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Thermo-Chemical Equilibrium Data for Oxygen System Fire Safety Analysis

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ABSTRACT: The oxygen safety community, in particular ASTM Committee G4, has avoided the standardization and promotion of chemical thermodynamic equilibrium practices in addressing the oxidant fire-safety hazard. It has been aware of its availability and validity yet it has demurred and often disparaged it (sometimes in flawed ways) in multiple cases. This worker whole-heartedly supports and has promoted and pursued it use with no success, for nearly two decades. The bases for its adoption are cited and an example draft standard proposal to define selected practical uses of these data including estimation of fire related parameters is presented.

KEY WORDS: Thermo-chemical equilibrium, HSC for Windows, Chemical Equilibrium for Applications, Factsage.

Thermo-Chemical Equilibrium (TCE) theory is well-established and valid especially for understanding combustion processes. However it is not a perfect tool nor is it without its challenges and issues. Chemical Thermodynamic Equilibrium is a powerful but complex body of study. As a result, it is not for the faint of heart or those with less than bull-dog tenacity, for in the writers estimation it lacks practical documentation for the masses. Even highly astute specialists have been daunted. However, its promise to oxygen safety practitioners justifies substantial effort to master its challenge.

TCE methods were first introduced to the oxygen safety community in 1992 in a paper by Steinberg, Wilson and Benz, [***1***][2] in which they assert:

> "The ready availability of computer codes for calculating complex chemical reaction equilibrium suggests that this thermodynamically consistent approach be used for discussing combustion of metals and alloys."

Unfortunately the quirks and vagaries of the NASA software they used were exhibited in the same paper with several apparent errors by the authors in extracting data from it. Later apparent similar errors in its use by these same workers led to results that again appeared

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[1] Retired. No address as this is an archive document.

[2] These authors and a number of their associates have been at greats odds with the present writer over a number of technical issues to the point they are considered nemeses and the several disputes have become personal. However, this worker is in complete agreement with this appeal and even herein seeks as yet another in a long series of efforts to advance and promote the ethic despite early disparagement by the very persons who originally proposed it.

flawed resulting in disparagement of the software in several excessive and perhaps unjustified ways [***2***]. These flawed as well as some implausible data appeared to sour the software's appeal to these most prestigious influencers and appears to have resulted in disdain within their community for their own software as was reflected in ASTM Committee G4's proceedings (and publications) by their representatives often exercising leadership roles. After 30+ years, there has been little-to-no significant use of the software in many appropriate cases, and even both disdain for its use in their community and the greater community[3].

However, just as TCE theory and related software are able to deal with some nasty situations, the particular quirky NASA software complexity can lead to misuse, and at least some of the assorted alternatives, perhaps more flexible, software that is vital to exploit the theory, has also exhibited bugs and quirks that one must be wary of, and finally there have been mechanisms in nature itself that can thwart a thermo-chemical equilibrium approach. In other words, it is not all-powerful. For that and a tragic series of reasons (including missteps), it has unfortunately *not* been exploited as it should be in analyzing the safety of oxygen systems from the fire-hazard point of view.

Nonetheless, thermo-chemical equilibrium analyses promises a quantum upgrade in the tools available to analyze oxygen system hazards, ...in those cases where it can serve. Furthermore, when carefully extracted and cataloged, TCE data that are challenging and onerous to generate, can be presented in a historically useful format that avoids actually dealing with the challenging software and theory and that is relatively easy to understand and apply with appropriate documentation and tutelage.

Following the introduction of TCE data and software in 1992 [***1***], that was then walked-back and largely abandoned, the writer has sought to pick up the torch and promote TCE data exploitation into a very reluctant ASTM Committee G4's practices since 2007 with no trace of success. Nor has this worker been the ideal standards bearer, struggling to learn the assorted necessary skills and having clearly made his own errors and misinterpretations while struggling in solitude. It appears that early efforts to deploy these data, that led to that series of errors apparently of understanding and flawed execution has generated an aversion to, or embarrassment about, its wider use. However, there may be other reasons as well, but as of today G4 has disdained numerous written and verbal appeals, and a negative ballot alleging dereliction in the pursuit of a proposed standard such as is also suggested by the text (among other material) presented here.

An appendix herein proposes how a first fledgling approach to a standard for generating and using specific thermo-chemical equilibrium data might be configured. It may also warrant fine-tuning or even major surgery. Specifically, the previously examined parameters such as burn ratio data that have been a mainstay of oxygen safety practice for decades, despite criticism of it by some of the Committee's cognoscente whomsoever also by implication oppose the cited improvements to these data.

The appendix is not an ASTM Standard, nor ASTM standard draft, but rather proposed-guidance the utility of which will hopefully someday aid in the pursuit of such a standard within G4 or elsewhere should NFPA, EIGA or any other group accept the challenge.

[3] In 2021, a negative ballot of an ASTM standard cited lack of thermo-chemical equilibrium uses was dodged (possibly wrongfully ignored and effectively ruled "non-persuasive") citing as a basis it not being a part of the "scope of the ballot". It is perhaps surprising that even today's modern ASTM permissiveness allows scope to be manipulated as a dodge against challenges to fitness for use.

However, since ASTM standards in particular of this kind are voluntary and subject to the acceptance and adoption by the user, this fledgling effort can serve as tutorial and an alternative embryonic resource “to reduce TCE analysis to practice”.

This approach seeks to specify a simplified data format that can be published, perhaps in atlas form, matured, and with suitable vetting should gain acceptance. It does not seek to address and may not be aware of all flaws and shortcomings that are possible, but rather suggests the resources and data shown here are valid even if needing fine-tuning. Users are welcome to consider this opinion and factor it into their hardware decisions in the same way that they consider the entire body of voluntary standards issued by ASTM Committee G4, including the “imperfect” burn ratio and related listings. Oxygen safety practitioners have always had to work with incomplete, flawed and/or conflicting data. In this case the new benefits outweigh such issues.

Intro to Thermo-Chemical Data

Thermo-chemical equilibrium behavior is not new and virtually everyone has some experience with it. Figure 1 exhibits some commonly recognizable behavioral data for water. This is actually TCE behavior and it becomes even more interesting at much higher temperatures, and can be generated with Outukumpu HSC Chemistry for Windows software Version 3.0 (circa 1992). This does not prove TCE data are equally good at predicting behavior for other materials however that is indeed the case in many, if not all, scenarios.

These data can be much more involved than for the very simple case of water yet can be realistically portrayed in what this worker calls a similar thermal profile. They can be used to determine or at least estimate numerous simplified behavioral data important to the fire hazard of materials. The burn ratio, the adiabatic combustion temperature, the heat of combustion, heat of dissociation, heat of formation, the upper and lower fire limits, and non-standard variants of all these properties.

Not all materials produce similar curves (though many do). Significantly different curves can be generated when materials mix or dissociate or react, or combust. However, just as one can pick significant property data from this curve, so too can significant property data be developed with other curves, and in many cases one could exploit curves like this without having to generate the curves using the software, ...if the curves were published in an atlas akin to the JANAF Tables which are also TCE data.

Closure

The likely unwarranted disdain within ASTM Committee G4’s leadership cognoscente centered on a NASA+ software contingent have thwarted the meaningful implementation of TCE approaches to oxygen safety analysis reviewed herein. Despite promotion by this less than ideal worker, one possible approach is suggested in the appendix, the significant merits of which will hopefully now begin to find purchase in the oxygen safety community and especially and maybe more importantly in the much less robust other-oxidant communities, as well.

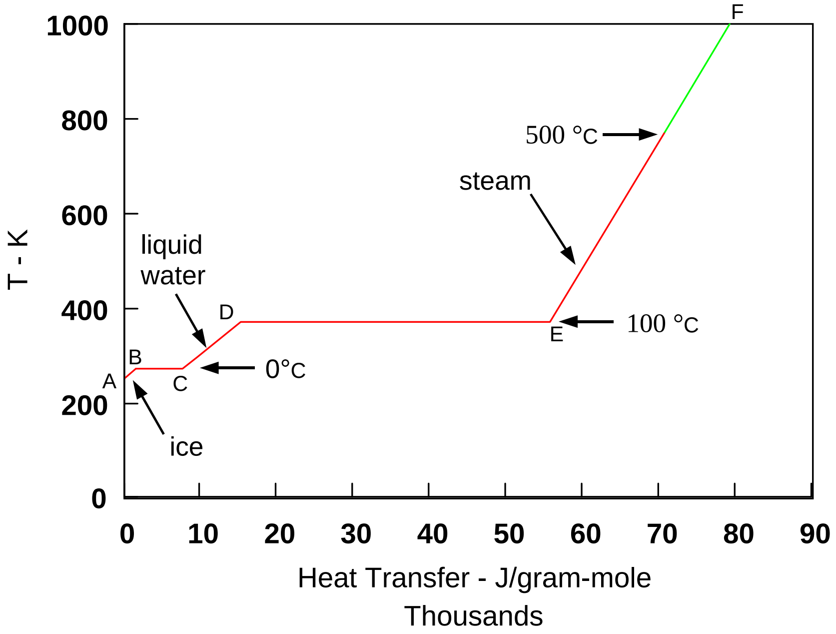

Fig. 1—*Simplistic thermo-profile for water.*

Acknowledgement

Appreciation is expressed to associates Dr. Shankar Nataraj and Joseph W. Slusser who have tried to tutor the writer on several specific topics discussed herein, and which the writer can only hope he has not messed up too badly.

References

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

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

Appendix

Proposed Format for a
Guide to the Use of Selected Thermo-Chemical Equilibrium Data for Evaluating Oxygen System Fire Hazards[A1]

1. Proposed Scope

This guide applies to the use of selected and appraised thermo-chemical equilibrium data in formats (called "profiles' herein) to characterize material flammability properties such are as cited in present or past ASTM Standards G 63 and G 94 and elsewhere such as comparative standard and nonstandard heats of combustion, standard and nonstandard adiabatic combustion temperatures, standard and nonstandard latent endothermic-process burn ratios (melting point, boiling point, dissociating, and derivative burn ratios thereof), and other yet to be configured properties.

This standard focuses on metals in oxygen but similar approaches can be valid, and have been used in some fields, for some nonmetals including gases and oxidants other than oxygen. Furthermore many other applications of thermo-chemical equilibrium data are possible that may lead to other parameters or useful data besides those shown herein that may be future inclusions.

Users of this voluntary (as is, use at your own risk) guide are expressly advised that notwithstanding any validation and commentary regarding opinions of the validity of any such evaluation methods and data, the risk of use of such evaluation methods and data are entirely their own responsibility.

As noted in standard ASTM documents[A1]: "In evaluating materials, any mixture with oxygen exceeding atmospheric at pressures higher than atmospheric should be evaluated from the hazard point of view for possible significant increase in material combustibility."

As is also noted in ASTM documents[A1]: "This proposed guide does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this proposed standard to establish appropriate safety and heath practices and determine the applicability of regulatory limitations prior to use."

2. Proposed Referenced Documents—*TBD* [To Be Determined]

3. Proposed Terminology

3.1 Proposed Definitions – TBD

[A1] Note: This draft standard proposal is not associated with any standards group including the often-cited ASTM or its related Committee G4, with which the author has had much participation, such efforts as this having been rejected by G4 leadership multiple times over nearly two decades (2008-2026). G4 or any other standards group is welcome to treat or incorporate this public domain information into standards or other works.

3.2 Proposed Description of Terms Specific to This Standard – TBD

4. Significance and Use

In the same way cited in all ASTM Committee G4 standards (which this is *not*[A1]), the purpose of this guide is to furnish qualified technical personnel with pertinent information in this case for use in obtaining and interpreting of thermo-chemical equilibrium data for the selecting of materials for oxygen service in order to minimize the probability of ignition and the risk of explosion or fire. It is intended for use in selecting materials for applications in connection with the production, storage, transportation, distribution, or use of oxygen. It is not intended as a specification for approving materials for oxygen service. It specifically focuses on methods of estimating ranking criteria based on theoretical and actual physical data based upon established thermo-chemical equilibrium theory. It may also find uses as a tool for understanding and explaining combustion and its hazards in incident investigations. Speculative future applications anticipates new approaches to evaluating materials, especially metals and alloys, and perhaps less costly ways to test alloys or at least estimate the risks of alloy compositions[A2].

5. Consensus/Dissent—This draft proposal has not been balloted, is *not* an ASTM or other society document, hence enjoys only the consensus of its solitary author. Dissent to the use of these data and the software in this way is reflected in several rejections to initiate a similar TCE activity within ASTM G4 dating to 2007, as well as the derisive way these data have been addressed by some of that Committee's most learned members in several published papers [***1,2***].

6. Generic Characteristic Behaviors—Although thermo-chemical equilibrium texts are considerably complex and mathematical, even introductory science courses commonly teach several basic material behavioral physical properties that can nonetheless often be explained with simplified TCE examples. Some aspects of the fire hazard can similarly be based upon

[A2] *Relative Amount of Data Available for Metals and Nonmetals*. The majority of materials testing for oxygen service historically has been directed at nonmetals since they are the more flammable (easily ignited and prone to burn). Hence there is a rather robust database of data collected with several formal and ad hoc test procedures for nonmetals. Metals test data through 1987 were scant and test procedures were scattered. Indeed in order to publish ASTM Standard G94 on Metals, an ad hoc test program based on NASA test hardware was commissioned by industry, that evolved into ASTM Standard G 94 and represents the core and bulk of metals test data available in ASTM Standard G94 to this day. As a result, and also due to economics, only a small number of the most commonly used metal alloys (or the closest alloys that could be obtained for testing as surrogates) have been tested for comparative fire-limit ratings, friction ignition ratings and particle impact ignition resistance. A majority of alloys and a significant number of commonly used alloys (that are also simply not attainable in configurations needed for testing) have *not* been tested. In comparison, for both metals and nonmetals there is a assortment of theoretical data based upon reliable physical property data such as heats of combustion, adiabatic combustion temperatures for elements, and "burn ratios" based upon formulae proposed by Southern Research Institute in the 1970s. Many alloys that have never been tested are similarly not listed for theoretical data for lack of a way to rank them. As a result many alloys are essentially blank slates with regard to their experience base, their lab test base, and their theoretically projected fire properties.

