_{mp} + \Delta H_{mp\text{-}vp} + \Delta H_{vp}) \quad (4)$$

Where:

BR_{mp} = Burn ratio at the melting point
BR_{vp} = Burn ratio at the vaporization point (boiling or sublimation)
ΔH_f = Heat of formation (often taken as heat of combustion) of the metal oxide
$\Delta H_{rt\text{-}mp}$ = Heat to warm metal from room temperature to the melting point
ΔH_{mp} = Latent heat of melting
$\Delta H_{mp\text{-}vp}$ = Heat to warm metal from melting point to vaporization point
ΔH_{vp} = Latent heat of vaporization (boiling or sublimation)

In this way, a range of Burn Ratios is defined that would cover the range of partial liquid or partial gas combustion possibilities. And the prospect of sublimation would also be covered. That range could be extended to address the range of oxides that might actually form, also. However, although this is more rigorous, one can still argue that some materials might have sufficient vapor pressure somewhat below the vaporization point to burn as a vapor and further examination and future refinement may be still be needed.

The range of oxides that form is important as indicated in [***2***]. Beyond the definitional issues, what if one calculates the burn ratios relative to the three oxides of iron that might form in combustion ($Fe_{0.947}O$, Fe_3O_4, or Fe_2O_3)? The results vary widely, and suggest

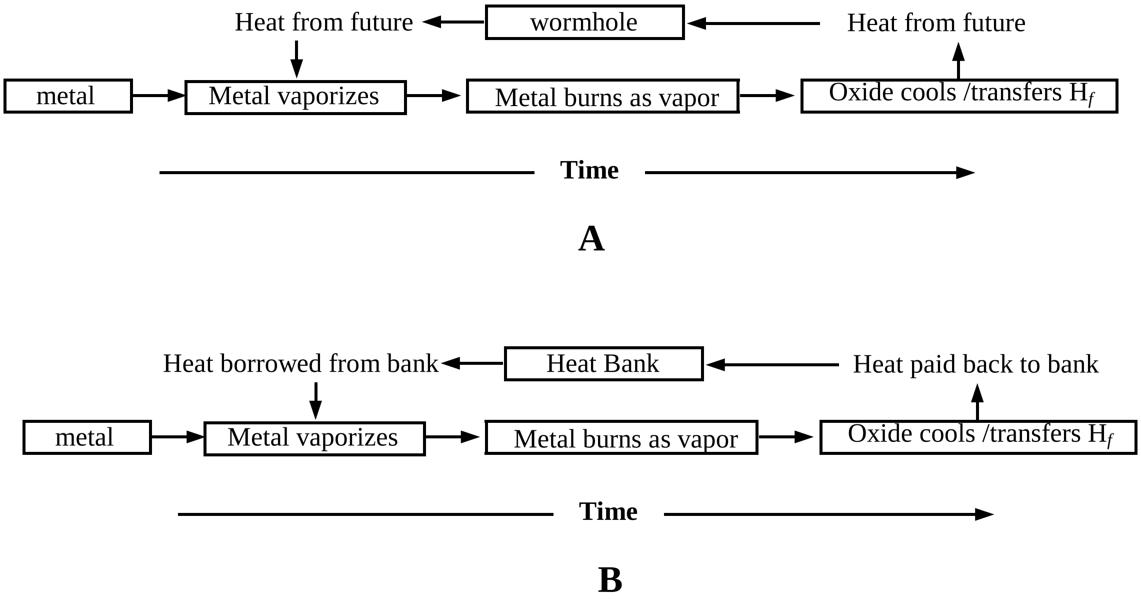

FIG. 1—*Fictitious combustion modes.*

significantly different levels of hazard depending upon the final individual oxides that form, or even worse, final mixtures of oxides, that actually result. How can a metal know how to burn without knowing what it is going to become (call this a "prophecy paradox"). But there is a still bigger problem: when a material has burned and its heat of formation (or combustion) has been "released", whatever that turns out to be, it no longer exists to be melted or boiled. Hence, to burn as a liquid or gas, it needs to be melted or vaporized *before* it burns. And, as is believed within today's paradigm (excluding science fiction scenarios such as from Star Trek, of course), a metal can not burn in bulk then retroactively transfer its heat of combustion via time travel (through a worm hole darkly) back into the past (Fig. 1, A) to melt or vaporize itself (call this a "temporal paradox"). Nor can it borrow heat it needs from the "thermal bank" to melt or vaporize itself (Fig. 1 B), then pay the heat back after the heat of combustion is released. Or can it?

Equilibrium Combustion

The concept of thermal equilibrium combustion (as distinguished from chemical-equilibrium combustion) is central to several test methods and this speculation. When sustained (meaning constant or repetitively variant) combustion occurs at its thermal threshold condition (a fire limit) there is a balance between the heat it needs and the heat it produces. At this fire limit, any further loss of (constant or varying) heat or temperature or any increase in requirements leads to ultimate, if not immediate, extinguishment of the fire.

The concept of equilibrium combustion is integrated by the ASTM Committee D-22 collegium into its body of work on the Oxygen Index standard D 2863 *Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)*. And ASTM G-4 incorporated and elaborated on some of the key thinking as it applies to oxidant safety testing in its derivative standard G 125 *Standard Test*

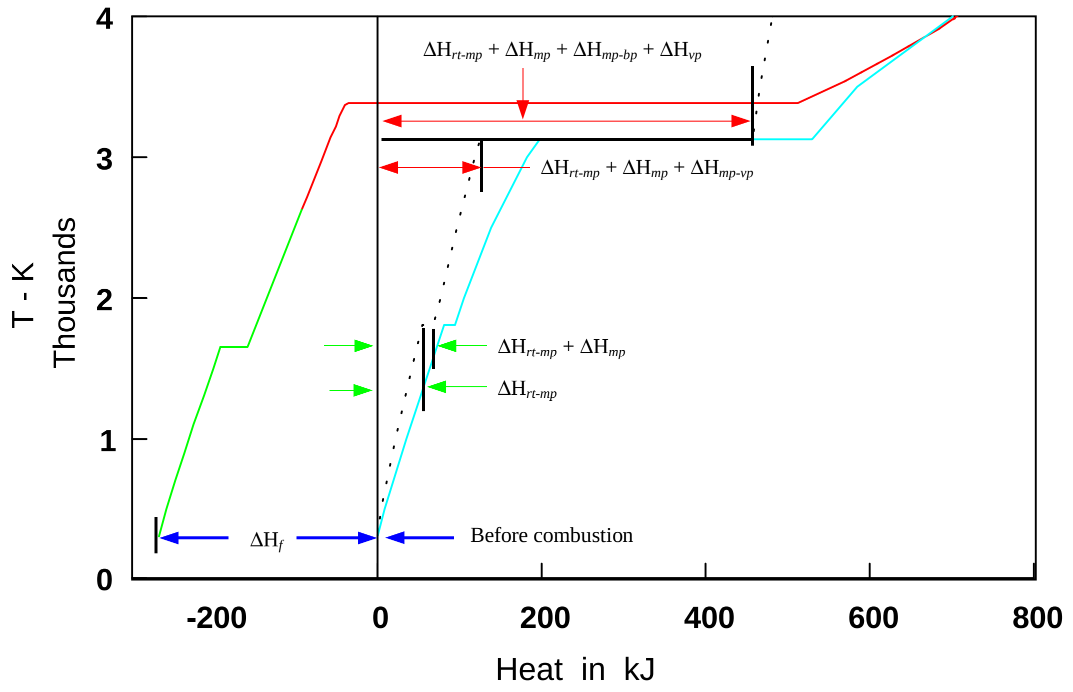

FIG. 2—*Iron Burn Ratios.*

Method for Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants.

In order to conclude that a metal will not burn in a specific mode (say as a liquid), one often draws worst-case conclusions as to how it might burn (say to its most stable oxides), then compares that to the perceived worst-case threshold equilibrium combustion requirements (such as in the numerators of Eqs 1-4). However, with less conservatism, one could also speculate (using thermochemical software) on how the metal *would* actually burn, and relate that to the threshold equilibrium combustion requirements that *would* actually apply. This latter approach can allow one to speculate on scenarios that would allow metals to be deployed more liberally than in the worst case, but it also allows insight into combustion scenarios that may seem to violate even the worst-case burn-ratio criteria.

Graphical Burn Ratios

Iron is a middling metal. It exhibits neither the highest nor lowest burn ratios. Fig 2 exhibits thermochemical data for iron and oxygen resulting from the stoichiometry for the stable oxide $Fe_{0.947}O$. The “before combustion” point (at the bottom of the blue and dotted black curves) is at the normal room temperature (~300 K), atmospheric pressure point, zero heat point on the abscissa. As the before-combustion metal and oxygen are heated, the thermal equilibrium condition tracks up the blue reactants curve to a latent heat plateau at which the metal portion melts then warms to the vaporization plateau (at which the metal boils) and then warms again until it ultimately becomes fully-dissociated purely-monatomic hot gases of monatomic iron and monatomic oxygen (some of which may also be ionized).

The after-combustion products curve is shown in green and red and is consistent with data from both CEA and HSC software, which were constrained to predict pure $Fe_{0.947}O$ at the lower temperatures, and the green portion is also consistent with thermo data from the JANAF tables for pure $Fe_{0.947}O$. This is consistent with rapidly cooled real world iron combustion which can quench to form this oxide even though it is not the precise state for room temperature chemical equilibrium.

The bottom of the products curve is at ~300 K and is –265kJ to the left of the bottom of the reactants curve (for one mole of $Fe_{0.947}O$, –281kJ for one mole of Fe reactant). This is both the heat and enthalpy difference between these two points and therefore the standard heat of formation (and therefore also the standard heat of combustion) of this oxide from iron and oxygen. Notice that the heat of combustion is for the reaction of iron with oxygen at the normal standard states (atmospheric pressure and ~300 K) and it is also the heat of combustion for iron combusted with room-temperature oxygen (because room temperature is the approximate standard state), a distinction that will be considered later.

As one heats the oxide, the CEA and HSC software predicts, its enthalpy increases and its temperature rises along the green segment to a latent-heat plateau at which the oxide melts then warms and transitions to the red segment, warms further to a second long latent heat plateau along which further heating also changes the chemical equilibrium with partial vaporization to FeO gas, as well as decomposition of the oxide into gaseous Fe, O_2, and O, and then upon further heating warms again fully decomposing the gaseous species until it ultimately merges with the light blue curve for mixed iron and oxygen and at sufficiently high temperature becomes the same fully-dissociated purely-monatomic hot gases of monatomic iron and monatomic oxygen (again, some of which may also be ionized).

Also shown is a dotted black curve also starting at the bottom of the reactants curve that represents the heating of the iron reactant constituent alone. This black curve tracks up to the melting point and through it, then to the boiling point and through it, ultimately changing into iron gas.

Note that if one takes the starting point as the standard condition (zero enthalpies for both the iron and oxygen), then the light blue reactant curve and the red/green curve represent the enthalpy of the reactants and products system relative to the origin. Similarly, with the standard states for both the iron and oxygen as zero at the origin, then the dotted black curve for heating of iron represents (has the same numeric value as) the enthalpy for the iron-oxygen system in which the iron is heated and then reacted with room temperature (zero standard state) oxygen.

If higher oxides of iron were to form, the heat of combustion would be a longer segment and the blue dimension line would point further to the left of that shown on Fig 2 (at – about –372 kJ per mole of Fe in forming Fe_3O_4 and at –411 kJ per mole of Fe in forming Fe_2O_3) [***3***]. Depending upon what oxide or mixture of oxides actually formed during combustion, the resulting heat transfer falls into the range of –281 kJ/mole Fe (for $Fe_{0.947}O$) to –411 kJ/mole Fe (for Fe_2O_3). But this analysis will focus only on the formation of $Fe_{0.947}O$.

Correspondingly, the heat required to just begin to melt the metal (minimum for onset of liquid combustion) is the green dimensioned segment designated $\Delta H_{rt\text{-}mp}$, and to melt it completely (minimum for full liquid combustion) is the green dimensioned segment designated [$\Delta H_{rt\text{-}mp} + \Delta H_{mp.}$]. Similarly, the heat to just begin to vaporize the iron (minimum[4] for onset of vapor combustion) is the red dimensioned segment, [$\Delta H_{rt\text{-}mp} + \Delta H_{mp} + \Delta H_{mp\text{-}bp}$], and to vaporize it completely (minimum for full vapor combustion) is the red dimensioned seg-

---

[4] Actually, there can be small amounts of gas in equilibrium with the solid at temperatures slightly below the boiling-point plateau temperature.

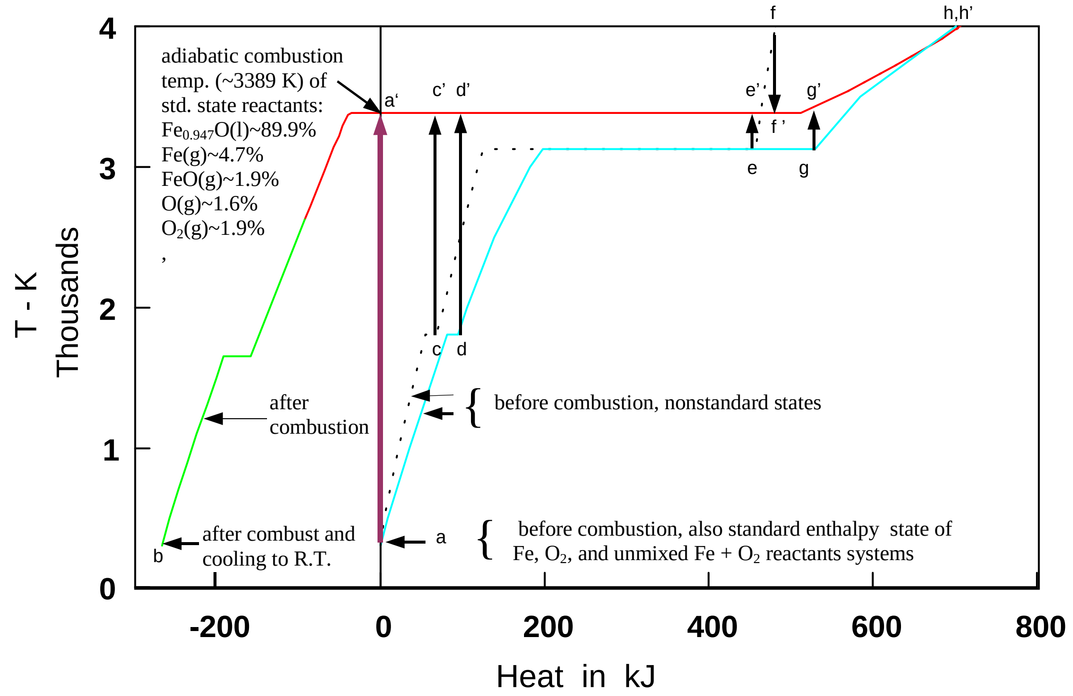

FIG. 3—*Iron combustion analysis (per HSC and CEA Software)*

ment $[\Delta H_{rt\text{-}mp} + \Delta H_{mp} + \Delta H_{mp\text{-}bp} + \Delta H_{vp}]$. Hence,

$$BR_{\text{(liq. onset)}} \approx 5.2 \approx \Delta H_f / \Delta H_{rt\text{-}mp} \leq BR_{mp} \leq \Delta H_f / (\Delta H_{rt\text{-}mp} + \Delta H_{mp}) \approx 4.1 \approx BR_{\text{(full liq)}} \qquad (5)$$

And,

$$BR_{\text{(vap. onset)}} \approx 2.17 \approx \Delta H_f / [\Delta H_{rt\text{-}mp} + \Delta H_{mp} + \Delta H_{mp\text{-}vp}] \leq$$
$$\leq BR_{vp} \leq \Delta H_f / [\Delta H_{rt\text{-}mp} + \Delta H_{mp} + \Delta H_{mp\text{-}vp} + \Delta H_{vp}] \approx 0.58 \approx BR_{\text{(full vap)}} \qquad (6)$$

The values for full liquid- and full vapor-phase burn ratios are approximately the traditional values published [*5*] as burn ratios to date. If a higher oxide with a higher heat of combustion is assumed, then the values of the burns ratios increase proportionately.

Graphical Combustion

Fig. 3 duplicates elements of Fig. 2. Note that for either reactants system (iron burning with oxygen of the same temperature (the blue curve), or iron burning with room temperature oxygen (the dotted black curve) the corresponding adiabatic chemical equilibrium condition is the point on the products (red/green) curve for the same amount of heating (same system enthalpy). Combustion of the starting points (e.g. the standard states of the elements at point “a”) results in transition directly up (e.g. along the purple arrow to the equilibrium point “a′”), and the composition and temperature (the adiabatic combustion temperature) of that standard combustion point are shown on Fig. 3.

The heat of formation (what the writer views as the in-situ heat of combustion) of point

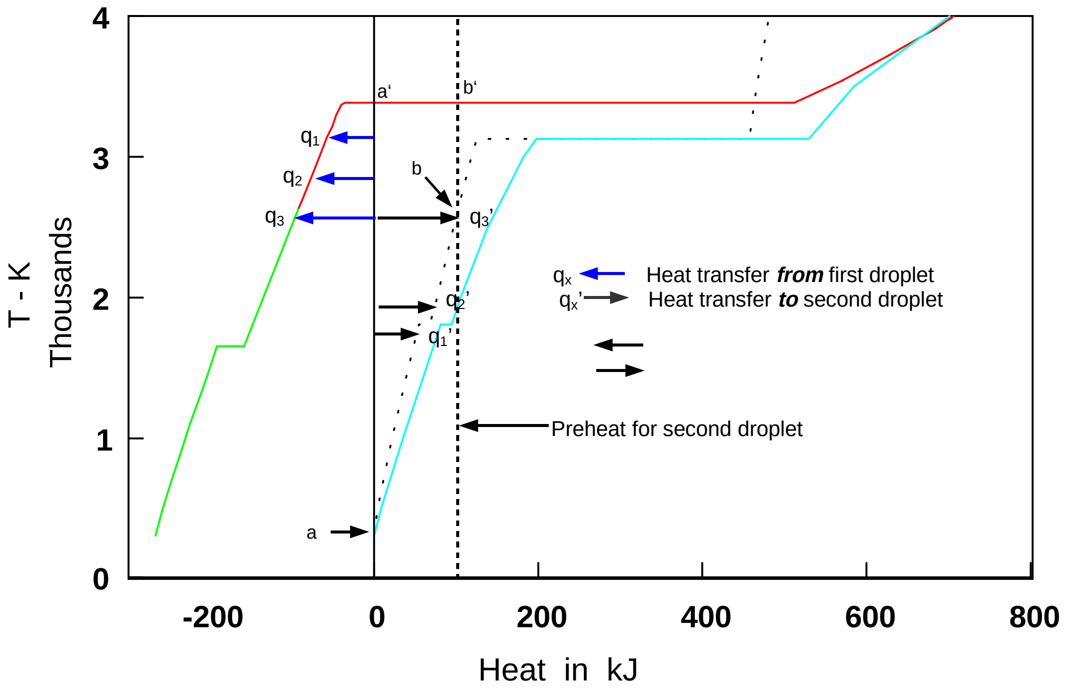

FIG. 4—*Adiabatic heat transfer, first to second droplet for 947Fe and 0.5 O_2 to form $Fe_{0.947}O$.*

“a′” relative to point “a” is *zero*, as it must be for adiabatic combustion. However, if the products at point “a′” are cooled to room temperature, point “b”, the standard heat of combustion will be transferred from the products.