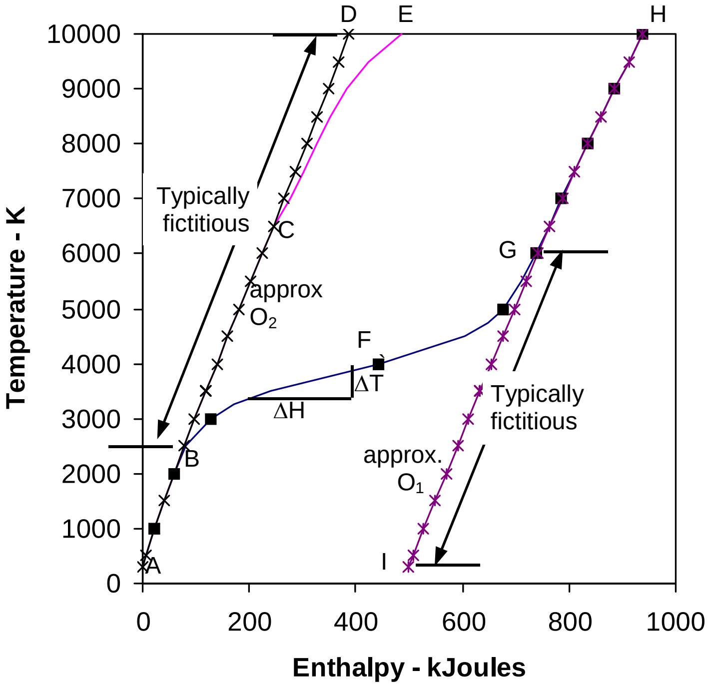

FIG. A1—*Examples of Sensible Heating of Oxygen*

a simplified behavior of materials as they are heated. The behavior of ice, liquid water, and steam are among the best known, and least complex, examples. Solid materials (like ice) can typically be heated till they typically melt (or sublimate or dissociate, or restructure or ionize or "activate" or otherwise). Liquid materials (like water) can also be heated till they typically vaporize (boil or dissociate or otherwise). Gaseous materials (like steam) can be heated until they dissociate, ionize or "activate" or otherwise). All of these practical behaviors can be cited in comparison to a reference condition ("standard" property) or at a specific (in-situ) condition and reflect a relationship between temperature and heating energy that are a central focus herein. There is a complex world of the more challenging behaviors of more complex materials for the more scholarly among us at still higher temperature and heating levels: plasma formation, atom breakdown, ultimately nuclear alterations, these latter prospects are not typical to the common combustion scenarios of oxidant system fires and are best avoided at this introductory level. However, those behaviors that relate to common combustion are typically analyzed using the free energy parameters of Gibbs and Helmholtz (Paragraph 8) and are based upon the commonly understood parameters of pressure, volume, temperature, and heat transfer (enthalpy changes) and the much less commonly understood yet crucial esoteric complicating (and poorly understood) parameter of entropy. Among these, heating (the adding of enthalpy) manifests as either sensible or insensible.

6.1 *Sensible Heating*—Sensible heating of a material is when heating always produces a measurable (sometimes at a constant rate) change (increase) in temperature. Fig. A1 exhibits how a few various materials (in this case including approximate "oxygen" data for diatomic oxygen, O_2, monatomic oxygen, O_1, and mixtures thereof) may sensibly heat over wide temperature ranges (perhaps excluding the near-absolute-zero level). Curve ABCD is "ideal" behavior in that the increase in temperature is taken as a linear function of the heat input and the material "nature" (like diatomic oxygen) likely does not change. The curve is roughly a straight line. Materials that are approximately ideal (solid, liquid, gas or supercritical fluid) will often heat linearly like this for substantial heat inputs. However, for most materials (even the noble elements: argon, neon, etc.) sufficiently elevated temperatures can result in a change in its "nature" including ionization or "activation", or other changes (perhaps even at ultra-low temperatures) that absorb additional or less heat and (as in curve ABCE) change the material (into activated or ionized diatomic oxygen) starting roughly at some point C, such that it absorbs additional heat energy (or in some cases might absorb less heat). If the resulting changed material can be treated as inherent (distinct), the changed material need not be analyzed as two different materials. However if there are circumstances in which the changes may be conditioned on other factors, such that sometimes it heats as in ABCD and other times heats as in ABCE then the heating may need to be treated as acting on two different materials. In other cases, the material may change upon heating into a different molecular form. In Figure A1, an approximate progressive shift from diatomic oxygen into monatomic oxygen is shown along curve ABFGH. If this behavior is inherent (or even just predominant for a specific scenario), it can be used for analysis as "oxygen" (rather than as a mixture of differing monatomic and diatomic oxygen). However, "oxygen" may also be resolved into these two distinct component behaviors: diatomic oxygen that heats along either curve ABCD or ABCE and monatomic oxygen that heats along curve IGH. In many systems inherent behavior renders the sections: BCD, BCE, CD and/or IG "fictitious" as oxygen is not expected, or has not been observed, to exist along their lengths even though it may be observed in mixtures. Instead. thermo-chemical equilibrium principles can use the nature of the partially fictitious diatomic and monatomic oxygen curves to estimate how a variable homogeneous mixture of the two gaseous materials might obtain and form as a function of temperature along the conversion segment BFG.

6.1.1—In cases of differing heating regimes in which the actual material may exhibit curvature as in Figure A1 segment CE, and the segment CD may never be observed physically, might be a fictitious expectation, but nonetheless can be evaluated as a hypothetical material. In these cases, one is not heating the exact original material but the altered material(s) it has become. Indeed, in at least some cases, perhaps all cases, sensible heating can be viewed as a combination of sensible and insensible (paragraph 6.2) partitioned heating where some heat goes to warm the material and some heat goes to convert its chemistry (typically called dissociation), its phase or other property. Along the central transition region BFG between the monatomic and diatomic curves, a roughly linear region indicates how an increment of added heat (ΔH) can produce a roughly proportional fractional sensible increase in mixture temperature (ΔT) that is greater than the heat required to warm it at lower temperature, as the heat also proportionally dissociates (splits) the oxygen molecules.

6.1.2—At point H of Fig. A1, virtually all of the material has dissociated and the reverse segments H to G to F to B to A and similarly H to G to I are now cooling curves for the dissociated resultant material. If one now considers cooling the hot material at point G, one can theoretically expect what the cooling curve might look like if reaction (reverse dissociation, re-association, "combustion") begins at point G or if a fictitious cooling expectation obtains

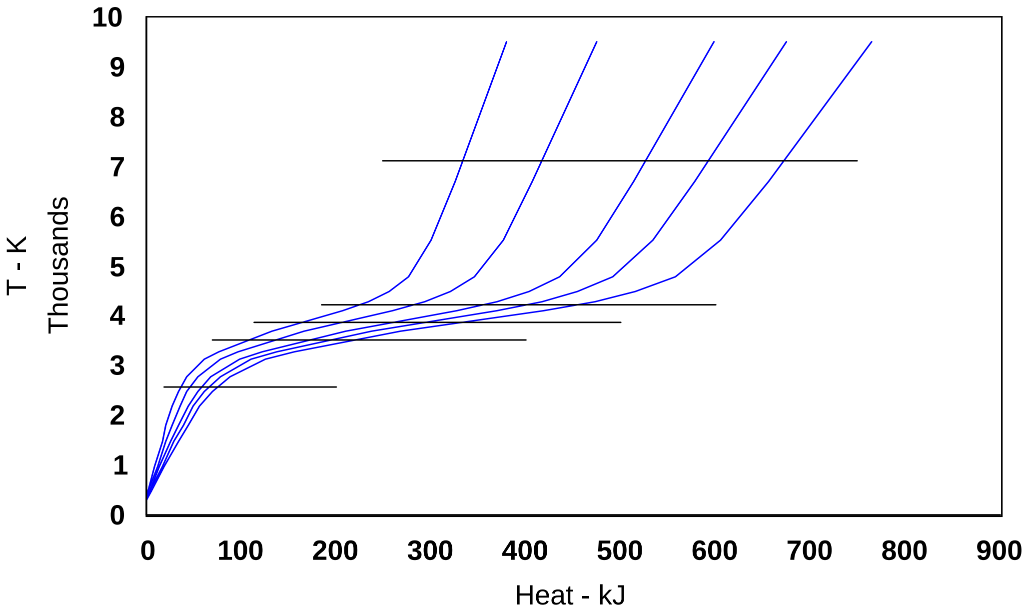

FIG. A2—*Effect of Quantity of Oxygen Gas on Heating*

as for the extrapolated segment GI, which may not be observed and may not exist in the real world but whose behavior can nonetheless be estimated as if it did. The following specific parameters are defined for this process.

6.1.3 Heat Capacity—the amount of heat energy required to raise the temperature of a substance a certain amount. Reported as a ratio: change in enthalpy, ΔH, divided by the mass, m, The ratio can be approximately constant over wide ranges in temperature but can also be variable. The heat capacity is directly proportional to the amount of material being heated. Fig. A2 exhibits how various amounts of oxygen require proportionally greater amounts of heat to achieve specific temperatures for greater amounts of oxygen.

6.1.4 Specific Heat Capacity—the heat capacity of a substance per degree of temperature change.

6.2 *Insensible Heating*—Insensible heating of a material (called "latent" heating) is when heating does not produce an increase in the material's temperature, hence can not be "sensed". There are regions of some heating curves where $\Delta H/\Delta T \cong \infty$ as for point D to E in Fig. A3. Figure A3 approximates the known heating of iron as solid, liquid and gas phases with latent melting and vaporizing transitions between them shown and dotted extrapolations for presumed fictitious regions that are not observed in real systems. In many if not all cases, latent heating/cooling occurs when the substance changes from one condition into a *segregated* second condition (melts into or freezes from a separate puddle or solid as between B and C), boils into or condenses from a separate gas or liquid as between D and E). In this case, a material can be sensibly heated or cooled until its achieves its transition temperature and then further addition or removal of heat is at constant temperature and the further heat transfer produces directly proportional change (melting, boiling, dissociation, crys-

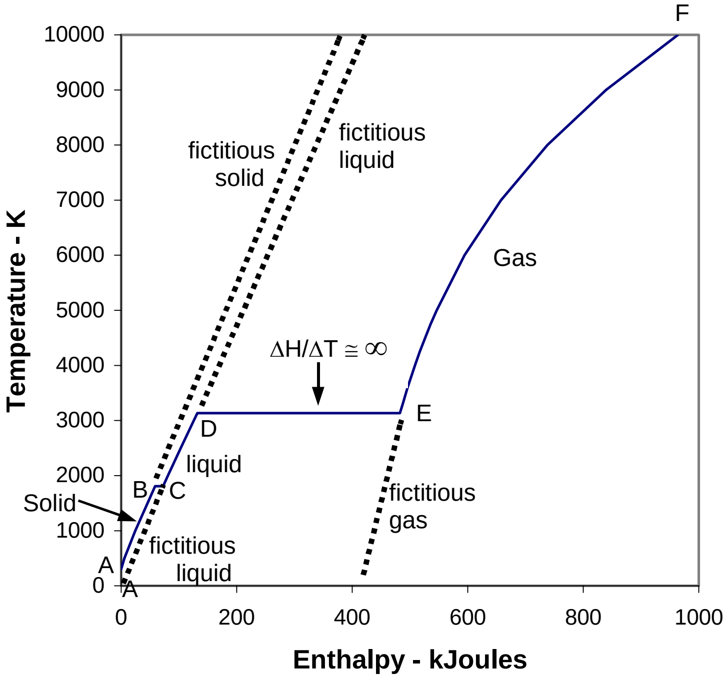

FIG. A3—*Heating of Iron*

tal change, etc). The added heat in cases of melting and boiling not only goes just to split the material apart but to also separate it into the separate phases. Well known, common examples of latent heating are many melting and boiling processes, such as the melting of ice and the boiling of water. But *not all melting or vaporization exhibit constant temperatures*. For example, some tin-lead mixtures exhibit a melting-point range, changing composition, phase and temperature at the same time. Less well-known cases of insensible heating can occur during dissociation, crystal lattice changes, and perhaps still other mechanisms. In cases of sensible heating some of the energy may go to change the material rather than just heat it. In the case of insensible (latent) heating, the extreme case can obtain in which all of the heating energy is absorbed in converting the “state” of the material rather than raising its temperature. Specific parameters are defined below for this process where latent behavior can be or is known to be present.

6.2.1 Latent Heat of Transition—the amount of heat energy required to change a substance from one physical state (phase, chemistry, crystal form) to a second physical state (or vice-versa) at constant temperatures, specifically at a defined transition temperature level and pressure. More specifically as follows:

6.2.1.1 Latent Heat of Fusion—the amount of heat energy required to change a substance from solid to liquid (or vice-versa) at constant temperatures, specifically at the substance’s melting/freezing point temperature for a specific pressure.

6.2.1.2 Latent Heat of Vaporization—the amount of heat energy required to change a substance from liquid to a gas (or vice-versa) at constant temperatures, specifically at the substance's boiling/condensation point temperature for a specific pressure.

6.2.1.3 Latent Heat of Sublimation—the amount of heat energy required to change a substance directly from a solid to a gas (or vice-versa) at constant temperatures, specifically at the substance's sublimation/deposition point temperature for a specific pressure.

6.2.1.4 Latent Heat of Dissociation/Association—the amount of heat energy required to change a substance from one chemistry to a second pre-cursor chemistry (or vice-versa) typically and specifically at a defined dissociation/association temperature level and for a specific pressure.

6.2.1.5—Latent Heat of Crystal Structure Change—Some elements and compounds can be assembled into various crystal structures. Some are more stable than others and so the change of a crystal can be associated with a latent (or sensible) heat of transition. These energies are often of smaller magnitude and so tend not to play a major role in combustion and are not addressed in this version of this standard.

6.2.1.6 Simultaneous Latent Transitions—Heat that is added to a material may produce more than one change/transition at the same time. In an example below, a fraction of the heat added to molten iron oxide (FeO) may vaporize it into gaseous FeO while simultaneously the remaining heat may dissociate some of the gaseous or liquid FeO into gaseous Fe and oxygen (as diatomic, monatomic or a mixture thereof). Hence a fraction of the transition heat can be a latent heat of vaporization (which may or may not dominate the resulting temperature in differing cases) and the remaining fraction will be the heat of dissociation (which may be latent or sensible and may or may not dominate the resulting temperature in differing cases).

6.3 *Transition Processes*—Transitions such as dissociation can occur when heating of a material is absorbed at least in part in changing a material. For example, dissociation splitting diatomic oxygen into monatomic oxygen, splitting simple compounds like FeO into elements: iron and oxygen, or splitting more complex molecules (e.g. Al_2O_3) into elements or less complex molecules (AlO, Al_2O, AlO_2, etc.). Dissociative or other heating may present as either insensible (latent) or sensible heating and usually, if not always, is determined by whether the material self-segregates (latent) into separate materials (e.g. phases: ice changing into separated liquid water, liquid water boiling into separated steam, or: diatomic oxygen splitting into separated monatomic oxygen), or remains homogeneous (diatomic oxygen splitting into a monatomic/diatomic oxygen mixture).