Consider points “c” and “d’ which respectively are the points at which the reactant iron and iron in thermal equilibrium with stoichiometric oxygen have been just fully melted and are about to be combusted with room temperature oxygen (in the case of “c” or same-temperature oxygen in the case of “d”). Adiabatic combustion again shifts these points directly upward to point “c′” and “d′”. The difference in heat (also enthalpy) between points “c” and “d” is the same as the difference between points “c′” and “d′” and is the heating necessary to warm the stoichiometic oxygen to the melting point of iron. Similarly points “e” and “g” correspond to the points at which the iron reactant is just fully boiled. Adiabatic combustion of these points is indicated directly above them at points “e′” and “g′”. Again the lateral difference in heat (also enthalpy) is the heat to warm oxygen from room temperature to the boiling point of iron.

Point “f” is for gaseous iron. Notice that when combusted with room temperature oxygen and shifted adiabatically to the products curve, the shift is directly downward to point “f′”. In this case *the effect of combustion is an adiabatic combustion temperature that is cooler than the reacting iron.*

Consider a chunk of room temperature iron burning according to the two prospects in Fig. 1. That is, it either burns completely in the future and is then put into heat exchange with itself in the past through a suitable worm hole, or else it goes to the heat bank which completely burns an identical chunk of iron and loans it for heat exchange and then after the iron burns, the heat is repaid to the bank.

Fig. 4 again contains the elements of Figs. 2 and 3. The before combustion point is again “a” (for either the iron or the surrogate chunk that is burned by the heat bank) and the adiabatic combustion point is “a′”. As the oxide cools from point “a′”, it transfers heat as a function of temperature as shown by the blue arrow segments, q_1, q_2, q_3, and as the temperature decays, the length of the heat release arrow grows. Since the iron at “a” is in heat exchange with either its future self or an equivalent surrogate hot oxide from the heat bank, it will warm as this heat is transferred into it. This warming is shown by the black heat transfer arrows q_1', q_2', q_3', which correspond to q_1, q_2, q_3, respectively. Notice that q_3 and , q_3' are the same length and at the same temperature. This is the limit to the heat that can transfer, because if the oxide were to cool further to transfer greater heat, then that heat would have to flow to a higher temperature in violation of the second law of thermodynamics. Notice that this point is a little more than half way between the melting point and boiling point of the iron. Hence, the iron has more than enough heat to entirely melt itself but not enough heat to begin to boil itself. *Or does it?*

TIP Combustion

Two graphical examples of iron combustion models will be reviewed here: TIP combustion and Batch combustion. Although Batch combustion will be taken as a necessary aspect in TIP combustion, TIP is easier to illustrate and examine and so will be reviewed first.

Commonly, metal combustion proceeds through a specimen and in many cases there is nothing remotely approaching temperature equilibrium throughout until the reaction is complete and settled. Nonetheless, as a specimen transitions from a metal to a metal oxide or combination of oxides, the incremental portion going through combustion may be locally in or near or at least closer to thermal equilibrium. As a result it can be informative to consider a transient/incremental/partitioned (TIP) combustion sequence as introduced in earlier work [***3***]. Two examples will be examined here that are adiabatic with regard to external heat loss but for which internal heat transfers and gradients will be allowed.

Accelerating/Decelerating TIP Combustion

In several metals combustion tests (including ASTM G 124) the specimen is suspended vertically and ignited at its bottom. Iron burns as a series of similarly sized drops each forming then falling away removing heat and heat capacity with them and thereby partitioning the combustion even though the combustion within each droplet may more nearly reflect Batch combustion behavior. The intensity of the combustion may nonetheless vary throughout the life-cycle of each droplet. Each droplet forms from a specific portion of the rod, and so the rod may be thought of as a number of connected nascent droplets. As each droplet is combusting, a portion of its heat is being transferred to the nascent droplet above until the droplet falls and partitions the combustion. Each droplet acts as a “heat bank” to loan heat to the nascent segment above, but instead of paying the heat back, the succeeding droplet pays that same heat forward (it passes it through).

For this example, each equal droplet will be viewed as going through equilibrium batch combustion (to be dissected later) and any heat transfer from it will be treated as passing only into the nascent room-temperature droplet above and not into subsequent rod segments. The iron will be treated as reacting only to form the lowest oxide, wustite, $Fe_{0.947}O$ and its equilibrium products (which generally applies at the higher temperatures and for which other possibilities will be examined at another time).

Since each droplet is taken to be the same size, the previously examined Figure 4, will be applied to each droplet on a molar basis and exhibits the thermo portrait for both iron in combination with (but not mixed with) stoichiometric oxygen (light blue curve), and for iron to be burned with separate room-temperature oxygen (black dotted curve), as well as for consequential $Fe_{0.947}O$ (red/green curve). Assume that the bottom segment of a test rod combusts (miraculously without added ignition energy) again yielding combustion from "a" to "a′". Initially, it is located at point "a" of the diagram, room temperature and atmospheric pressure. If it batch-combusts completely to form a droplet, its condition shifts upward to point "a′" on the products curve. Point "a′" is the chemical-equilibrium condition (per NASA CEA or Outukumpu HSC software codes) and is on the latent plateau for the products and is comprised of a combination of species (as indicated on Fig. 3). The standard heat of combustion for the rod segment has been transferred into its products at this point and the system enthalpy is still zero.

If one were to cool the segment back to room temperature, the heat of combustion of the segment could be recovered at point "b".

The hot droplet at "a′" is now transferring heat internally to the nascent segment above, taken to be identical in starting size. The maximum heat it can transfer is limited to the point at which its decaying temperature as it cools matches the temperature of the subsequent initially room temperature segment above it, as that segment warms. Hence the analysis is the same as before in which the iron chunk was in heat exchange with its future self or with a surrogate from the bank.

As this first droplet cools and its state moves along the products curve to the left, evolving heat and then cooling, the cumulative amount of heat evolved is given by the length of the succeeding black segments, q_n. As the heat is transferred (as actually might occur much like but even without the use of a wormhole or bank) into the unburned segment (but not its associated oxygen) of the same origins, the next segment temperature increases as the corresponding black segments, q_n', show. At points, "q_3 and q_3'" the two temperatures match, the heat evolved therefore matches the heat absorbed, and heat transfer must stop as further transfer would violate the laws of thermodynamics by going from a lower to a higher temperature.

If the droplet now falls away, it partitions the combustion nicely (by removing heat capacity) and a new life cycle starts for the second droplet. However, this second droplet begins its reaction "preheated" at a higher temperature than for the first droplet, at the second droplet preheat level for which a second dotted vertical axis is shown on Fig. 4.

Figure 5, which begins where Fig. 4 left off, exhibits the second droplet combustion, and batch-combustion of this segment from point "a" to "a′" shifts its condition directly upward again to the products curve to a point which is still on the latent heat plateau for the products and so is about the same temperature as for combustion of the first droplet but which is at a higher heat (and enthalpy) level because of its preheat. However, the chemical equilibrium composition of the combustion products is different (it contains less liquid $Fe_{0.947}O$ and more of the decomposition products that are gases, as shown on Fig. 5). Therefore, it is further to the right (higher enthalpy, higher temperature) than for the combustion of the first droplet and so is capable of greater heat transfer as it cools (assuming heat can be recovered from the gases in this worst case scenario).

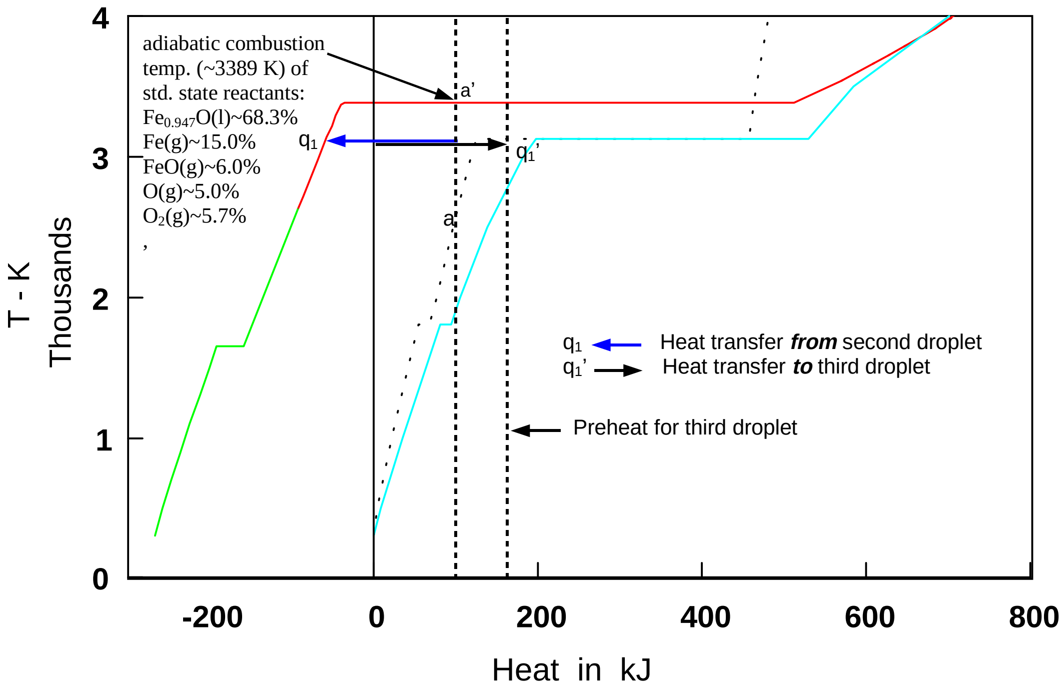

FIG. 5—*Thermochemical portrait of the combustion of 0.947Fe and 0.5*O_2 *to form* $Fe_{0.947}O$ *wustite.*

As this second droplet and associated gas cools and transfers heat as it moves along the curve to the left, again a blue segment, q_1, exhibits one level of transfer. If this heat, q_1 is transferred into the unburned third segment which is initially at the same initial room temperature as the second segment was at the beginning of its combustion cycle, the temperature of the third segment increases to the boiling point of the iron as indicated by the black heat segment q_1'. At this point, the two temperatures again match, the heat evolved again matches the heat absorbed, and heat transfer must stop as temperature equilibrium limits the maximum amount of heat that can transfer.