6.3.1 *Transition Temperature*—Simple transitions such as dissociation can often present with an (insensible) latent temperature. Then as is the case with insensible melting points and boiling points, one can similarly circumstantially speak of dissociation "points" and latent heats of transition/dissociation for which the extent of change may (or may not) be directly proportional to the added heat. However, transition like dissociation may also present

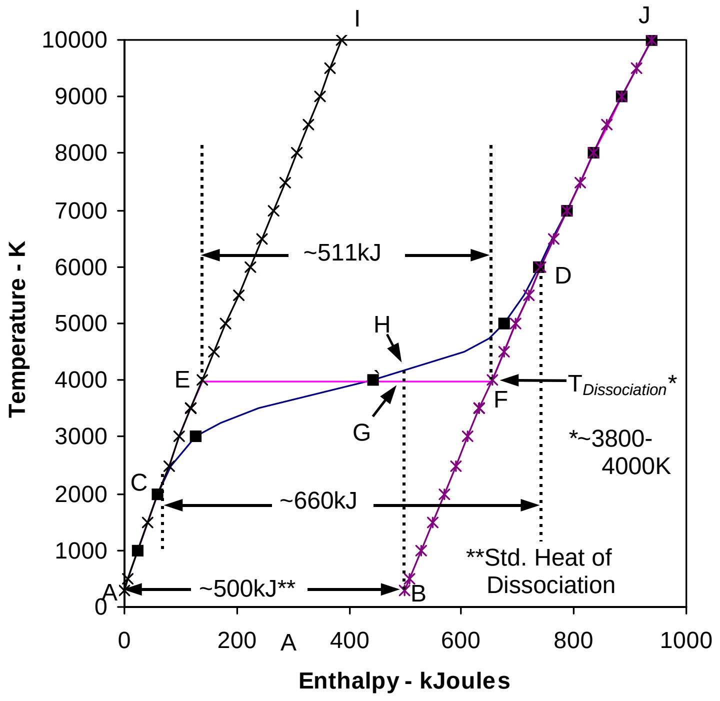

FIG. A4—*Heats of Standard and Nonstandard Dissociation of 1.0 Mole* O_2

for some materials as a sensible transition for which the extent of change occurs with a constantly changing temperature and no precise starting or finishing temperatures and the extent may be a variable function of the added heat, and at least some heat will be diverted to produce the sensible increase in temperature. Fig A4 expands upon the approximate data of Fig A1 for 1.0 mole of diatomic oxygen and exhibits thermo-chemical equilibrium estimates (from HSC for Chemistry 3.0) for the simple case of dissociation of diatomic oxygen (O_2, curve ACEI) into monatomic oxygen (O_1, curve BFDJ) for both purely sensible (one homogenous gas phase, curve ACHDJ as was earlier seen in Figure A1 and as is commonly seen in nature) heating and also shows theoretical purely insensible (latent, two separated gas phases, curve ACEGFDJ heating that that does not appear to have been observed in nature). The sensible transition is treated as inherent in most instances, but the latter insensible dissociation can nonetheless be estimated mathematically and may actually be possible in some specific circumstances.[A2] Note that the theoretical insensible transition indicates a latent heat of about 511 kJ would be required to dissociate diatomic oxygen from point E to point F at about 3800-4000K. However, to dissociate sensible diatomic oxygen through points CHD, where C is close to zero-percent O_1 and D is close to zero-percent O_2 would require ~660 kJ due to the extra sensible heat needed to also raise the temperature of the

[A2] Although monatomic and diatomic oxygen gases would normally be expected to mix, or to form homogeneously, during dissociation, the diatomic oxygen has twice the mass of monatomic oxygen and likely could circumstantially be separated centrifugally, gravimetrically, with membranes or otherwise. Such stratified gases are known to be possible. In partial dissociation of more complex molecules, even more easily segregated products are reasonable, so distinct multiple gaseous oxygen phases may be possible.

changing mixture from roughly 2000K to roughly 6000K. However, regardless of which path (latent ACEGFB or sensible ACHDFB to go from A to B at 298K dissociation transition would be about ~500 kJ that is in keeping with some estimates based upon chemical bond energy calculations. The slightly greater value of 511 kJ between points E and F is due to the smaller number of molecules of diatomic oxygen of greater heat capacity in going from point A to E, compared to the larger (double) number of monatomic atoms of oxygen of lesser heat capacity going from point F to B.

6.4 *Association/Recombination (Reverse Transition)*

Materials that dissociate or change upon heating may (but not always quickly) re-associate (re-react) upon cooling. Cooling hot monatomic oxygen of Fig A4, point J, would normally spontaneously result in a return (reaction, possibly combustion [Paragraph 6.5])) to re-form equilibrium diatomic oxygen whether sensibly or insensibly with a large heat release. Monatomic (free radical) oxygen is so reactive the prospect of a cooling quench to capture the circumstance (as can be done to capture iron oxides) and to produce room temperature monatomic oxygen does not appear to be possible. If it were the combined O_1 might prove to be a very brisant (angry) explosive.

6.5 *Combustion and Spontaneous Reactions*

In many (perhaps *not* all) cases, reactive heating results when two or more materials (of differing or even the same chemistry) can come together spontaneously (automatically) to form a new or more complex material. The combination may be slow (rusting of iron) or fast (combustion/explosion). Reaction and combustion are in many ways the reverse of dissociation and self-generated heat is released into the products rather than being added from external sources. The reacting materials are heating the products they change into as they change, but may also heat nearby starting material to facilitate propagation of combustion. For example: iron and oxygen can combust or slowly combine (rust) to form iron oxide. Similarly, monatomic oxygen atoms could combine (literally combust) to form diatomic oxygen with a heat release. In any case, the combustion heating may produce further temperatures so high that they may resist and limit the further extent of combustion/reaction. Iron that is being heated is being encouraged to react but that can release heat that can encourage dissociation. Ultimately a balance between the two effects (combustion/reaction and dissociation) results in what is called equilibrium. Numerous specific parameters are defined for this process that can be estimated from thermal profiles as are developed herein.

6.5.1 *Standard Heat of Combustion/Reduction*—Heat energy (enthalpy) released is commonly cited for a reactant material at a standard state (usually room temperature atmospheric pressure) that is ignited and burns “completely” (or to a self-limiting point) in oxygen (or other oxidant scenario) and produces naturally occurring products that are then cooled back to the standard temperature (and pressure) during which time further reaction and heat release may or may not situationally occur. Combustion may be considered “complete” when all of the materials are reacted as far as is chemically possible (Fe might react to yield Fe_2O_3) if cooled slowly and supplied with abundant oxygen, but it may also be considered “complete” in a practical sense when it has burned to the maximum extent it can in its present situation. Fe might alternatively combust/cool to yield FeO, Fe_3O_4 or Fe_2O_3, or assorted mixtures of FeO, Fe_3O_4 and Fe_2O_3, and in some cases may even contain un-reacted Fe depending upon its cooling, quench rates, ambient oxygen availability, temperature, etc.). The variable pure products and mixtures of products yield heat releases that are at least to a first approximation linear combinations of the fraction of specific-oxide heats produced. The total heat release may also depend upon whether the products of combustion are homogeneous mixtures or segregated phases, which is an important factor in many cases, but in cases where the heat differences are small, the consequences of the phase variations can also be small. To avoid confusion, heats of combustion should always be referenced to the circumstances and products that obtain either explicitly or by inference. The reverse of combustion (reduction) exhibits heats that are the negative of the heats of combustion.

6.5.1.1 *Nonstandard Heat of Combustion/Reduction*—The heat of combustion with nonstandard starting and/or equal or differing finishing conditions of temperatures or pressures.

6.5.2 *Standard Heat of Formation*—The amount of heat released when specific materials in their standard states are changed into specific materials in their standard states can be non-typical regardless of whether the overall reaction occurs or is unlikely to occur in nature or during combustion or under external heating. The standard heat of formation of an oxide is equal to its standard heat of combustion ...if combustion occurs or can be made to occur in a way that reflects the specific reaction. The heat of formation of a metal oxide from the metal and oxygen is then the negative of the heat of formation of the metal and oxygen from the metal oxide. However often the desired heat of formation data, especially for mixtures, must be mathematically teased from actual natural reactions that occur during tests that may produce assorted results. To wit, the standard heat of formation of specific metal oxides may oftentimes be inferred even if those oxides do not naturally form purely during combustion or other processes.

6.5.2.1 *Nonstandard Heat of Formation*—The amount of heat released when specific materials or specific compounds at temperatures and/or pressures differing from the standard temperature and/or pressure react or dissociate with specific elements or specific compounds to produce specific product compounds regardless of initial and final states whether the particular reaction occurs or is likely to occur in nature.

6.5.3 *Standard Heat of Dissociation*—By analogy, a common “standard” heat of dissociation would be the heat required to transition a material at a standard temperature and pressure into its simpler constituents (typically elements) at the same standard temperature and pressure. However, dissociation by simple heating may stop far short of complete reversion into elements and this has led to confusion. This is still more challenging when the material does not exhibit latent (sensible) heating and when the dissociated materials are not commonly seen in nature (as for monatomic oxygen at standard conditions). Often dissociation data have apparently either not been reported or measured but are calculated from bond energies for these scenarios. Published dissociation heats for the simpler insensible transitions are commonly reported much like heats of fusion and vaporization *at* a dissociation temperature and pressure for cases of latent (insensible) dissociation. The discussion of para-

graph 6.3.1 in reference to Figure A4 illustrated how these various situations can obtain and how confusion can result for a sensibly heated material like oxygen, and how thermochemical equilibrium calculations can allow a standard dissociation parameter between points A and B to be surmised owing to its relationship to either real-world sensible heating of oxygen and analogous insensible heating of oxygen which would both have the same standard heat of dissociation in at least many cases. Although the standard heat of dissociation can often be close to the calculated insensible (potentially real or not) value avoiding such confusion can be and has been a challenge. For an energy to fully dissociate a material at temperature like diatomic oxygen at point C of Figure A4 to monatomic oxygen at point D (660 kJ) can be much greater that the calculated insensible amount (between point E and F, 511 kJ) or the standard amount between points A and B (500 kJ) that applies to either case[A3] and the latter case would be equal to the standard heat of formation/combustion. This discrepancy would be even greater for dissociations initially at point A and are due to the additional heat that is necessary to raise the temperature of the dissociating materials. Similarly, Figure A4 indicates also that while the reaction/combustion of monatomic oxygen at point B would release the standard heat of formation/combustion (equal to the negative of the heat of dissociation) when transitioned to point A, that the reverse heating (putting back) of those products with the exact same standard heat of dissociation would not return (convert) the products to their original state at point B. It would at most only move them to partial dissociation at either point G (for an insensible transition) or H (for a sensible transition). Returning them to the initial point B would require “decombusting” them at points G or H by also reversing their “standard entropy of combustion” (paragraph 7.3.1.4).
START HERE

6.5.3.1 *Nonstandard Heat of Dissociation*—By analogy, the amount of heat that must be added to a material where its initial state and/or products state or both are not standard. In many cases the nonstandard heat of dissociation are tabulated for the heat needed to dissociate the substance *at the temperature* at which it dissociates. For example the heat to dissociate oxygen gas in an insensible condition is indicated on Figure A4 where also shown is the heat to dissociate oxygen in a sensible scenario in which the dissociated oxygen is produced at an increased temperature which may be cited either in combination with the dissociation heat or separately.

6.5.4 *Standard Heat of Transition*—The amount of heat that must be added to a material in its standard state to change it into a specific differing state of standard temperature and

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[A3] The focus of oxidant safety design is typically on combustion that proceeds from reactants to products, however a subtle confusion (mistaken belief—fallacy) and error on dissociation in particular on this point is cited several times by some of the oxidant safety communities most learned and distinguished members in past controversy and contention [***1-4***). For example, in 1992, in [***1***] (page 204) it was argued “...complete dissociation [of a metal oxide] would produce elements, and the enthalpy of dissociation would be the negative of the enthalpy of combustion (i.e. formation) never greater than it”, then later regarding Gordon-McBride code, “dissociation was forced in the computation, that is, the input species was the metal oxide and the input energy corresponded to the enthalpy of formation (negated) of that compound. This is equivalent to using the entire enthalpy of formation of the oxide for dissociating the product metal oxide”, and in 1997 in [***2***] (page 244) the code was used to show “dissociation of FeO(l) where the thermal energy input is the negative of the enthalpy of formation.” This reinforces the posture of this standard that thermal profiles need to be scrupulously extracted so that wider practical use by even the less than-extensively-learned can be of benefit.

pressure. For example crystal structure changes and ionization changes. Dissociation and combustion are specific more commonly known transitions. Any transition may exhibit the same complexity in standard versus nonstandard changes that dissociation exhibits.

6.5.4.1 *Nonstandard Heat of Transition*—The amount of heat that must be added to a material at nonstandard initial, final or both states to change it into or out of a specific final state.

6.5.5 *Standard Adiabatic Combustion Temperature (ACT)*—By analogy a “standard” adiabatic combustion temperature would be the temperature that combustion of a material and stoichiometric oxidant (if required) in standard initial temperature and pressure states can produce in the products of that combustion at the standard final product pressure when no external heat is gained or lost during the combustion process. Clearly the final temperature may not be at the standard initial state temperature. If combustion yields equilibrium and initial and final stoichiometries are precise, the ACT can be a theoretical maximum.

6.5.5.1 *Nonstandard Adiabatic Combustion Temperature*— The adiabatic combustion temperature of a material and oxidant (if required, stoichiometric or not) resulting from a nonstandard initial temperature and or initial or final pressure in the products of that combustion when no external heat is gained or lost during the combustion process.

6.5.6 *Standard Burn Ratio*—Two original “standard” burn ratios were initially (1970s) defined as the ratio of the heat that is released in combustion relative to the heat necessary to melt (burn ratio at the melting point, BR_{mp}) or perhaps more precisely vaporize (burn ratio at the “boiling or vaporization” point, BR_{bp} or BR_{vp}) the material [***5,6***]. These parameters were and still are a useful tool in coarse evaluating flammability of elements that exhibit melting and/or boiling points. Combustion that does not melt or boil a solid material is possible (a charcoal or coal fire that sublimates its fuel or burns into a gas on its surface) but tends (in most but perhaps not all cases) to be relatively slow and much less of a dire hazard. Materials that can fully melt during combustion are capable of a much more rapid and hazardous (liquid phase) combustion. Materials that can fully vaporize during combustion are capable of a still more rapid and hazardous (gas phase) combustion. Most published data for burn ratios of metals have cited metallic elements because data for melting points and heats of combustion are better known and defined for elements. Burn ratios for alloys have tended to be based on linear combinations of the heats of combustion of the elemental constituents but best estimates of melting and boiling points can be flawed in complex cases such as where melting point range alloys are involved rather than latent melting and boiling points. The concept is still valid but the manual calculation can be daunting. The procedures of thermo-chemical equilibrium herein can readily estimate both the heat of combustion and the heat needed to achieve full or partial melting or vaporization.

6.5.6.1 *Mixed-Phase Combustion*. In 1992, Steinberg, et al. [***1***] first addressed mixed-phase combustion (partial burning as a solid, liquid, gas and/or combinations) that are not precluded. They applied thermo-chemical equilibrium theory and software to illustrate these mixed-phase contingencies. Indeed, in the iron combustion example herein there is a fraction of the metal that is estimated to obtain in an adiabatic combustion scenario. Tabulated burn ratios are largely based upon standard heats of combustion, and standard heats of melting or boiling (and could be similarly extended to rare sublimating circumstances). Alloy burn ratios are more complex because the interactions of the various melting and vaporizing mechanisms are vastly more complex than for simple element melting and boiling. However, alloy behaviors can be at least be estimated with the methods of this standard. More interpretation of mixed phase combustion and its implications is needed.

6.5.6.2 *Note:* Burn ratio data appear at present to be more valid as parameters to rank metals fire behavior than to decide whether metals are or are not flammable in a specific hardware circumstance.

6.5.6.3 Burn ratios are an evolution of the Theory of Sir Humphry Davy [*7*] whose early study argued a flammable gas can not support a flame unless its heat of combustion is sufficient to raise the temperature of the gas to its ignition temperature. Burn ratios extrapolate this thinking to argue metals can not combust in various ways unless their heat of combustion (in-situ) is sufficient to support the required changes. In this regard, burn ratios are thresholds that are more valid in surmising whether a material *might* burn rather than surmising it *will* burn, on the basis that other factors besides heat availability may thwart combustion.

6.5.6.4 *Nonstandard Burn Ratio*—Nonstandard burn ratios can be based upon nonstandard heats of combustion and/or commensurate non-standard melting or boiling or sublimating heats for systems that would be considered non-standard in their operation or are at nonstandard initial temperature or pressures.

6.6 *Other Characteristic Elements*—Other characteristic elements or unique combinations of these elements may provide useful data in certain cases. Their potential existence is noted but they not addressed in this version of this standard.

6.7 *Overlapping Effects*—Among the more complicated aspects of TCE are the possibilities of overlapping effects wherein heating or cooling may produce more than one effect at the same time. For example: heating molten Wustite oxide (~FeO) TCE theory predicts that a significant fraction of the heat will go to vaporize the liquid FeO product into gaseous FeO, but that an even larger fraction of the heat will go to produce gaseous Fe, O_2 and O_1 (whether as a dissociation of the gaseous FeO or perhaps less likely as a dissociation of the liquid FeO into liquid Fe and gaseous O_2 and gaseous O_1 followed by vaporization of liquid Fe). When all the temperature-limiting liquid is “gone” in a latent process (for this material), further gaseous dissociation is then predicted as a sensible heating process unless additional insensible transitions are possible.

7. Circumstantial TCE Thermal Profiles

7.1 *Creating a Thermal Profile*—This standard specifically addresses what it refers to herein as “thermal profiles”. To create a thermal profile involves identification of a specific scenario of interest, what materials should be present in what amounts, and what species might form at the initial temperatures and pressures present, and how those initial conditions might change during combustion. To simplify the math, often "certain" behaviors like latent melting/fusion with a specified heat of transition are inferred or assumed and consideration of solid material above the melting point or liquid melted material below the melting point are ignored. Other parameters may also be important. One must also identify critical factors like heat losses and phase formations, and more. And this standard presumes these issues are all best addressed by a body of astute practitioners of TCE theory. Then the astute practitioners of the theory apply TCE mathematics (actually use one or more TCE software codes like HSC Chemistry for Windows, NASA CEA for Applications [formerly, Gordon–McBride code], FactSage or other[A4]) to estimate what the equilibrium outcome will be relative to the initial conditions. In this standard a thermal profile is generated for temperature versus heat input (enthalpy). Other relationships may prove additionally useful for future evolution of the standard (for example, temperature versus entropy input, heat input versus entropy input, etc.). Finally to the extent possible, the thermal profile should flag known key aberrations of the data that may obtain and how they are handled. Indeed, to the extent possible all such aberration "traps" should be cataloged and tutored for the users of these data. In some cases thermal profiles may factor in such behaviors into the curves themselves. Practitioners of oxidant fire safety have never enjoyed complete knowledge of any fire hazard, and often have had to deal with conflicting data, and must here again apply their experience and skillful intuition to assess the degree to which they will trust and apply these data and tools.

7.1.1 Example Aberration 1: Nitric oxide, NO, is quick to form at high temperatures but slow to dissociate upon cooling. Rapid combustion of the fuel within a split-second in an internal combustion engine can rapidly form nitric oxide but the rapid quenching of the combustion products as occurs following that combustion versus long term open combustion in free space can quench the nitric oxide produced into what is called a "frozen equilibrium" that may persist even for long periods thereafter. These data were well-known sometime before the 1970s. This must be factored into a thermal profile.

7.1.2 Example Aberration 2: Combustion of iron in oxygen largely forms molten FeO slag near or at the adiabatic combustion temperature, at which higher oxides do not appear to form[A5] and if slowly cooled can revert to more stable higher oxides but if rapidly quenched can form solid FeO oxide at room temperature in another example of "frozen equilibrium". Over long periods of time solid FeO can revert to more stable equilibrium forms but can seem to behave as a stable oxide during a system incident.

7.2 *Example Thermal Profile for Iron Combustion in Oxygen*—Since iron (in particular steel) is the most commonly used material in contact with oxygen, a putative (albeit prelimi-

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[A4] Although there may be differences among the calculations from assorted software, to the extent surveyed to date the thermal profiles generated have been remarkably similar, especially in the most important lower temperature regions.

[A5] Although only FeO oxide has been observed at the high adiabatic combustion temperatures, that does not mean only FeO oxide (liquid and/or gas) can be present. Indeed, Fe liquid and/or gas and/or either or both monatomic and diatomic oxygen may all be predicted to be present.

Table A1—*Input/Output Species for iron in Fig. A5.*

Lower Tier	**Upper Tier A**	**Upper Tier B**	**Upper Tier C**
Gas Phase O(g), O_2(g), 0.5 kgmol Fe(g)	**Gas Phase** O(g), O_2(g) ~0.5 kgmol, Fe(g)	**Gas Phase** O(g), O_2(g) Fe(g)	**Gas Phase** O(g), O_2(g) Fe(g)
Liq/Solid Phase 1 Fe(s,l) 1.0 kgmol	**Liq/Solid Phase 1** Fe, 1.0 kgmol	**Liq/Solid Phase 1** Fe	**Liq/Solid Phase 1** Fe
	Liq/Solid Phase 2 Fe_3O_4	**Liq/Solid Phase 2** Fe_3O_4	**Liq/Solid Phase 2** Fe_3O_4
	Liq/Solid Phase 3 Fe_2O_3	**Liq/Solid Phase 3** Fe_2O_3	**Liq/Solid Phase 3** Fe_2O_3
O_2 to form FeO.	O_2 to form ~FeO	O_2 to form ~Fe_3O_4	O_2 to form ~Fe_2O_3
Fe and Oxygen segregated.	FeO is only oxide.	FeO, Fe_3O_4 only oxides.	FeO, Fe_3O_4, Fe_2O_3 oxides
	Adiabatic Combustion Temp. ~3330K	**Adiabatic Combustion Temp.** ~3190K	**Adiabatic Combustion Temp.** ~3157K

nary unvetted[A6]) prototype thermal profile is included as an example herein, subject to future upgrade. More sophisticated (and complicated) examples may differ and the general shapes and effects exhibited by iron may not always apply even to other metals and especially to alloys. Thermal profiles illustrate how numerous useful data affect material behavior. Table A1 lists configurations for the iron/steel scenarios to be examined herein.

7.2.1 *Lower Tier Data*—Figure A6 Part A, page 21, exhibits the predicted heating curve possibilities (from HSC Chemistry 3.0 software) for segregated 1 mole of iron and one-half mole of diatomic oxygen. Part A shows both an “s”-shaped (single phase) curve and a plateau (latent) curve for each material. Based upon a-priori knowledge (1) that Fe liquid and gas do not mix well, a two-phase condition can be imposed on the iron and (2) that highly reactive bilk monatomic oxygen is not observed at lower temperatures and also because monatomic oxygen gas and diatomic oxygen gas are expected to mix easily (in normal situations) a single-phase condition is imposed on the oxygen. Therefore, the composite heating curve for the *segregated* materials is shown as a summation in part B. This is the presumed realistic curve for the most likely lower tier behavior and this curve was shown as the lower tier curve in Figure A5. If greater input amounts of either component were present the curve would stretch out to the right as was shown in Figure A2.

7.2.1.1 These data are actually rather robust at least at lower temperatures. At very high temperatures differing mechanisms may be factored in that can change the shape of the curve significantly, however they will at least in most cases similarly change the highest tempera-

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[A6] Thermal profiles must be considered preliminary even though as was described, they here were first proposed in 2007, however, have been largely disdained by key members of the oxidant safety community.

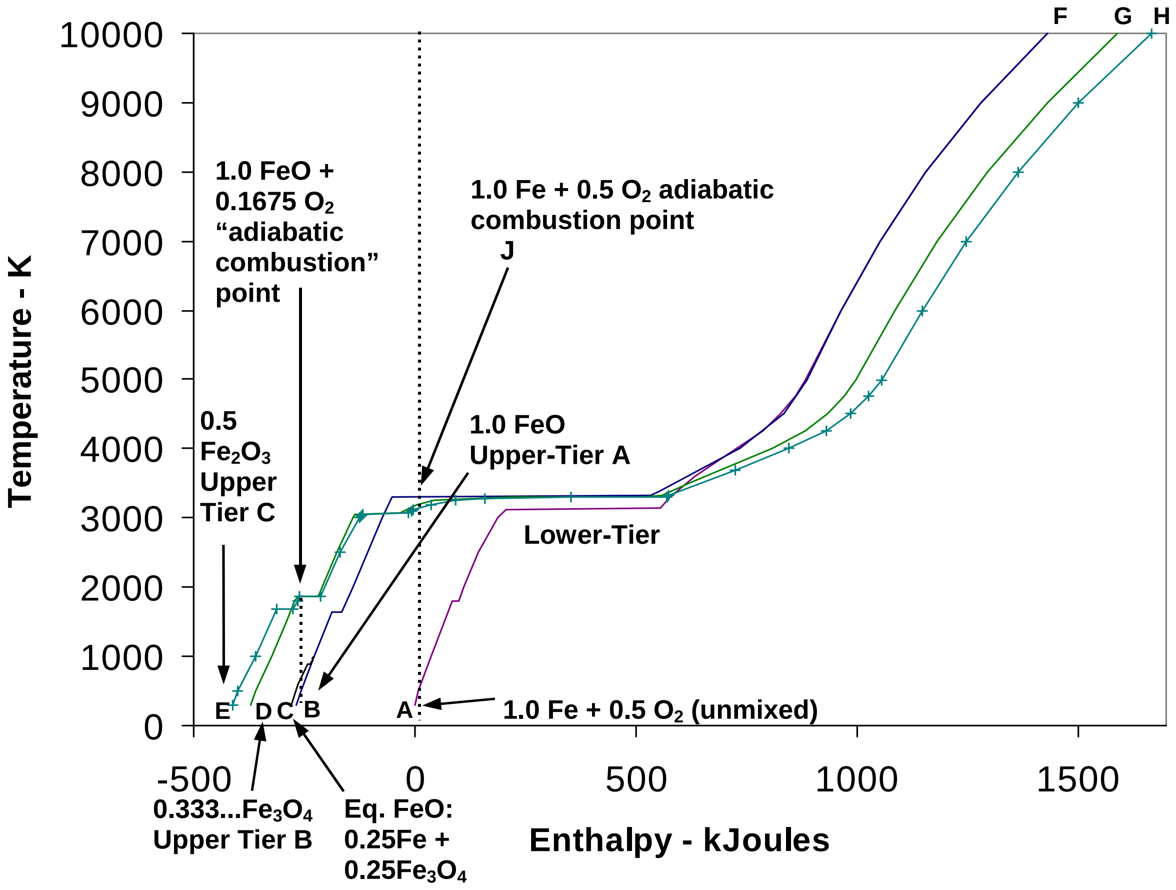

Fig. A5—*Heating/cooling of maximum composite grail results.*

ture portions of the upper tier curve to be developed below and will be offsetting as to numerous subsequent conclusions.

7.2.2 *Upper Tier Data*—Figure A5 also exhibits four upper tier curves (end points at points B,C,D,E) as follows:

7.2.2.1 The curve at point B is based upon thermo-chemical equilibrium calculations performed with HSC 3.0 for 1.0 mole Fe allowed to react with 0.5 mole diatomic oxygen (stoichiometric for the production of oxide FeO). Oxides Fe_3O_4 and Fe_2O_3 were not allowed to be produced (calculated). The high-temperature end-point of this curve B merges with the end-point of lower tier curve A at very high temperatures (at point F) . This low temperature point B of this curve is largely physically achievable with a rapid quench of adiabatically combusted iron of curve A. The low temperature end-point of this curve at ambient temperature is more precisely Wustite (either pure FeO or a series of wustite oxides of form Fe_xO where x is commonly cited as 0.9475, but can vary significantly) and tends to form because the solid formation process omits approximately one iron atom for every twenty oxygen atoms, ~5% more oxygen or less iron than for FeO). The enthalpy difference between

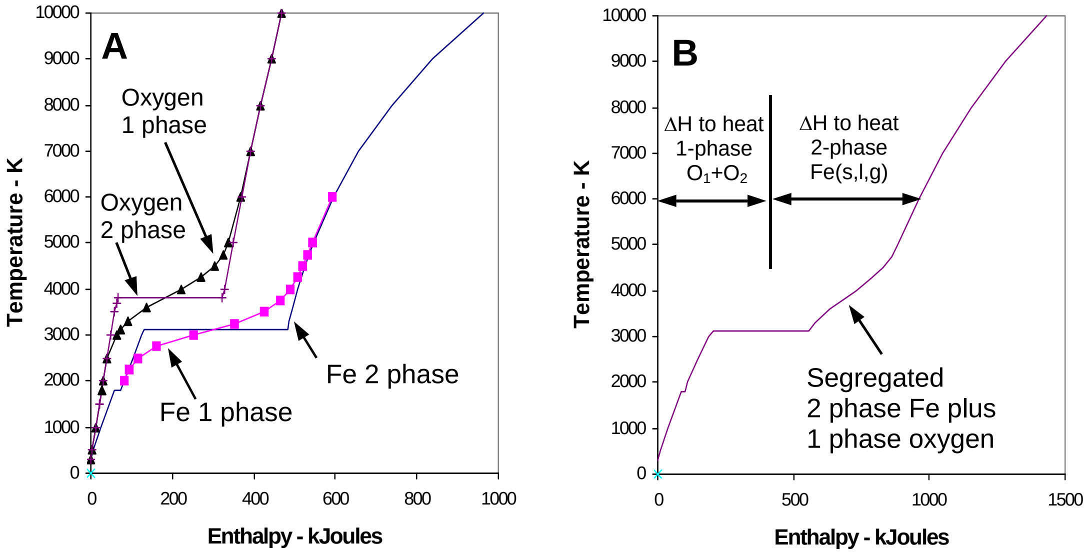

FIG. A6—Summing of Separated Materials Enthalpies

points A and B is the standard heat of formation/combustion for iron given by the reaction equation:

$$1.0Fe + 0.5O_2 \rightarrow FeO$$

with a heat of formation/combustion of about -266 kJ/gmol-Fe consistent with tabulated data.

7.2.2.2 The curve at point D is based upon thermo-chemical equilibrium estimated calculations performed with HSC 3.0 for 1.0 mole Fe plus 0.666... mole diatomic oxygen (stoichiometric for the production of oxide Fe_3O_4, magnetite). This curve is not typically produced even in skillful normal or fast quench actions, so is theoretical. The low temperature end-point of this curve at ambient temperature is magnetite, Fe_3O_4. Oxides FeO, Fe_3O_4 and Fe_2O_3 are able to form. The high temperature end-point of this curve is shown as point G shifted slightly to the right due to additional heating necessary to raise the temperature of the additional O_1 oxygen that would be present. A curve to exhibit separated heating of the Fe and O_2 components has not been shown to avoid clutter but would merge with point G. The enthalpy difference between points A and D is the standard heat of formation/ combustion for iron given by the reaction equation

$$1.0Fe + 0.666O_2 \rightarrow 0.333Fe_3O_4$$

with a heat of formation/combustion of about -368 kJ/gmol-Fe consistent with tabulated data.

7.2.2.3 The curve at point E is based upon thermo-chemical equilibrium estimated calculations performed with HSC 3.0 for 1.0 mole Fe plus 0.75 mole diatomic oxygen (stoichiometric for the production of oxide Fe_2O_3, hematite). Oxides FeO, Fe_3O_4 and Fe_2O_3 wereallowed to form by the software. The high temperature end-point of this curve is shown as point H shifted slightly to the right of point G due to additional heating necessary to raise the temperature of the additional O_1 oxygen that would be present. A curve to exhibit separated heating of the Fe and O_2 components has not been shown to avoid clutter but would merge with point H. The enthalpy difference between points A and E is the standard heat of formation/combustion for iron given by the reaction equation

$$1.0Fe + 0.75O_2 \rightarrow 0.5Fe_2O_3$$

with a heat of formation/combustion of about -411 kJ/g-mol-Fe consistent with tabulated data. With much larger oxygen presence and a slow quench, Le Chatelier's principle would suggest a low-temperature approach to complete hematite formation might occur.