If the second droplet now falls away, it again partitions the combustion nicely (by again removing heat capacity) and a new life cycle starts for the third droplet. However, this droplet begins its reaction at a still higher temperature than for the first two droplets, as indicated by the new dotted black axis on Fig. 5 indicated as the third droplet's preheat level.

For the third droplet, again shown on Fig. 6, the starting point "a" is part way along the latent plateau and so a portion of this droplet is burning as a vapor. Its batch-combustion shifts it upward to the products curve, point "a" to "a′", which is still on the latent heat plateau for the products and so is again about the same temperature as for combustion of the first two droplets but at a higher heat (and enthalpy) level. However, it is still further to the right and so is capable of still greater worst-case heat transfer than for the first two drops as it cools.

As this third droplet and associated gas cools and moves along the curve to the left, evolving heat and cooling, the key amount of heat evolved is again given by the length of the now larger heat transfer, q_1. As this same heat is internally transferred into the unburned fourth

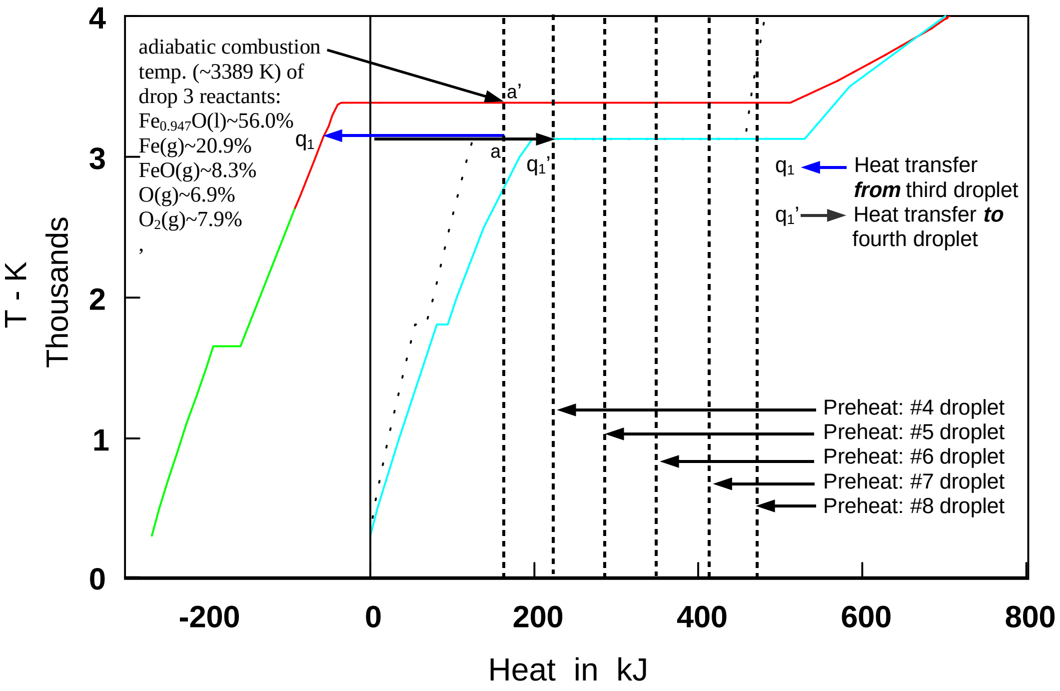

FIG. 6—*Thermochemical portrait of the combustion of 0.947Fe and 0.5O_2 to form $Fe_{0.947}O$ wustite.*

segment which is at the same room temperature as the first, second, and third segments were at the beginning of their combustion cycles, its temperature increases and ultimately places it still further to the right on the latent than did the preheat for the prior droplet. Hence a greater fraction of this droplet after partitioning will burn as a vapor. At point q_1' the two temperatures match, the heat evolved matches the heat absorbed, and heat transfer must stop as this is maximum amount of heat that can transfer.

If the third droplet now falls away, it once again partitions the combustion nicely (by again removing heat capacity) and a new life cycle starts for the fourth droplet. However, this droplet begins its reaction at a still higher preheat temperature than for the first three droplets, as indicated by a dotted vertical axis indicated as the fourth preheat level.

Notice that for each of the first three droplets, the heat levels increased ultimately until portions of the latter droplets were preheated to the point of partial vaporization which would suggest partial gas phase combustion would be a prospect. Such gas phase combustion could be a significant heat loss mechanism but has been treated as being captured for this extremal case analysis. Figure 6 also indicates where the preheat axes would fall for similar droplets five through eight and by which time the eighth segment would be preheated to the point of complete vaporization and fully to gas-phase combustion. Hence as a specimen burns in an environment that is above its fire limit, combustion acceleration may occur and later droplets may exhibit an increasing tendency to exhibit partial or full gas-phase flaming combustion features. This may explain the powder that forms during standard tests of iron.

This extreme-case analysis has shown the sequence of droplets accelerating and growing sequentially hotter under internal heat transfer until the adiabatic segment combustion temperature is limited by the latent heat plateau. In real combustion the segment combustion might fall

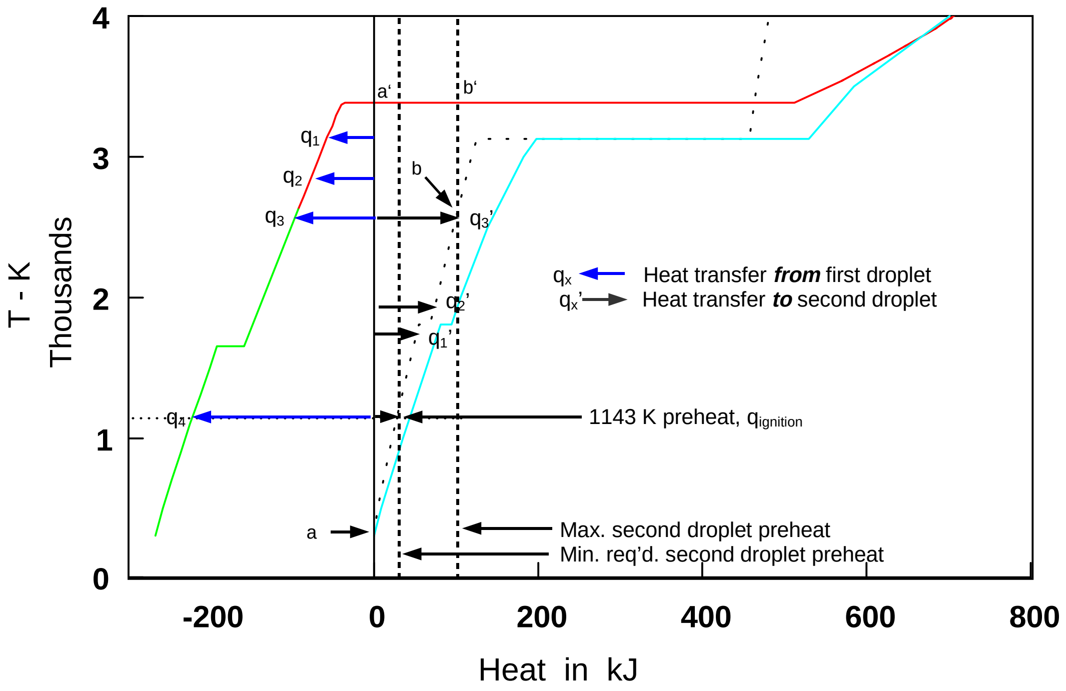

FIG. 7—*Adiabatic heat transfer, first to second droplet for 0.947Fe and 0.5* O_2 *to form* $Fe_{0.947}O$.

far short of being adiabatic and that is to be considered next.

A Taste of Reality—Thermal Equilibrium Combustion

The "ideal" adiabatic combustion of the previous TIP combustion model exhibits accelerating combustion that finds partitioned iron combustion ultimately burning as a vapor. However, if a little reality is injected into the model, the worm turns. Perfect heat transfer from droplet to droplet is not realistic. Each droplet would lose significant amounts of heat through radiation and convection and also to conduction, although conduction is less an inhibitor since at least most of any heat lost (that passed through) to subsequent segments beyond the next in line would aid combustion a little later when that segment's turn came to combust.

Consider the ignition condition for iron. The writer has heard laboratory commentary that if one heats a steel rod to the point of glowing and thrusts it into oxygen it will ignite and burn. There are other such gross observations that can be cited. When oxy-acetylene cutting is accomplished the standard procedure is to heat the target metal to the point at which it glows red or even exhibits molten metal and then to start the oxygen blow and burning proceeds. And Linnert [7] cites a specific temperature of 1143 K (1600°F) as the threshold at which iron "combines readily with purified oxygen". So for the sake of this analysis, assume that iron will achieve both its minimum *in-situ* ignition temperature and *in-situ* minimum ignition energy if heated to 1143 K, and that it will also satisfy any other thresholds and will ignite.

So consider the previous combustion scenario with potential heat loss included. Figure 7 again exhibits the thermo-curve of Fig. 1 for a first droplet of burning iron (that miraculously ignites at room temperature) for which the first droplet is preheating the second segment of rod.

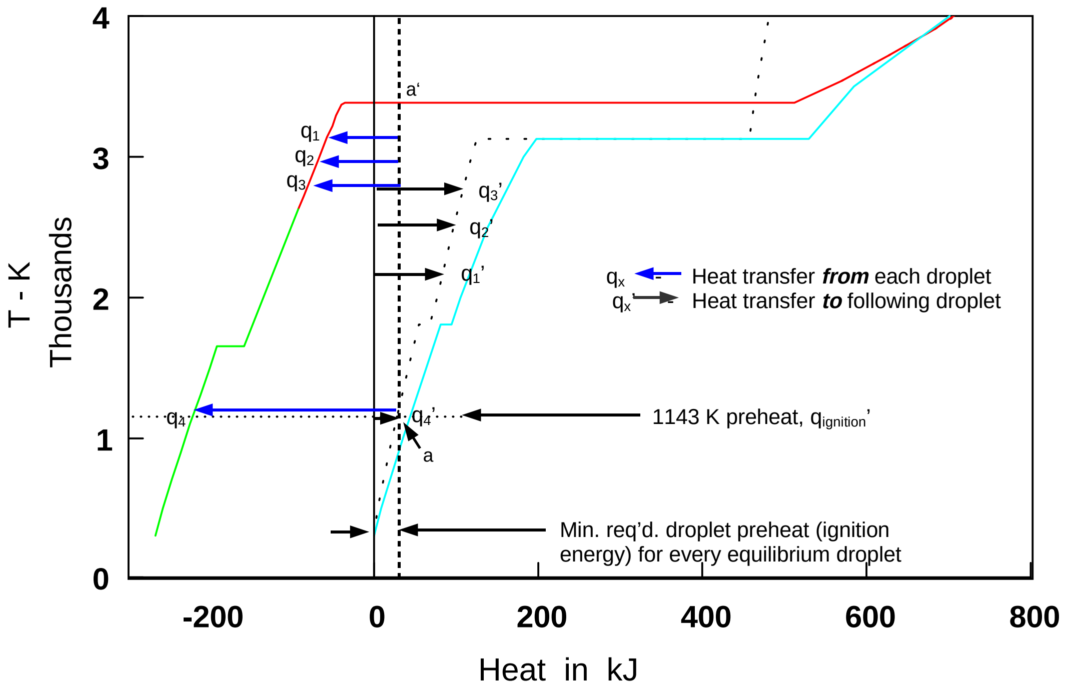

FIG. 8—*Threshold minimum equilibrium heat transfer, from each droplet to its successor for 947Fe and 0.5 O_2 to form $Fe_{0.947}O$.*

Shown again are the heat transfers q_1 , q_2, and q_3, heat transfers *from* the first droplet, and q_1', q_2', and q_3', heat transfers to the second droplet. Also shown is a q_4 which is the maximum heat transfer from the first droplet at or above the 1143 K ignition threshold. Finally, also at the 1143 K threshold, q_4', is shown which is the minimum amount of preheat that will raise the second segment and resulting droplets to achieve ignition, $q_{ignition}$, and allow combustion to continue. Note that the minimum required to sustain combustion is only a small fraction of the maximum amount available indeed, $q_4' = q_{ignition}$, is only about 14% of q_4. In other words, about 86% of the available heat to ignite the next segment can be lost elsewhere and in the heat capacity of the falling droplet and the second droplet can still achieve its assumed ignition condition.

However, miraculous combustion at room temperature can not be expected. For combustion to proceed indefinitely under these assumptions, the first droplet and every droplet must have an initial preheating to at least the 1143 K point. More than this will act to accelerate the combustion (in speed, intensity or even just facility). Less than this will lead to extinction. However, if each segment and its resultant droplet receive this amount of preheat and no more, then the combustion will be at its minimum thermal equilibrium condition. This amount of preheat that leads to ignition is the minimum amount of "pass-through heat" analogous to the heat that passes back through time in a worm hole in Fig. 1 A, or that is borrowed from the heat bank in Fig 1 B.

Fig. 8 adjusts Fig. 7 slightly to incorporate the minimum preheat that the first droplet requires from an ignition source, its ignition energy. In this case the first droplet burns from the same initial conditions as the second and every subsequent droplet and this adds a small constant amount of additional "pass through" heat to q_1 , q_2, q_3, and q_4, and as a result the maxi-

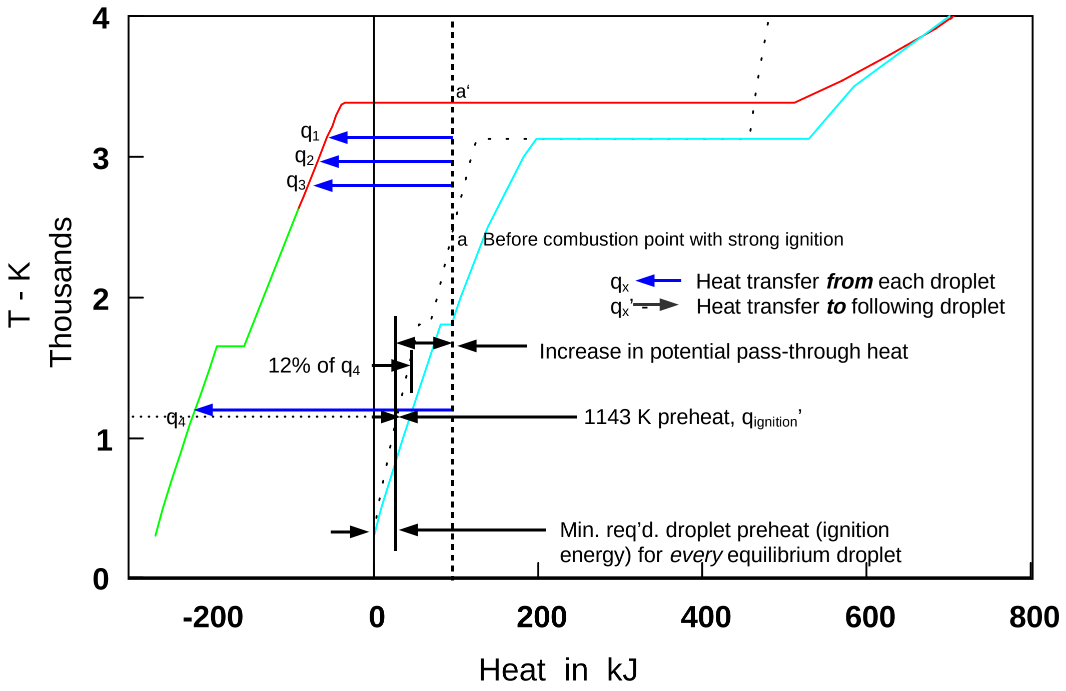

FIG. 9—*Threshold minimum equilibrium heat transfer, from each droplet to its successor for 947Fe and 0.5* O_2 *to form* $Fe_{0.947}O$.

mum amount of heat transfer possible *from* the droplet increases so that the minimum pass-through required to sustain equilibrium combustion is a somewhat smaller ~12% portion. In addition, the adiabatic case is now at a somewhat higher level shown as q_3 and q_3'.

Every droplet proceeds on Fig. 8 through the sequence, point "a" to "a′" and then the slag cools to release q_4 of heat, 12% of which represents q_4' and is the minimum amount required to heat the next segment of the rod to its minimum ignition temperature of 1143 K. This is equilibrium combustion.

Note that if a greater preheating of any droplet is provided, then a greater recovery (a greater pass through) is also possible and despite losses, a higher level of greater-than-minimum equilibrium combustion might obtain.

Suppose an ignition energy that is twice or three times that for minimum equilibrium combustion were employed (observed combustion exhibits residual molten slag and that is at least two times hotter than 1143 K), point "a" of Fig. 9, and so might transfer heat at much higher temperatures. When that slag cooled to the minimum ignition temperature point it would transfer a larger amount of heat as q_4. Furthermore, estimate that the heat loss rate for the excess ignition energy is the same 88% as for the minimum equilibrium case. In this case, the estimate would suggest some 12% of the extra ignition energy might pass-through to the succeeding droplet and yield higher than minimum combustion, and a 12% portion of these portions would pass through to the droplet after that. Fig. 9 indicates where the preheat might be for the second droplet if 12% of q_4 were passed through. Of course a more complex relationship would apply, but nonetheless, *excess ignition energy can have a legacy for numerous droplets*.