7.2.2.4 Curve C is based upon the input conditions of curve B, but for which the formation of Fe_3O_4 is allowed. The end-point, C, would be an uncertain (segregated or homogeneous) combination of Fe and Fe_3O_4. All of the oxygen in the FeO of point B, shifts at equilibrium to form Fe_3O_4 leaving pure iron behind.

$$1.0Fe + 0.5O_2 \rightarrow FeO \rightarrow 0.25Fe_3O_4 + 0.25Fe$$

with a heat of combustion/formation of about -280 kJ/g-mol-Fe. In order to produce this scenario, one must allow long periods of time for FeO to achieve this equilibrium at ambient temperature where the solid materials impede changes, or heat the FeO to the latent transition temperature where the materials are more active and conversion might be more rapid but still rather slow since both materials are solid. And this is apparently why rapid quench of molten FeO slag produces a "frozen equilibrium" of "unstable" FeO.

7.2.2.5 *Excess Oxygen*—Table A1 presented the bases for the several curves of Figure A5. Other possibilities may be meaningful or even more meaningful than these, and some of those may be currently possible to calculate with present software or may become possible in the future. For example, some workers argue a series of ferrite ions are present[A7]. If so, they would compete for existence and they would have to be accounted for and might alter all of these curves and even require new and different curves as well. This aspect has been a significant factor in the dereliction in pursuing a thermo-chemical equilibrium approach to

[A7] During the early 1990s, discovery was claimed of massive "excess oxygen" in the molten slags of iron burning in oxygen [***8***]. Later, the experimental methodology was obliquely admitted to be flawed but a follow-up study [***9***] asserted that at least copious amounts of excess oxygen *are* present and that the copious excess must be in the form of ferrite ions [$FeOx^{n-}$]. In the intervening 30 years numerous learned workers have treated this work as "settled science" but no efforts have been made to measure or calculate the properties of these putative ions. Dissent to this discovery over the period 1995-2025, has been largely censored. A re-examination in 2025 [***10***], argues the original study had error margins that precluded drawing the conclusion, and that the oblique correction [***9***] was similarly flawed. Hence such massive or even copious presence may not be proven and may not to be present in significant amounts to significantly alter the thermo-chemical equilibria estimated in Figure A5.

Table A2—*Derivative estimates of properties based upon Figures A5-A12.*

Property	"Standard" Environment (Ambient, 298.15K, 70°F)	"Nonstandard" Environment (1000K, 1340°F)
$\Delta H_{c,f}$ FeO	~266[a] (Fig. A5) A↔B	~266[a] (Fig. A7) A'↔B'
$\Delta H_{c,f}$ *	~280[a] (Fig. A5) A↔C	not applicable
$\Delta H_{c,f}$ Fe_3O_4	~368[a] (Fig. A5) A↔D	~368[a] (Fig. A7) A'↔D'
$\Delta H_{c,f}$ Fe_2O_3	~412[a] (Fig. A5) A↔E	~412[a] (Fig. A7) A'↔E'
ΔH_D (FeO)	~736[a] (Fig. A8) K↔M	~736[a] (Fig. A9) K↔M
ΔH_D° (FeO)	~950[a] (Fig. A8) B↔M	~907[a] (Fig. A9) B'↔M
ACT(FeO)	~3245K (Fig. A5, A↔J=B↔J)	~3245K (Fig. A7, A'↔J'=B'↔J')
ACT(Fe_2O_3)	~3135K (Fig. A5, A↔J=D↔J)	~3135K (Fig. A7, A'↔J'=D'↔J')
ACT(Fe_2O_3)	~3082K (Fig. A5, A↔J=E↔J)	~3082K (Fig. A7, A'↔J'=E'↔J')
	→← [c] / →→ [d]	→← [c] / →→ [d]
$BR_{MP(FeO)}$:	~2.7[b] / ~1.25 (T/S)[f]	~4.2[g] / ~2.6 (T'/S')[g]
$BR_{MP(Fe3O4)}$:	~3.9[b] / NS[e], >1.25[f]	~6.0[g] / NS[e], >2.6[g]
$BR_{MP(Fe2O3)}$:	~4.3[b] / NS[e], >1.25[f]	~6.6[g] / NS[e], >2.6[g]
$BR_{BP(FeO)}$:	~0.47[b] / ~0.21 (T/U)[f]	~0.50[g] / ~0.27 (T'/U')[g]
$BR_{BP(Fe3O4)}$:	~0.67[b] / NS[e], >0.21[f]	~0.71[g] / NS[e], >0.27[g]
$BR_{BP(Fe2O3)}$:	~0.75[b] / NS[e], >0.21[f]	~0.79[g] / NS[e], >0.27[g]

***0.25Fe_3O_4 + 0.25Fe** **[b] fig. A10, text p.32** **[d] Co-Current** **[f] fig. A11, text, p. 34**

[a] kJ/gmol Fe **[c] Counter-Current** **[e] Not Shown** **[g] fig. A12, text, p. 36**

oxidant safety and even opposition to its use. However, if present, the thermo-chemical properties of these alternatives would have to be measured or estimated, and as such apparently no data have been sought since the 1990s. Here again the inclusion of additional "extra oxygen" would tend to reduce the temperatures achieved and could yield a less conservative result.

7.3 *Thermal Profile Analysis*—Table A2 presents data estimates extracted from the curves that HSC 3.0 produced in Figure A5 and later figures. These include the standard heats of formation of the several real and potential oxides that may obtain (Paragraphs 7.2.2.1-7.2.2.4). Among the power that this standard provides is the option to explore additional credible estimates of numerous both standard and nonstandard circumstances. This perhaps includes estimates of how higher operating ("standard-like") temperatures might affect oxidant system combustibility. Since there are an infinite number of possible nonstandard conditions that may be of interest in any given situation (and the variations might even be plotted to estimate trends) hence only a few are tabulated in Table A2. Since this standard discourages user extraction of data with the complex and expensive HSC or other software, the extracted data are illustrated for the reading of the Figure A5 graph which boils down to astute reading of the distances between specific points and ratios of various point values and distances between points on the curves. This can be challenging by eyeball, so often use of devices such as vernier calipers and scale factors can be useful (though rather labor intense), and in perhaps a preferred case, "reader" software can be desirable to not only allow placement of cross-hairs on specific points to allow readout to the limit of accuracy of the plot but to perform needed calculations as well. As described herein, this would facilitate easier extraction of, and less error in, properties such as the previously presented heats of formation/ combustion but also: latent transition points such as melting, boiling, and sublimation points, and heat capacities as simple slope measurements, and also parameters such as burn ratios with some sophistication..

7.3.1 *Equilibrium Combustion and Products*—On Figure A5, the reactants (1.0Fe and $0.5O_2$) are shown as segregated, summed, and heated between points A and F, then also shown as mixed at point F and cooled to point B (to form FeO) or C (to form $0.25Fe_3O_4$ + 0.25Fe). However, adiabatic combustion follows a different path. The heat of formation/ combustion was indicated as the heat between points A and B or A and C. On Figure A5, adiabatic equilibrium combustion is indicated by a vertical transition (meaning no added or lost heat) from point A to point J. Adiabatic combustion of the same environment at elevated initial temperature is also indicated by any direct vertical transition from that point on the lower-tier curve between points A and F to the upper tier curve between points B and F directly above it.

7.3.1.1 *Local Equilibria in Transient Combustion*—Separated iron and oxygen at any temperature can each be in equilibrium and "stable" locally throughout their separate respective masses. When allowed to mix and interact, a new equilibrium can obtain. If the two were at the 10,000K temperature of Fig. A5 point F, then mixing them would be expected to produce little or no change in temperature. However, if the two were at the standard conditions of point A in Figure A5, then internal energy could be converted into temperature and raise the combined in-situ result to point J, the adiabatic combustion temperature, were they to achieve equilibrium. When iron is in oxygen and ignited locally a transition of the two stable materials can proceed (called propagation) in which a third local equilibrium region of the products is produced and if it obtains quickly would to be called local adiabatic combustion. The more rapidly the propagation occurs, the more closely the temperature of the local equilibrium would reflect the adiabatic combustion temperature. A fine iron powder that can be thoroughly intermingled with oxygen (as in a dust cloud) may propagate very quickly and may even be explosive, while chunky iron might not burn or might burn so slowly as to behave like coal burning in a furnace. The ability for a local equilibrium to move through a medium can be crucial to the speed of propagation, the required strength of ignition to launch propagation, and even the ability to propagate at all (the fire limit).

7.3.1.2 Standard Heat of Combustion (ΔH_c) for iron—When any iron combustion occurs, the input condition A of Figure A5 has a specific (in this case standard) temperature, entropy and enthalpy (internal energy in constant volume systems) and heats the material to point J by converting enthalpy energy and entropy change into temperature and composition changes. At point J of figure A5, heat of combustion has been released into the products of combustion (in this case largely if not entirely FeO), from whence they can be rapidly quenched to the standard temperature at point B, and measured to determine the standard heat (Enthalpy) of combustion, ΔHc, for the FeO products, as the length of the segment AB on the enthalpy scale. This is why standard texts such as Glassman [***11***] cite adding the heat of combustion back into the products of combustion as a way of computing the adiabatic combustion temperature, but that is not nearly a trivial task compared to measuring the length of segment AB.

7.3.1.3 *Combustion Variations*—Note the in-situ heat of combustion depends upon the combustion products that form. If iron slag at point J is rapidly quenched, FeO is the principal product that is cooled. If the slag is more slowly cooled, mixtures or discrete regions of FeO, Fe_3O_4 and Fe_2O_3 may form in various proportions. As the materials are cooling, further reaction is occurring and releasing additional heat of (further) combustion. Hence any final heat release may range from the segment lengths AB where only FeO is formed) to AE where only Fe_2O_3 is formed. If only Fe_3O_4 were to form, the heat of combustion would be segment AD. Mixture heats of combustion might fall anywhere in between. Note that the release of heat greater than that represented by segment AB tends not to be a consequence of the initial combustion but a delayed and slower reaction.

7.3.1.3.1 *Products of Combustion*—The products of combustion can vary in many additional ways. In the previous example, if adiabatically combusted FeO is not quenched rapidly, and if additional oxygen is present, as it cools and releases enthalpy (heat) it may solidify progressively freezing a varying composition and fractionally quenching the combustion during cooling, also altering the in-stu heat of combustion/formation.

7.3.1.3.2 *"Complete" Combustion*—Heat energy (enthalpy) released when a material at room temperature is ignited and burns "completely" (till it stops burning) in oxygen (or other oxidant scenario) and is cooled back to room temperature can vary in real scenarios. Typical laboratory test procedures tend to use abundant high pressure oxygen at constant volume testing so that pressure/volume work is not a factor and so that the combustion will tend to react with a maximum amount of oxygen possible (Le Chatelier's Principle). However, for time and other reasons often even this natural combustion does not form the most extreme products possible and so the resultant "complete" measurement must be qualified or adjusted to provide the necessary result.

7.3.1.3.2.1 Sometimes the adiabatic combustion point is altered by differing phases that may form (e.g. liquid and gaseous FeO). For example on Fig. A5, if the iron is combusted in abundant oxygen from the starting point "A", assuming the combustion is adiabatic, without added heat or heat drain to the un-reacted bulk oxygen and so combustion would progress vertically upward. Many different compounds might form and change as the reaction proceeds and the temperature rises. Ultimately a temperature above those at which Fe_3O_4 and Fe_2O_3 exist would obtain and one can visualize the reaction of the iron with a stoichiometric amount of oxygen to form largely FeO at point "J" (bulk oxygen is assumed absent or unheated). This indicates the adiabatic combustion limit. HSC predicts that at point J, at about 3258K, the composition of the combusted iron will be FeO. This may be alternatively understood also by assuming the heat of combustion/formation of FeO has been added to solid

FeO starting at point B and heating it through its solid state and liquid state and further heating it with the consequence that at the adiabatic combustion temperature point J on the latent plateau, a small amount of it has been vaporized and/or dissociated.

7.3.1.3.2.2 If the molten slag at point "J" were to be rapidly quenched, it could (and does) tend to form a largely solid FeO slag plus doubtless gaseous oxygen and perhaps a small amount of pure iron. However, if it is allowed to cool more slowly its temperature would drop to where it would tend to incorporate more of the ambient oxygen: releasing heat that would slow the rate of cooling. The slower cooling would actually enable the further combustion of the oxide. Hence the slag enthalpy and temperature would both decay along the upper tier curve shifting to various amounts of Fe_3O_4, Fe_2O_3, FeO perhaps homogeneous perhaps stratified or both. Rapid quenching at any point along this upper tier curve would tend to produce a slag of the same composition as the TCE software predicts for the higher temperature point on the curve. Continued slow quenching might produce a still different slag composition depending upon the path the cooling took to return to room temperature. Slag compositions also tend to show variations in the compositions depending upon the temperature gradients that form during cooling: outer regions near a cooling surface tend to reflect the local equilibrium conditions for a lower temperature. Indeed, in heat of combustion testing, often the final composition of the products must be analyzed to be able to compensate for variable reaction of the test material. [A8]

7.3.1.4 *Standard Entropy of Combustion (ΔSc)*—Whereas combusting elements (or other input conditions) at point A of Figure A5, allows one to estimate the various possible heats of combustion between points A and B, A and D, and A and E, note that adding the heat of combustion back into the products does not return one to the initial elements at point A but rather to the adiabatic combustion point at J. This is because there is an entropy change that also occurs during combustion that defines a standard entropy of combustion ΔSc. In order to reverse combustion all the way back to elements one must reverse both the heat of combustion *and* the entropy of combustion. Indeed future versions of this embryonic standard might include not only thermal portraits for T versus ΔH, but thermal portraits of T versus ΔS. Note also that combustion between Points A and J releasing heat of combustion/ formation of segment A to B can be rapid with a high hazard effect, but that release of the greater heat estimate by segment A to D and A to E, tend to be much slower and can facilitate and protract ambient combustion but would not tend to be nearly as explosive as might be the heat release of segment A to B, because the later heat releases only occur during cooling and not during the fast or even explosive high temperature combustion stage, A to J.

7.3.1.4.1 *Adiabatic versus Isentropic*. Note that whereas a pressurized gas can be adiabatically expanded (without added or withdrawn external heat) a process that is also isentropic, when combustion occurs without adding or withdrawing heat the process is also adiabatic but not isentropic. The entropy at point J on Figure A5 is much different than that at point A

[A8] Note that this conflicts with the perspective of the excess oxygen proponents cited in footnote A5 that argue during cooling, copious oxygen dissolved into the slag is both desorbing and venting and reacting internally.