Fig. 9 attempts to illustrate the first step of this negative cascade. However, just as adiabatic combustion ratchets upward with each droplet above the fire limit, excess ignition ratchets

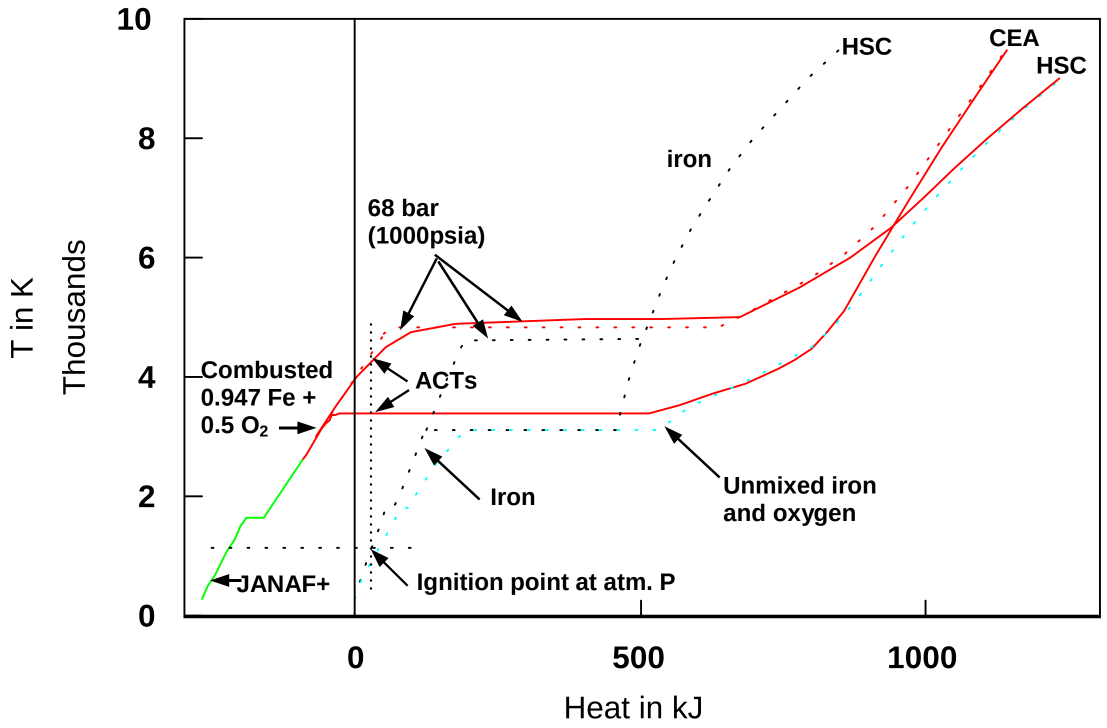

FIG. 10—*Thermochemical portrait of the combustion of 0.947Fe and* $0.5O_2$ *to form* $Fe_{0.947}O$ *at two pressures (atmospheric and 1000 psia).*

downward in a series of steps below the fire limit. Just as excess energy facilitates combustion above the equilibrium threshold, anything that acts to increase the heat loss rate acts to extinguish combustion though it may take a series of droplets for that extinction to obtain. However, if the heat loss rate is less at the higher heats, then the number of steps to extinction may be increased.

Higher pressure

At elevated pressures, experiments show that propagation thresholds decrease (metals such as iron are easier to burn) and iron will burn at lower oxidant concentration [8]. Why? Fig 10 exhibits the previous thermo analyses per HSC and CEA software but adds HSC software data at 68 Mpa (1000 psia), a common test pressure. This figure is more detailed than a similar attempt in the writer's earlier manuscript [3] which incorporated data from CEA software while this figure includes additional and more expansive data available from HSC.

Worth noting is that the ends of the curves match at both pressures (though the high temperature ends of the CEA and HSC curves are slightly different as described previously [4]), the predicted heats of combustion from the software are the same at both pressures as are the heats to produce monatomic gases that form at extremely high temperature (ignoring ionization). The biggest difference is that the boiling points are elevated at 1000 psia. Very importantly, for most materials the ignition temperature decreases with increasing pressure but the

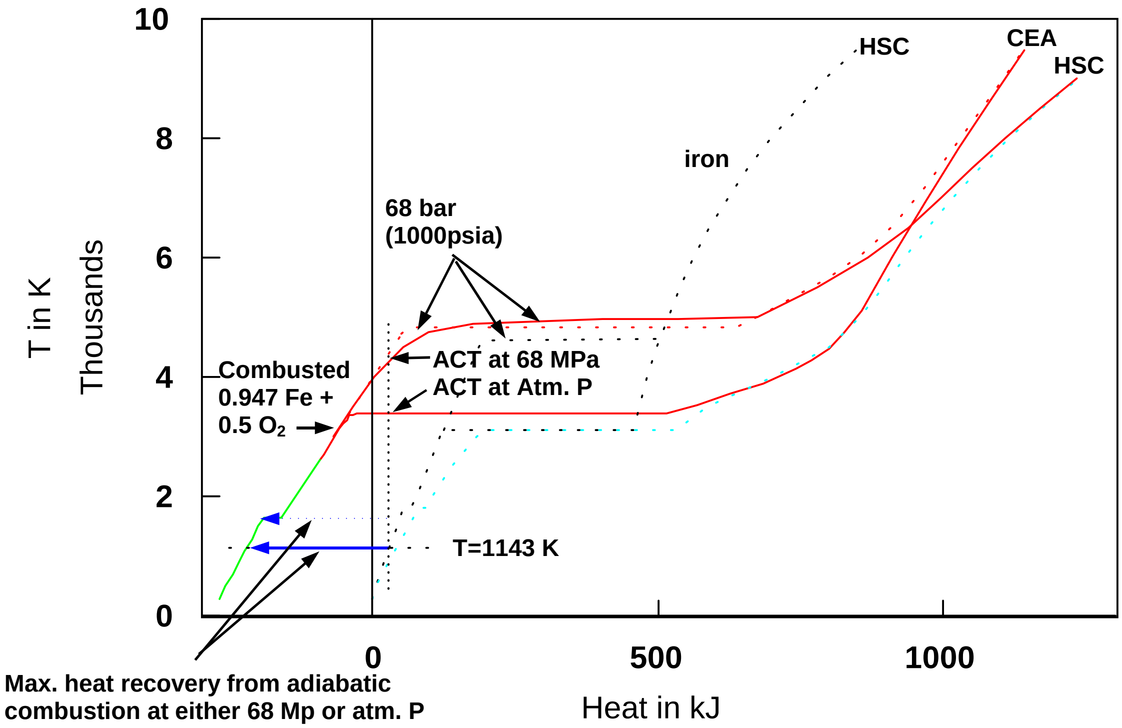

FIG.11—*Thermochemical portrait of the combustion of 0.947Fe and 0.5*O_2 *to form* $Fe_{0.947}O$ *at two pressures (atmospheric and 1000 psia).*

writer has no data with which to quantify this prospect for iron. Hence the ignition point at the elevated pressure might be lower than indicated for atmospheric pressure.

The adiabatic combustion temperatures are indicated and are higher for the elevated-pressure case than for the atmospheric-pressure case. However, HSC software does not attribute any elevation or depression in the melting points due to increased pressure for any of the materials.

Figure 11 duplicates the data of Figure 10 and illustrates the maximum heat recovery at 1143 K from adiabatic combustion of a droplet ignited at 1143 K that has just fallen (assuming the droplet could fall as a solid, a more precise maximum would terminate the heat arrow slightly higher and shorter at the oxide melting point transition, as shown with a dotted arrow). The maximum recovery is the same regardless of pressure according to these data. However, the early heat transfer would occur at a higher temperature, and therefore perhaps more efficiently, in the higher pressure case which might be a factor in the lower combustion threshold at higher pressure. The previously mentioned lower ignition temperature at the higher pressure may also imply significantly less heat may need to transfer at higher pressure. With data on the ignition temperature at 68 MPa one could estimate the minimum fraction of heat recovery that would be required as compared to the previous estimate of 12% percent for atmospheric pressure.

Note also on Fig. 11 that at 68 MPa, there are fewer gaseous combustion products than at atmospheric pressure (the ACT at 68 MPa is on the warming curve for the liquid products, while the ACT at atmospheric pressure is on the latent vaporization plateau). The higher boiling points at higher pressures, result in the greater ACT and greater radiation losses (tending to re-

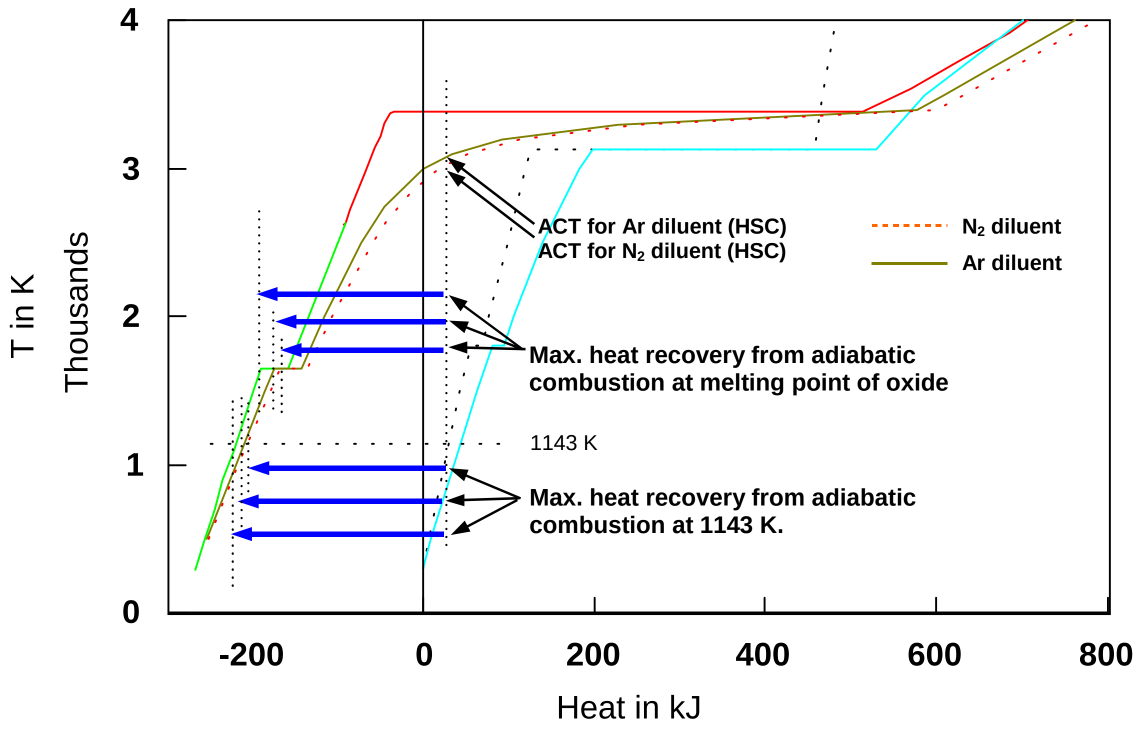

FIG.12—*Thermochemical portrait of the combustion of 0.947Fe and 0.5*O_2 *to form* $Fe_{0.947}O$

duce the actual combustion temperature), but more of the combustion products are liquids and therefore more of the products are retained in the molten droplet, hence the combustion products are more liquid and therefore the combustion could be more adiabatic at higher pressure and heat conduction to the next segment may be improved. Future analyses will be interesting.

Diluent Effects

As the oxidant in which a metal is ignited is mixed with a “diluent[5]” the ability of the metal to burn can change. It can become more or less combustible. It may burn faster or slower or hotter or colder or not at all. These changes may be due to kinetic or physical effects or they may be due to thermochemical changes.

Figs. 12 exhibits the basic data of Figs. 2-9 for atmospheric (1 bar) pressure, but also with oxidant mixtures (containing the same amount of oxygen) but as 50% oxygen with 50% nitrogen and 50% oxygen with 50% argon. For many materials, dilution does not greatly alter ignition temperature. The lower set of three blue arrows indicate the maximum heat recovery possible at 1143 K for the three cases. In these cases, if a specimen segment is at 1143K when it begins combustion and the heat is returned to the next segment, then to preserve the 1143 K initial temperature which corresponds to the room-temperature equilibrium combustion scenario, then the pass-through heat would have to increase from the 12% minimum for oxygen (lowest blue arrow) to ~12.5% for argon-diluted oxygen or for nitrogen-diluted oxygen. At a higher transfer temperature (e.g., above the oxide melting point), the minimum pass through heat

---

[5] Diluents (gases, liquids and solids) are discussed little in the literature. Inert gases are diluents but in many cases reactive gases may also dilute and decrease combustibility, but in some situations any of them (including the inerts) may increase combustibility instead.

would be greater for all three prospects.

These changes are small and my not be important but are in the correct direction for a thermo chemical basis for the decreased combustibility of materials in diluted oxidants. This thermodynamic aspect may or may not be the dominant reason why a material is not combustible (again, other mechanisms that establish a still higher threshold may be operative), but it establishes a thermodynamic threshold that may be of value in oxygen system design.

Batch Combustion

So far, TIP combustion has been examined in which a "batch" behavior is asserted for the combustion of each incremental region of a specimen when the increment (segment/droplet) is suddenly shifted from its before-combustion state (typically, point "a" on the figures) to its after-combustion state (typically, point "a′" on the figures). The smallest and perhaps truest example of batch combustion is when a single iron atom representing a batch of iron comes together with a single oxygen atom representing a batch of oxygen to form a single FeO molecule representing a final product batch. This scenario occurs in an instant of time, and is therefore a true batch process. If accomplished adiabatically, (which is a certainty for some period of time however brief) the atoms would move on Fig 2 from the origin point "a" to the ACT point at "a′". However where a bulk specimen of iron is present, the reaction of any one atom would not remain adiabatic for long before it collided with other molecules or atoms or radiated heat and transferred some of its heat to them. Nonetheless, when an entire specimen combusts adiabatically, where the entire batch of it reacts too quickly for external heat loses, it too would shift from point "a" to point "a′".

In combustion textbooks, the point "a′" (at the adiabatic combustion temperature point) is established by assuming the heat recovered from room temperature products of combustion (be that a single FeO molecule or a larger batch of molecules) that have been combusted (yielding the heat of combustion of the products,) is transferred *back* into the products thermo curve warming it/them along the curve shown, to and through the melting point and then further to the vaporization point and partially along the latent heat of vaporization plateau to the batch combustion point which estimates the adiabatic combustion temperature.

To consider batch combustion, the approach here will be to apply the same reasoning to cumulative PIT combustion that has been incremented but is not partitioned at each stage. Hence the results of a series of adiabatic PIT steps will be combined to get the bulk result.

Heat Accumulation in Batch Combustion

In the case of batch combustion as treated here, the concept of accelerating combustion from drop to drop is moot since there is only one uniform batch under consideration. However, within that one batch there is an operative progression. In the case of TIP combustion, each step in the process began with an identical rod segment having a potentially different preheat. In the case of batch combustion herein for each succeeding "step" (increment of combustion), this analysis begins with identical additions of heat and conversions to oxide to a batch that is in adiabatic thermal equilibrium but is changing in composition . The combustion may begin at one spot and spread to create a batch that is partially oxide with the remainder unreacted iron (and the treatment here will assume they do not mix), but if the temperature grows to a sufficient level, there is the prospect that the oxide and iron may form an altered chemical equilib-

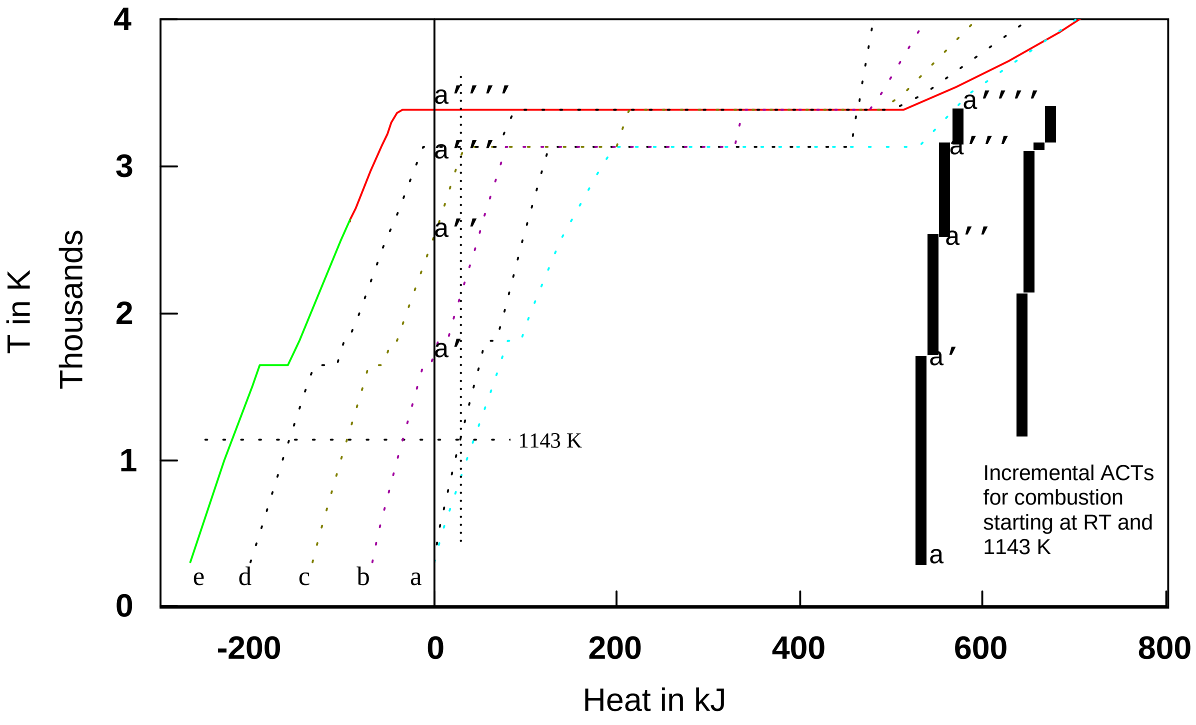

FIG.12—*Thermochemical portrait of the combustion of 0.947Fe and $0.5O_2$ to form $Fe_{0.947}O$ in batch combustion mode showing four stages of combustion .*

rium.

Fig. 12 exhibits this incremental batch analysis and corresponds to Fig 3 for TIP combustion. It illustrates the same governing equilibrium curves as Fig 3. However, since each increment of combustion is going to add heat to a changing droplet, there are stages (three intermediate stages are shown) of the combustion from the beginning room-temperature point, “a”, to the final room temperature complete combustion point, “e”. Fig. 12 shows the initial room temperature point, “a”, and three intermediate room-temperature stages of the combustion, “b”, “c”, “d”, each reflective of a 25% increment of the iron that has been converted to the assumed final oxide’s fractional combustion point, between points “a” and “e”. We can now return the heat of combustion of each of these end conditions to the respective thermo curves and surmise the behavior during a Batch combustion process.

At each of the three intermediate stages, the thermo curves are shown for combustion of 25% of the segment which converts to $Fe_{0.947}O$ oxide ala Fig 10, hence “b” is the unmixed combination of a product that is 25% oxide/75% iron. Ditto the remaining two thermo curves which are for 50% oxide/50% iron, and 75% oxide/25% iron respectively. These three intermediates are generated with HSC/CEA software and represent the chemical equilibrium that would obtain at the staged combustion points.

The presence of the fraction of unburned iron during combustion drags down the composite intermediate adiabatic combustion temperatures indicated as a′, a′′, and a′′′. These temperature break points are also illustrated to the right of the Fig. 12.