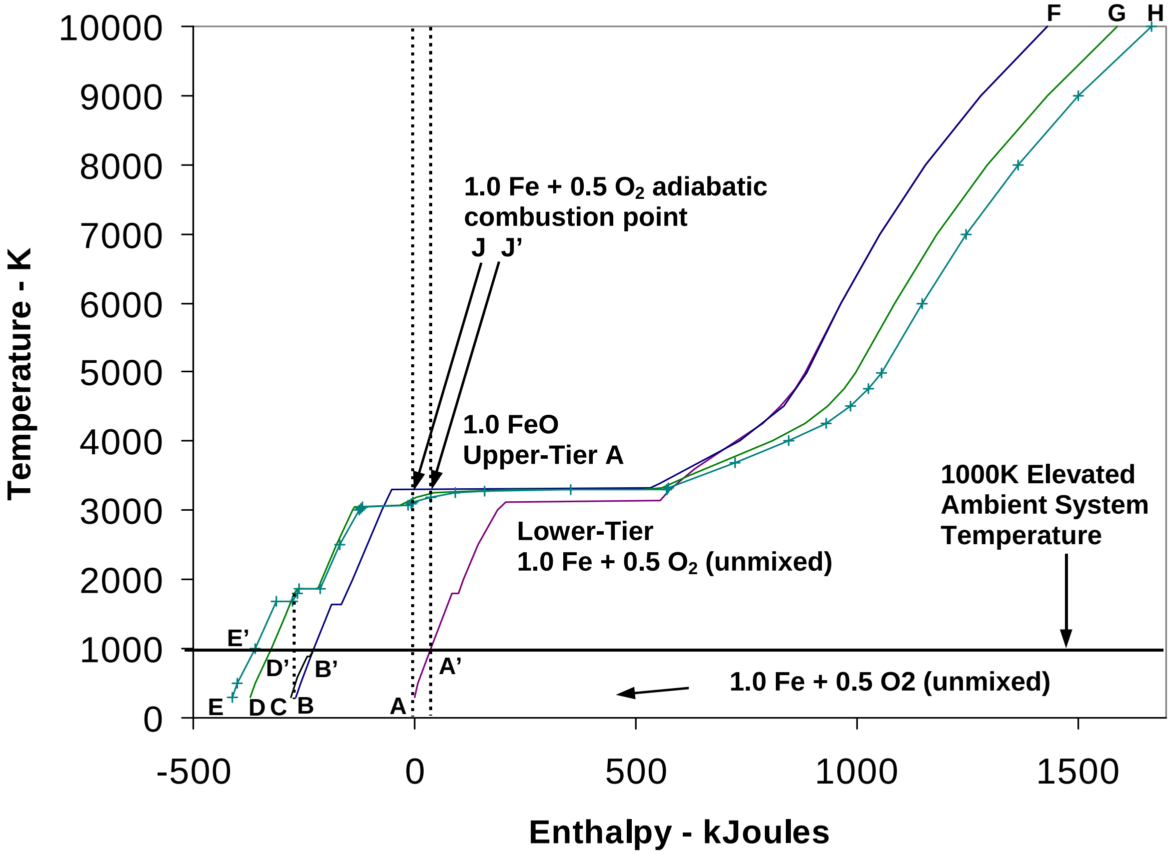

Fig. A7—*Heating/cooling of maximum composite grail results.*

even though Point J is adiabatic relative to point A.

7.3.1.5 *Nonstandard Combustion and Nonstandard Heat of Combustion*—Nonstandard combustion is when any of the initial and final standard conditions are not present, in particular when the initial and/or final temperatures or pressures are different. These data can be of interest. Indeed the initial and final temperatures/pressures may in some cases be different from each other and can still be meaningful. On Figure A7 an elevated temperature system at, say, 1000K is indicated and might have a nonstandard input condition at A', combust to J', quench to FeO at B' and the nonstandard heat of combustion would be the length of the segment between A' snd B'. In this case, but not every case, the nonstandard and standard heat of combustion/formation are nearly the same. The nonstandard adiabatic combustion temperature at point J' is about the same as the standard at point J (both about 3258 K) since both fall in the latent boiling-point transition plateau. These properties are essentially unchanged by the higher ambient temperature *but that does not mean the fire hazard risk of these two systems is the same*.

7.3.2 *Standard Heat of Formation*—The standard heat of formation is typically taken as the heat produced when elements in a standard state are converted into a specific compound in the same standard state. During combustion, a specific transition may or may not occur in

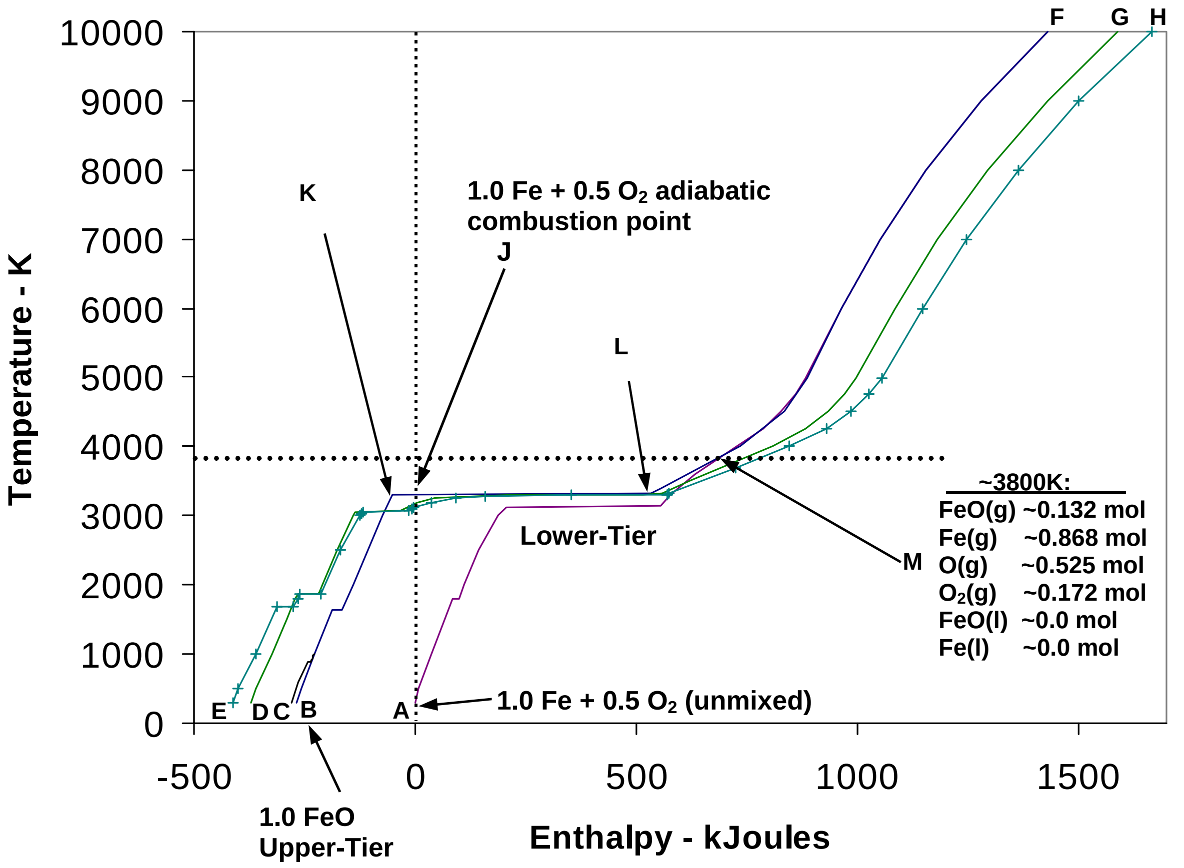

Fig. A8—*Standard and non-standard heat of dissociation interpretations.*

nature. For example when iron is combusted its slag will typically cool to form an assortment of oxides and if one seeks the heat that was produced by any one oxide, one may have to tease the result from a series of tests and mathematically infer the desired result. If one seeks the result that a test produces naturally then the heat of formation and heat of combustion are equal (the entropy of combustion and entropy of formation would also be equal).

7.3.2.1 *Nonstandard Heat of Formation*—As before, nonstandard heats of formation apply to heats determined for nonstandard initial and/or final conditions whether in terms of differing initial or final temperatures or pressures or with non standard starting or final materials.

7.3.3 *Standard Heat of Dissociation*—The dilemma of dissociation is described in paragraphs 6.2.1.4, 6.3, 6.3.1, and most especially 6.5.3. The standard heat of dissociation is often taken as the heat required to reverse an association/reaction of specific compounds when elements in a standard state have been converted into a specific compound or mixture in the same standard state. As was detailed in 6.5.3, such a transition may or may not occur in nature upon such heating. For example, in the case of Figure A8, when iron is combusted its slag will typically cool to form an assortment of oxides and if one seeks to determine the heat that was produced by any one oxide, one may have to tease the result from a series of tests and mathematically infer the desired result. If one seeks the result that a test produces naturally then the heat of formation and heat of combustion are equal (the entropy of combustion, paragraph 7.3.1.4, and entropy of formation would also be equal). As was examined in 6.5.3 for diatomic oxygen gas, a similar dissociation dilemma obtains for iron combustion. For example in Figure A8 (which repeats Figure A5 with less clutter) HSC software predictions of thermo-chemical equilibrium behavior are shown for iron and oxygen and the product FeO (or any of the slightly differing non-stoichiometric Wustite variations cited in paragraph 7.2.2.1) is shown starting at or near input point B. The standard heat of dissociation is the negative of the heat of combustion/formation and is the length of the segment between point B and point A. However, if FeO (or other wustite) at or near point B is simply heated with this heat in seeking to produce dissociation, the resulting condition is at point J, not point A as has been elaborated in footnote A3. This is irreversible in the case of iron combustion which requires additional changes to recover to point A.

7.3.3.1 *Nonstandard (In-Situ) Heat of Dissociation*

The nonstandard (meaning at nonstandard starting and/or finishing heat transfer that will produce (complete) dissociation is often of interest in other than equal temperature and pressure standard starting and finishing scenarios [A9]. For example, earlier Figure A4 (from HSC software) and paragraph 6.3.1 examined how diatomic oxygen would dissociate if the heated monatomic oxygen were either a segregated phase (latent insensible transition) from the diatomic source or fully and homogeneously mixed as would be expected (and is apparently seen) in most situations. There was substantial differences. Note that for the case of heating FeO (or other wustite), Figure A8 exhibits an even more complicated scenario. On Figure A8, principally liquid FeO is present at point K, and heating is insensible to point L while the FeO is both vaporizing and partially dissociating to point L, at which point the liquid is gone, but the FeO is not completely dissociated. Then between Point L and point M, a sensible heating results in further dissociation of the remaining FeO as a gas and at roughly point M (FeO is about 87% dissociated). Note this point is where the upper-tier curve nearly “merges” with the segregated reactants curve from point A. The nonstandard heat that is predicted to dissociate the FeO this far is the segment between points B and M, about 964 kJ/gmol-Fe, and to roughly dissociate the liquid FeO at point K is the segment between points K and M, about 736 kJ/gmol-Fe while the latent heat to partially in-situ dissociate/vaporize just the latent portion of the curve (K to L) is roughly 585 kJ/gmol-Fe and all three significantly exceed the standard heat of dissociation/formation/combustion indicated by the segment between points B and A (about ±258 kJ/gmol-Fe).

7.3.4 *Standard Heat of Transition*—Whenever a material or system change is possible that can have enthalpy or entropy effects, equilibrium analyses are a viable way to estimate the transition in the same way that they are useful to evaluate transitions produced by combustion, melting, boiling, dissociation, etc. Again a standard designation would be applied to initial and final states at an assigned temperature and variations from the standard state would be designated nonstandard transitions. Such less frequently addressed transition in-

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[A9] The role of standard versus nonstandard dissociation heating is vigorously debated in references [***1,3,4***].

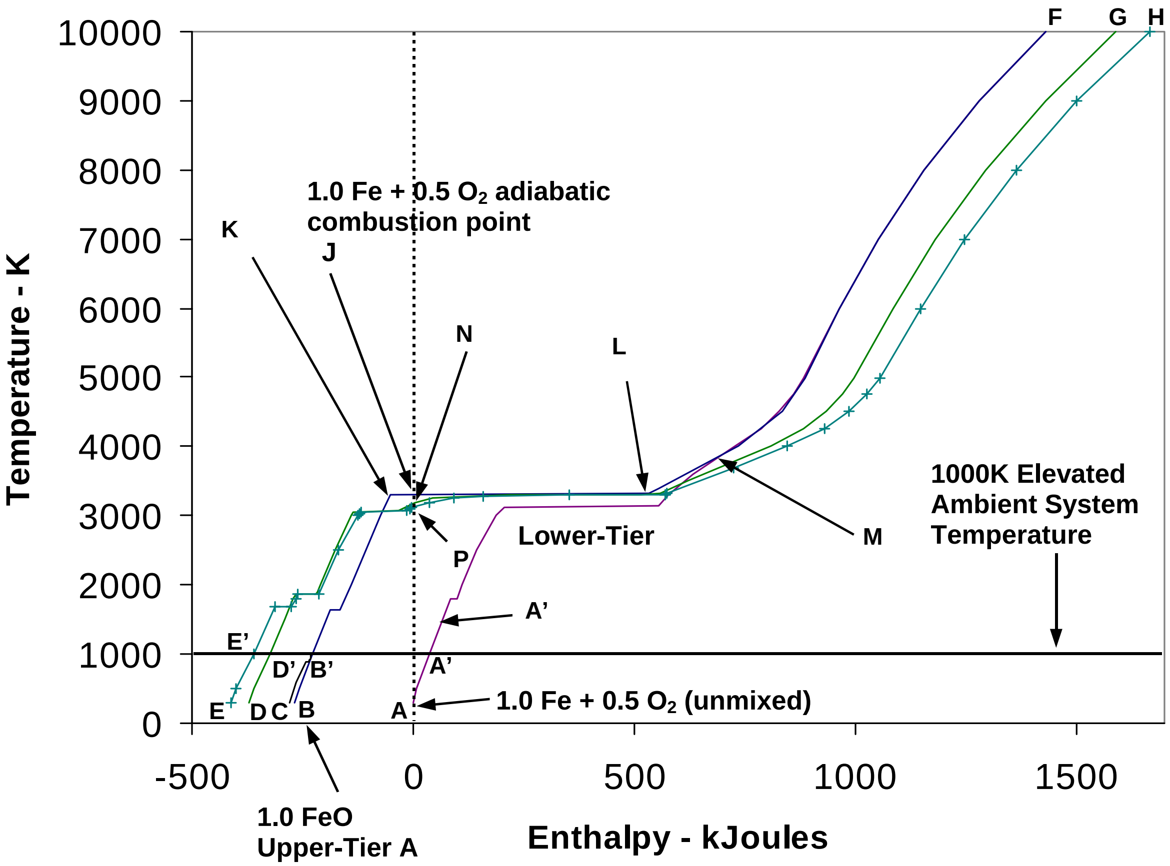

Fig. A9—*Adiabatic combustion interpretations.*

clude crystal structure changes (which tend to be of much smaller effects), sublimation (which obtains for a small number of materials, such as carbon, or special system configurations), or perhaps even some super-critical fluid situations. Transitions of pressure may also be of interest.

7.3.4.1 *Nonstandard Heat of Transition*—Nonstandard heat of transition change is when nonstandard initial of final temperatures or pressures are involved.