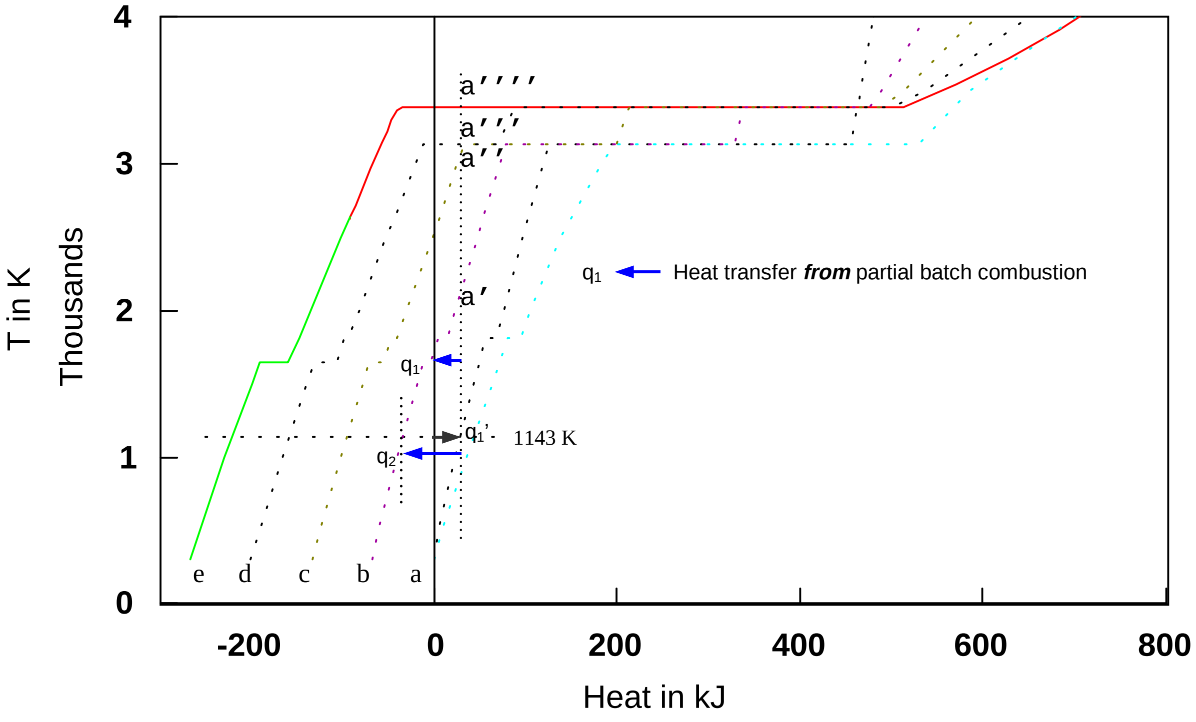

FIG.13—*Thermochemical portrait of the combustion of 0.947Fe and $0.5O_2$ to form $Fe_{0.947}O$ in batch combustion mode showing potential heat transfer .*

This analysis estimates what the temperature versus reaction relationship would be for a batch combustion in thermal equilibrium. However, as before this analysis is for “miraculous” combustion starting at room temperature. As we have seen, ignition requires an ignition temperature and energy from an external source, and that temperature is presumably at 1143 K, also shown on Fig. 12 along with a vertical dotted line through all of the stages of combustion. This estimates a different relationship between temperature and the stages of combustion that is also shown to the right of Fig. 12.

Fig. 13 repeats the key data from Fig. 12 and exhibits how combustion of one pre-heated partial batch in thermal equilibrium can make heat transfer available. The ignition of the batch at 1143 K, on curve “a”, begins its sub-batch combustion and at the 25% combustion point on curve “b” has progressed to point “a′”. When the combustion had progressed to the 50% point curve “c” it would be at the point “a′′”, and so forth.

More Reality Equilibrium Combustion

Combustion of specimens in much laboratory work exhibits both batch and TIP combustion features, however, in work in microgravity in which droplets of slag do not detach, the combustion exhibits results much more nearly like batch combustion throughout.

In the batch combustion example, as is also the case for the previous TIP combustion example, the product of combustion was taken as a single oxide, $Fe_{0.947}O$, which is a common and even probable result. However, in more complex real combustion scenarios, other more stable oxides can form and may need consideration. This has been considered to some extent in earlier analysis [***3***] in showing that regardless of the oxide or mix of oxides that forms, regardless of the burn ratio that might be calculated, the adiabatic combustion condition is typically the same. The situations in which differences may obtain are left for another paper.

Present and Future Work

This manuscript is third among a sequence of fledgling manuscripts begun in 2007 to explore the thermal and chemical equilibria of metal combustion using thermochemistry software. All three are baby steps. This software challenge and the issues associated with its use have not been trivial [***4***]. In the immediate predecessor opinion [***4***], the writer called upon ASTM Committee G4 to create a Blue Ribbon Task Force (or even full regulation subcommittee) to validate (or dispute) the proposals made so far and to serve as a software users group. This paper serves to build the case for such a specialty and will be followed simultaneously and over a longer term by further examinations of this approach.

This particular manuscript graphically illustrated the concepts of traditional burn ratios and exhibited the basis for some of the criticism they have received, while pointing the way to new parameters and analyses that might be both more powerful and more valid. This treatment may evoke criticism for being too protracted or too brief. The specific appraisal of several more possibilities is left to later papers when the approach is at least a little more mature, when flaws in the effort so far may surface, and when perhaps some reaction to the approach from the oxygen safety community forms. In addition, the case for interpreting combustion in two extreme modes “TIP” and “batch” combustion is also made. Many more interpretations for many more metals types are strong candidates for further work.

However, the techniques so far may already allow for the inference of extreme thermodynamic thresholds below which certain combustion scenarios can not sustain. In some cases, these thresholds may be so conservative as to be trivial. Nonetheless, more sophisticated interpretations someday may allow for less conservative, yet valid, parameters to be defined.

This paper also serves as an introduction to a subsequent paper [***9***] to launch on it heels, to serve as dissent and protest to recent committee efforts to redefine criteria for establishing self-sustaining propagation in its *G124 Standard Test Method for Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres*.

This paper builds on the basic approach of applying thermo-chemical portraits like those in this paper to the evolution of safe oxygen systems design when suitably validated. As a result, the generation of a series of these basic portraits for various metals and oxidants remains high on the agenda, not to mention again the much more difficult issues in the combustion of alloys from among these same metals, the issues of diluent metals, inhibiting metals, synergistic and real-gas effects that might all provide for further insight into the performance of combinations, and the need for practical software tools (utilities) that would greatly benefit and facilitate the use of these data. ASTM G4 would do well to answer these needs.

Workers in the field will still need judgment to factor-in all of these issues and to compensate for inadequacies in the software due to theoretical ideal gas assumptions, but hopefully this is a step, again a baby step, toward a deeper understanding.

Conclusions

- The results of thermochemical calculations continue to provide new perspectives on metals combustion, and many more are needed pending evaluation of their validity or the adjustment of their formulation.
- A binary approach to describe and delimit metals combustion (“TIP” and “Batch”) may help illuminate thresholds that may allow for greater exploitation of metals safely.
- Thermochemical portraits provide a graphical understanding of traditional burn ratio parameters and suggest numerous more sensitive ways and likely more meaningful ways to interpret the spirit of minimum required thresholds for combustion.
- Graphical approaches allow for an understanding of conditions in which thermal processes (heat recovery and feedback from the fire-front to the base metal, heat pass-through from any ignition energy or prior combustion) become possible or can be excluded. Among the more important considerations regarding metals combustion is the issue of equilibrium combustion (meaning thermal equilibrium) as a minimum thermal criterion for sustained fire.
- The roles of diluents and pressure can be interpreted though the use of burn ratio thresholds but the thresholds they suggest may be very conservative compared to other circumstantial thresholds established by kinetics and other physical effects.

Summary

The definitions and shortcomings of traditional burn-ratio data for metals combustion have been examined graphically and suggestions for improvements made. Even more powerful analysis of metals combustion employing apparently new approaches called partitioned incremental transient combustion and batch combustion modes have been elaborated and examined for normal and elevated pressure cases and for pure and diluted oxygen scenarios. A much improved insight into the subtleties of metals combustion has been asserted and even more benefit has been forecast for the future. But the need for much more work is also acknowledged.

References

[1] Davy, H., **"Some Researches on Flame,"** *Philosophical Transactions of the Royal Society of London for the Year MDCCCXVII, Part 1*, January 16, 1817, pp. 45-76.

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

[3] Werley, B. L., **“A ‘Simplified’ PC-Based Thermo Analysis of Iron During Combustion”,** Personal opinion paper, *BWOpinion* Website, www.enter.net/~bwerley, 2008, 50 pages.

[*4*] Werley, B. L., **“A Comparison of CEA and HSC Software for Oxidant Safety Thermo/Equilibrium Analysis”**, Self-published opinion, *BWOpinion* Website, www.enter.net/~bwerley, To be published in 2010, ~31 pages.

[*5*] Monroe, R. W., Bates, C. E., and Pears, C. D., **"Metal Combustion in High-Pressure Flowing Oxygen",** *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres, ASTM STP 812*, B. L. Werley, Ed., American Society for Testing and Materials, Philadelphia, 1983, pp. 126-149.

[*6*] Steinberg, T. A., Wilson, D. B., and Benz, F. J., **"Response to Comment by I. Glassman,"** *Combustion and Flame*, 93, 1993, pp. 343-347.

[*7*] Linnert, G. E., **"Carbon and Alloy Steels,"** *Welding Metallurgy*, Volume I, Fundamentals, American Welding Society, 1994, pp. 634-637, 710-713.

[*8*] Benning, M. A., and Werley, B. L., **"The Flammability of Carbon Steel as Determined by Pressurized Oxygen Index",** *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Second Volume, ASTM STP 910*, M. A. Benning, Ed., American Society for Testing and Materials, Philadelphia, 1986, pp. 153-170.

[*9*] Werley, B. L., **"Dissent and Protest to Revision of ASTM Standard G 124's Criteria for Defining Fire Limits: Influences of Ignition and Extinction Processes"**, Self-published paper, Website, www.enter.net/~bwerley, to be published in 2010, ~32 pages.