7.3.5 *Standard Adiabatic Combustion Temperature*—The standard adiabatic combustion temperature (paragraph 6.5.5) is the temperature that combustion produces when no external heating is applied or withdrawn (effective insulation) during combustion and the initial material temperature and both initial and final pressure are at standard values typically 298K, atmospheric pressure. As was previously examined in 7.3.1, Figure A9 (which is the same data as Figure A8 but with differing annotation) exhibits initial standard (input) conditions at point A, and combustion produces a vertical increase in temperature to the equilibrium curve at point J (about 3258K). Note that if there is oxygen beyond stoichiometric for the formation of FeO, a different adiabatic combustion temperature would obtain due to both the need to heat additional un-reacted oxygen or to form and to heat additional oxide species that might form or that might release additional reactive heat. Hence, a different adiabatic combustion temperature and composition could result.[A10] An increased oxygen presence stoichiometric to Fe_3O_4 would also originate at point A but its adiabatic combustion temperature estimate with HSC software would be as indicated vertically above at point N. A still greater Oxygen presence stoichiometric to Fe_2O_3 would once again originate at point A but its adiabatic combustion temperature estimate with HSC software would be as indicated at slightly lower point P vertically above A. Furthermore note that as described in Paragraph 6.5.5, the adiabatic combustion temperatures at these points can be calculated by introducing the respective heats of combustion (for example the heat of combustion to produce FeO indicated by the segment between points B and A are added into the curve from points B to J) and estimate the standard adiabatic combustion temperature . Similarly the heat of combustion to produce Fe_3O_4 is indicated by the segment from point D to point A are in effect added into the curve between point D and point N. And also the heat of combustion of Fe_2O_3 indicated by the segment from point E to point A are in effect added into the curve between point E and point P. The same approach applies to other mixtures of produced oxide mixtures that might lie on the segment between E and A when returned to similar curves (not shown on Figure A9) all of which would terminate at points below J.

7.3.5.1 *Nonstandard Adiabatic Combustion Temperature*—When initial temperatures and/or pressures and/or final pressure of materials are at other than standard values, combustion can produce other than standard adiabatic combustion temperatures (6.5.5.1). For example if the initial temperature at ignition of Figure A9 is increased to the point A’, then a vertical shift to the respective equilibrium curve directly above it yields the nonstandard adiabatic combustion temperature as was shown on Fig. A7 which in this case is essentially the same as it was for the standard case due to the insensible (latent plateau) temperature controlling effect of vaporizing/dissociating the liquid FeO that is present there for this example but may differ for other materials.

7.3.6 *Standard Burn Ratio*—Burn ratios (Paragraph 6.5.6) are an extension of Humphry Davy’s observations [***7***] that certain material behavior is limited by specific properties. To wit: a gaseous material that incrementally burns must transfer enough heat from the burning increment (the flame/combustion-zone) to subsequent increments to ignite them. Similarly, incrementally burning solid materials must transfer enough heat to melt or vaporize an equivalent incremental amount of material as a minimum if it is to sustain the more hazardous propagating combustion modes of the material (and perhaps combustion itself) as a liquid or gas. Heat transfer is commonly analyzed in two limiting modes; counter-current and co-current.

7.3.6.1 *Counter-Current Heat Transfer*—Traditionally, “standard” burn ratios were based upon a coarse implied maximum heat transfer in which the ratio of the entire standard heat of combustion is divided by the standard heat to melt or vaporize a material. In hazardous

[A10] The formation of ferrite ions in iron combustion would be an example of new species that may require additional heating and/or might release additional heat to yield either a higher or lower ACT but as discussed in footnote A7, there are no data to allow such calculation nor does this standard ascribe to any substantial presence.

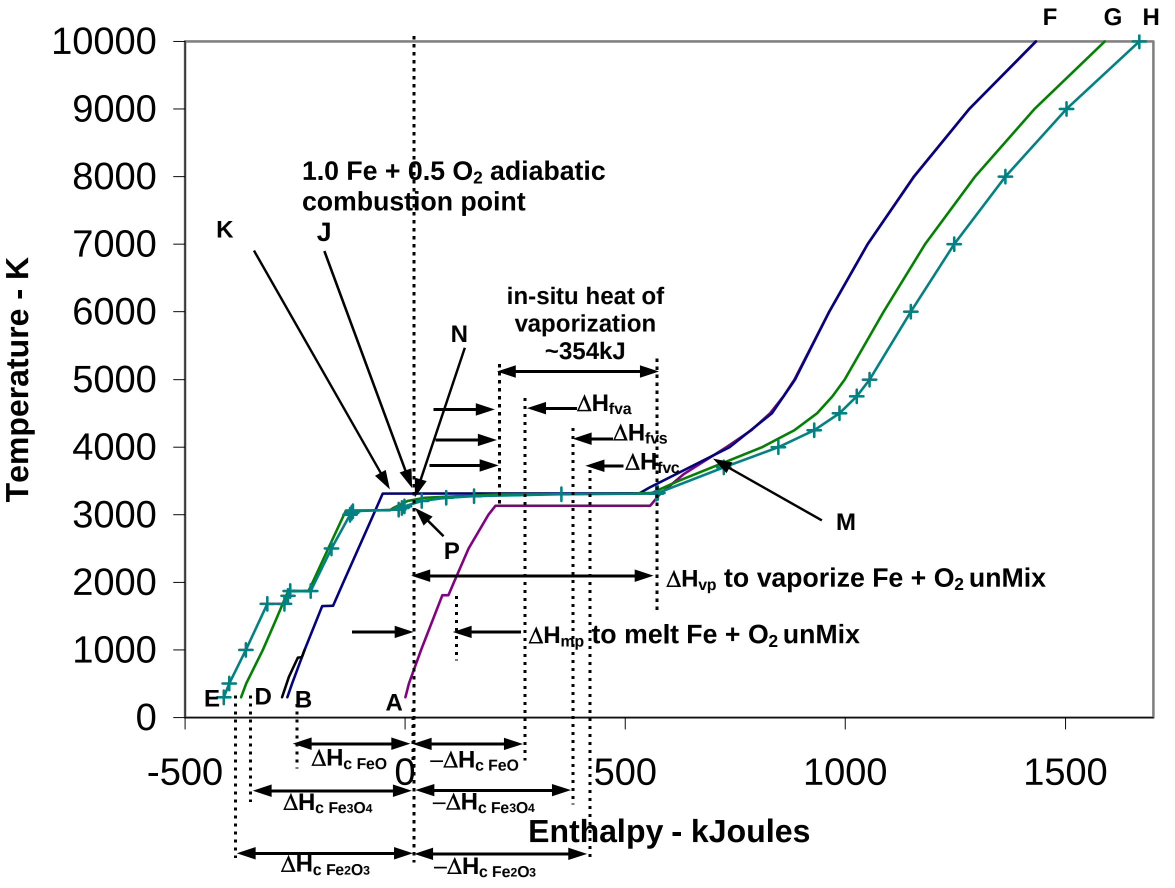

Fig. A10—*Counter-current heat transfer burn ratios.*

fires, such extensive, even complete, exchange of heat between streams is characteristic of counter-current heat exchangers, a mechanism unlikely to be seen in real-world fires where the fire front and heat transfer tend to move in the same direction. In laboratory testing counter-current heat transfer might be most like top ignition of a vertical tube such that the molten slag can flow down the inside of the tube and preheat the incremental combustion zone. Though this scenario increases combustibility and can even exhibit an accelerating combustion, the results tend to be erratic and so bottom ignition is used in testing such as by ASTM Standard G 94 [***12***]. In the case of iron, there is the problem that iron first combusts to FeO (or other similar wustite variations) with a rapid heat release but can then further combust *during cooling* to release additional heat *as the slag cools* and can react to form magnetite (Fe_3O_4) and/or hematite (Fe_2O_3) in mixtures or segregated oxides. This source of further (delayed) heating/cooling mechanisms would not tend to occur in the most hazardous (fire-front) regions of propagation of combustion wherein the slag would often tend to just drain away with little or no protracted heat transfer. This counter-current-like heat transfer mechanism would be most important to a fire hazard if it can contribute to sustain later or secondary propagation. Consequently, Figure A10 exhibits how to extract burn-ratio data for all three oxides (that include herein heat needed to warm stoichiometric oxygen for each increment):

FeO Burn Ratio at melting point: $BR_{mp} = \Delta H_c\,(FeO) / \Delta H_{mp} = \sim258/96 = \sim2.7$
Fe_3O_4 Burn Ratio at melting point: $BR_{mp} = \Delta H_c\,(Fe_3O_4)/ \Delta H_{mp} = \sim370/96$[A11] $= <\sim3.9$[A11]
Fe_2O_3 Burn Ratio at melting point: $BR_{mp} = \Delta H_c\,(Fe_2O_3)/ \Delta H_{mp} = \sim410/96$[A11] $= <\sim4.3$[A11]

FeO Burn Ratio at vaporization: $BR_{vp} = \Delta H_c\,FeO / \Delta H_{vp} = \sim258/545 = \sim0.47$
Fe_3O_4 Burn Ratio at vaporization: $BR_{vp} = \Delta H_c\,(Fe_3O_4) / \Delta H_{vp} = \sim370/545$[A11] $= <\sim0.67$[A11]
Fe_2O_3 Burn Ratio at vaporization: $BR_{vp} = \Delta H_c\,(Fe_2O_3) / \Delta H_{vp} = \sim410/545$[A11] $= <\sim0.75$[A11]

When these BR_{mp} data are greater than unity, they suggest combustion *may* occur in the liquid state, but more importantly, when they are less than unity, they are an even more persuasive suggestion that rapid sustained propagation of combustion is unlikely. When these BR_{vp} data are greater than unity, they suggest combustion *may* occur in the gas state, but more importantly, when they are less than unity, they are an even more persuasive suggestion that the even rapid (oftentimes explosive) sustained propagation of gaseous-phase combustion is unlikely to occur although in some cases a liquid phase or fractional gas phase fire may result. Figure A10 indicates the in-situ (latent) heat of vaporization of the segregated iron/oxygen materials. Note that the indicated $-\Delta H_c$ for the three oxides provides enough heat to vaporize portions of the segregated Fe/O_2, shown as $\Delta H_{fva,\ fvb,\ fvc}$ (fractional vaporization heat). This suggests that a small amount of gas-phase combustion heat (ΔH might accelerate the combustion marginally, but only a small amount of FeO powder (characteristic of gas phase combustion, should result from typical Fe combustion. Indeed FeO powder is not observed in many tests, nor does upward combustion of vertical iron rods tend to produce visible smoke, whereas known vapor-phase upward combustion, to wit; aluminum, tends to smoke and produce oxide powders that completely obscures visibility.

7.3.6.2 *Co-Current Heat Transfer*—Thermo-chemical equilibrium theory enables less conservative but in at least some cases more sophisticated, yet likely more realistic, burn-ratio parameters. These are based upon the Second Law of Thermodynamics that states basically that heat flows only *from* a higher temperature *to* a lower temperature. Heat transfer stops when temperatures equilibrate. As a result, the way in which heat transfers *from* combusting material to un-combusted material can be crucial. If slag drains away from the combustion zone as occurs in bottom ignition of rods in testing by ASTM G 94 [***12***], heat transfer from earlier combustion can be lost, or if (as in early Glassman teachings [***13***]) the adiabatic combustion temperature is less than the melting or boiling point temperature, then combustion is not likely to proceed rapidly or perhaps at all. If the heat transfer is akin to a counter-current heat exchanger (7.3.6.1, above) a maximal fraction of the heat of combustion will serve to heat incoming material. However, a more likely co-current form of transfer will transfer a smaller fraction of the combustion heat or even just a fraction of the incremental combustion heat to an incremental un-combusted region to where their temperatures equilibrate, even when adiabatic. This is a situational maximum preheating. Hence

[A11] The heat to melt, ΔH_{mp}, and the heat to vaporize, ΔH_{vp}, in this case is estimated by the somewhat smaller segregated respective values for the segregated FeO example since the segregated curves for the higher oxides are not shown on the figure. Hence the ratios are somewhat smaller than indicated.

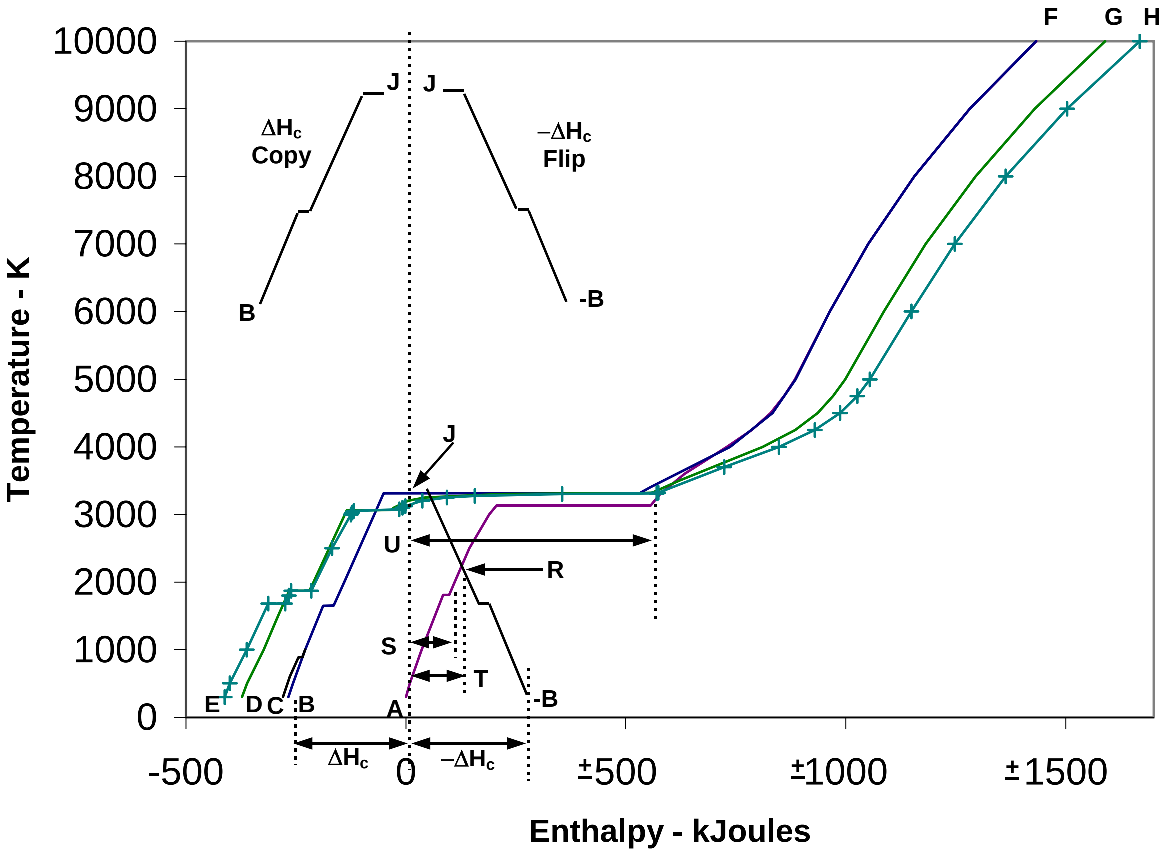

Fig. A11—*Co-current heat transfer burn ratios.*

while the standard burn ratio is an ideal (and conservative) worst case, if a more realistic co-current scenario burn ratio is less than 1.0, then propagation as a respective liquid or gas may also be not likely. However, propagation may be very unlikely even in some cases where standard burn ratios are greater than 1.0 if there are sufficient heat losses or if the heat exchange mechanism between combusting and source material are inefficient. The co-current data to estimate burn ratios for iron combusting to form FeO are exhibited on Figure A11 (with the same data of Figures A5-A9 but differing notations). The cool-down sector of the curve from points J to B exhibits the standard heat of combustion (ΔH_c) for the formation of FeO, is replicated above the curves as "**ΔH_c Copy**" and its horizontally flipped image is shown to its right as "**$-\Delta H_c$ Flip**", and then shown also on the data curves as the curve between points J and -B. This converts the region of the abscissa above a heat of zero to both positive and negative curves depending upon which curve is being read. The cool-down of the adiabatically combusted Fe is from point J to point –B while the warming curve of the segregated Fe and O_2 intersects it at point R. R is the point where the cooling slag temperature and the warming iron/oxygen temperature are equalized and is the maximum incremental co-current heating possible. The co-current burn ratios for this scenario are then:

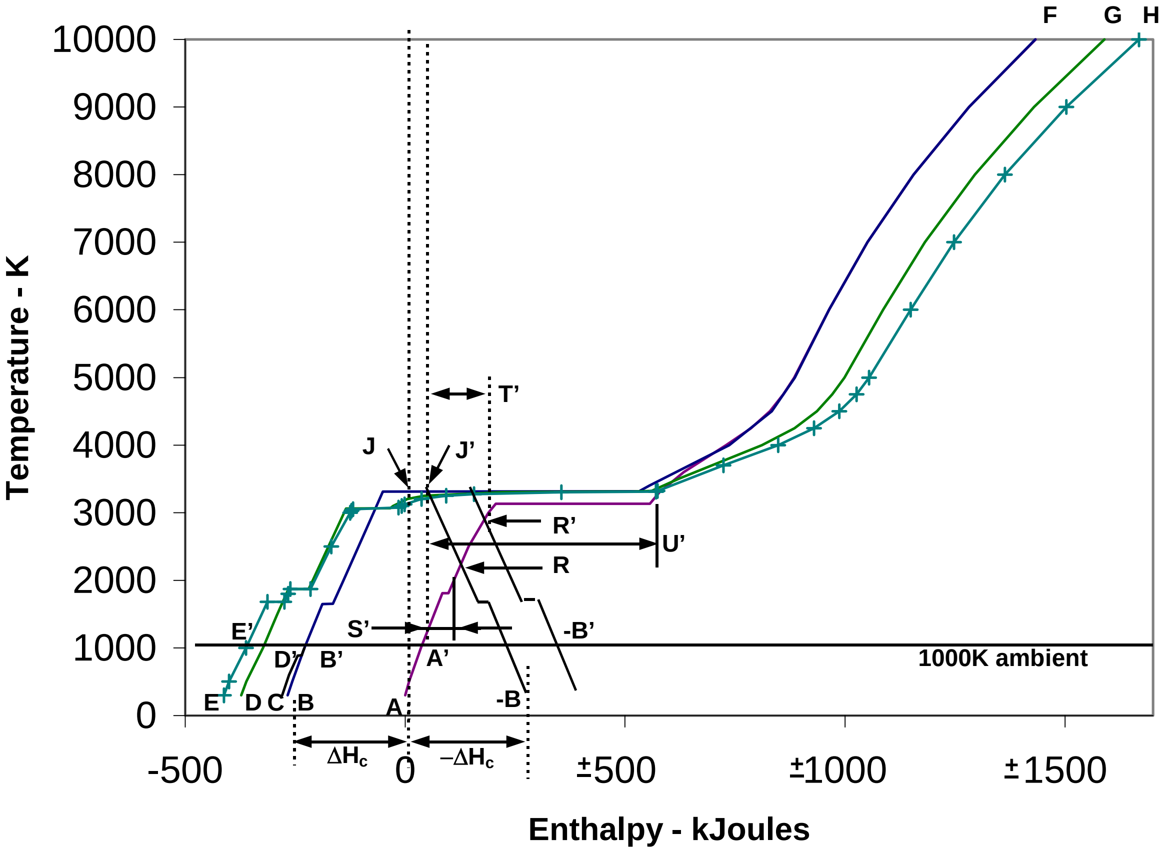

Fig. A12—*Increased ambient temperature effects.*

Burn Ratio at melting point: BR$_{mp}$ = Segment T /Segment S = ~121/96 = ~1.25

Burn Ratio at vaporization point: BR$_{vp}$ = Segment T/Segment U = ~121/554 = ~0.21

Here again, when these BR$_{mp}$ data are greater than unity, they suggest combustion *may* occur in the liquid state, but more importantly, when they are less than unity, they are an even more persuasive suggestion that rapid sustained propagation of combustion is unlikely. When these BR$_{vp}$ data are greater than unity, they suggest combustion *may* occur in the gas state, but more importantly, when they are less than unity, they are an even more persuasive suggestion that the rapid (oftentimes explosive) sustained propagation of gaseous-phase combustion is unlikely to occur although in some cases a fractional liquid phase or fractional gas phase reaction may obtain. Furthermore, the maximal heat transfer in this case does not estimate any partial vaporization of the iron that is being heated. Note that both these formulations are smaller than the counter-current burn ratios estimated in paragraph 7.3.6.1. These indicate less combustibility than for the counter-current scenario and are perhaps more consistent with actual combustion test results and real-world hazards of iron in oxygen.

7.3.6.1 *Nonstandard Burn Ratio*—Burn ratios that apply to nonstandard starting temperature and pressure and/or finishing pressure and heat transfer patterns (Paragraph 6.5.6.4) can vary greatly from the conservative standard estimates above. Figure A12 exhibits the same higher temperature ambient of Figure A7 for the systems previously examined at 300K ambient (point A) increased to 1000K (point A'). This results in the adiabatic combustion points and temperature changing from point J to point J' (which is the same temperature ACT) value due to the latent transition. The cool-down heat transfer curve changes from between point J and –B to between points J' and –B'. Hence the temperature equalization point changes from point R to point R' which is significantly greater. Although the adiabatic combustion temperature and heats of combustion for the two temperatures change by at most small amounts, the co-current heat transfer equalization changes significantly indicating why preheating causes increased combustibility. This is precisely why oxy-acetylene torch cutting of steel first preheats the metal locally before spraying oxygen onto it.

7.3.6.2 The nonstandard counter-current burn ratios corresponding to the standard burn ratios of paragraph 7.3.6.1 (p.32) are:

$$\mathrm{FeO}\ \mathrm{BR}_{mp} = \Delta H_c\ (\mathrm{FeO}) / \Delta H_{mp} = {\sim}258/61.8 = {\sim}4.2$$
$$\mathrm{Fe_3O_4}\ \mathrm{BR}_{mp} = \Delta H_c\ (\mathrm{Fe_3O_4}) / \Delta H_{mp} = {\sim}370/61.8^{A11} = <{\sim}6.0^{A11}$$
$$\mathrm{Fe_2O_3}\ \mathrm{BR}_{mp} = \Delta H_c\ (\mathrm{Fe_2O_3}) / \Delta H_{mp} = {\sim}410/61.8^{A11} = <{\sim}6.6^{A11}$$

$$\mathrm{FeO}\ \mathrm{BR}_{vp} = \Delta H_c\ \mathrm{FeO} / \Delta H_{vp} = {\sim}258/520 = {\sim}0.50$$
$$\mathrm{Fe_3O_4}\ \mathrm{BR}_{vp} = \Delta H_c\ (\mathrm{Fe_3O_4}) / \Delta H_{vp} = {\sim}370/5520^{A11} = <{\sim}0.71^{A11}$$
$$\mathrm{Fe_2O_3}\ \mathrm{BR}_{vp} = \Delta H_c\ (\mathrm{Fe_2O_3}) / \Delta H_{vp} = {\sim}410/520^{A11} = <{\sim}0.79^{A11}$$

7.3.6.3 The nonstandard co-current burn ratios corresponding to the standard burn ratios of paragraph 7.3.6.1 (p.32) are:

$$\mathrm{FeO}\ \mathrm{BR}_{mp} = \Delta H_{c\ \mathrm{FeO}} / \Delta H_{mp} = {\sim}142/55.4 = {\sim}2.6$$

$$\mathrm{FeO}\ \mathrm{BR}_{vp} = \Delta H_{c\ \mathrm{FeO}} / \Delta H_{vp} = {\sim}142/521 = {\sim}0.27$$

7.3.7 Other Parameters—Many other scenarios can be surmised and estimated. Too many to include herein. Which of them is most important in a safety regard depends on the specific circumstances. Indeed, competing material curves may differ in degree and even in shapes, yet such comparisons can often be useful to know.

8. J. Willard Gibbs's Theory of Equilibria.

8.1 Theories to predict the shapes of these curves are based upon free energy, a combination of heat energy and statistical probability. This was developed by J. Willard Gibbs for systems at constant volume (variable pressure, no mechanical work). In equilibrium, systems tend to settle into the lowest GFE (Gibbs Free Energy) possible. Systems at constant pressure (variable volume, variable work production) settle into an analogous Helmholtz Free Energy (HFE). Heating a system tends to drive up its free energy. Cooling a system tends to reduce its free energy. The free energy change is often cited as the maximum amount of mechanical work that can be extracted.

8.2 *Interferences/Complicating factors*. While free energies dictate the ultimate equilibrium states of a system, free energy minimization in nature is not instantaneous. Nor is it always rapid. Nor is it the same for all materials. Lightning fast for some materials, sometimes it is doggedly slow for other materials . Hence while there are many systems that can be rapidly heated and cooled and will reasonably closely track a curve like that of Figure one. For example: compression heating, combustion and expansion cooling in an internal combustion engine can be effected in as little as one tenth of a millisecond and yet astute thermochemical equilibrium concepts allow useful analysis, yet some constituents can be exceptional. “Frozen” equilibria (paragraphs 7.1.1, 7.1.2) is just one exceptional issue.

8.3 *Phase Issues*—The various phases of materials that form can alter the thermal profile. This is a basis for cataloging vetted thermal profiles rather than running them in real time as needed. Several analyses comment upon this issue [***1,2,14***]. As examples: whether materials mix (like gases usually do or like some but not all liquids often do) or whether they segregate (like many materials do when melting or boiling). In the case of, iron oxides at present HSC software recommends citing each oxide as a distinct separate phase. However, as an oxide like Fe_2O_3 warms when solid and changes into solid Fe_3O_4, the prospect of either random (homogeneous) mixtures of the two or segregated separate phases or regions of both homogenous and segregated oxides needs to be considered, again the reason why vetted and well-documented thermal profiles are preferred herein. In many cases, software like HSC combine phases. For example: iron solid/liquid is cataloged as a single entry in which it is assigned solid status below a melting point and liquid status above and the free energy minimization algorithm does not consider other options, but it is not impossible that some systems might alter this scenario, ...another reason for creation and use of an atlas of vetted qualified thermal profiles.

8.4 *Effect of Carbon*—Carbon has a major influence on the combustion of iron, but it is transient. This is the basis for modern production of steel. Carbon is protective of iron combustion while it is present (that is until it burns off). Indeed, in some cases of re-processing steel, steel scrap plus carbon (as coke or charcoal, etc.) is heated until molten iron is present along with dissolved carbon (as coal or other) in a vat (blast furnace) and commercial grade oxygen is sprayed directly into the melt, something that is not recommended in oxygen system design ethics. However, the slower-burning carbon prevents the iron from reacting with the oxygen, ...while the carbon is burning off instead. Typically the molten iron is periodically tested until the carbon falls to a desired level to meet a specification for steel. And then the oxygen flow is interrupted. The steel production is done. If the oxygen flow were to continue after all of the protective carbon were consumed, the molten iron would abruptly become a very potent destructive fuel and a very intense combustion mode might obtain. Other examples of protective performance of other metals are less well documented.

8.5 *Excess Oxygen*—In the case of iron and some other metals, the molten oxide slags have been postulated and experimental data are published to argue it absorbs large amounts of "excess oxygen" [oxygen well in excess of what is needed to form the viable oxide in the form of complex "ferrite ions" (of form $FeO_n^{n-}x$ where n is speculated to be at least as large as 7) [9]. The lack of thermodynamic data for these ions has been cited as a disqualifier of thermo-chemical equilibrium data [2] for use in material combustion analyses, and has discouraged such standardization use for several decades. The experimental results are disputed [10,15] as to the scale of any such ion presence perhaps even to the point of insignificance as a major factor in the origins of this draft standard proposal.

8.6 *Strong Ignition*—In combustion testing, materials that are not in ultimate thermodynamic equilibrium (for example, iron and oxygen), can be triggered into a combustion that shifts them closer to equilibrium. Typically in the laboratory, this involves "ignition" with a heat source. The heat source locally raises the temperature of the reactants to where they can combine spontaneously into different compounds and if there is a concomitant release of heat of sufficient scale the ignition may set up a propagating conversion of iron into oxides. Such propagation may be transient and the propagation may proceed until the temperature falls below a threshold value needed to sustain. Conversely, the propagation may accelerate if the transient propagation releases enough heat to more than offset any local or systemic losses. And finally, the propagation may settle into a constant "equilibrium combustion" that may consume the entire iron source, yet may be fragile and extinguish if it encounters an upset or disruption of various kinds. The strong ignition literally locally lowers the threshold for combustion that then "coasts" to its ultimate condition. The stronger the ignition, the further a transient combustion tends to proceed. A combustion that is ultimately unable to sustain, may proceed before achieving its ultimate status. Hence industry practice is often to use strong ignition so that transient combustion can more readily settle into a equilibrium final state. This is because during the chaos of weak ignition materials especially when near their equilibrium thresholds may "stumble", fluctuate or encounter a local variation and fail to sustain propagation (be false negative results) even though brief some transient sustained combustion may be possible.

8.7 *Combustion Hazard Modes*—The hazard of combustion is largely due to the undesired transfer of enthalpy (heat, whether transient, equilibrium propagating, or accelerating in combustion) that damages system components, damages or ignites area materials, or injures or takes life. For the most part, the rate of release of the enthalpy transfer is important. Small and slow enthalpy release tends to be much less hazardous than large and fast energy release (the worst of which we call explosions). To a large extent, combustion that is (a) slow (charcoal burning in air), is less hazardous than combustion that can (b) melt and spread a fuel material and increase the accessibility of the oxygen to the fuel, which is in turn less hazardous than (c) combustion that is capable of vaporizing a material and makes the accessibility of the oxygen to the produced gaseous fuel still greater, which is again in turn less hazardous than combustion that occurs in scenarios where (d) the oxygen and the materials are natively more homogeneous or even completely homogeneous (mixtures of fuel particles with oxygen liquid oxidant, or even nitrated chemicals). These latter cases are often classed as "high explosives'. In these cases system specifics can be crucial. Organic molecules that combust to produce gases tend to be more hazardous the closer their compositions are to stoichiometric and the more favorably their atomic arrangements are. However, in the case of mixtures of fine-structured materials, for example aluminum in liquid oxygen that can combust to produce liquid products, extra liquid oxygen can exacerbate the hazard of a resulting explosion by producing left-over gases at high pressure and high temperature. In comparison materials like thermite (one example: aluminum fines mixed with stoichiometric iron oxide fines) produces no gases and despite large transfer of enthalpy may produce little or no pressure damage but can produce extensive heat damage.

8.8 *Local TCE Points*—Although FeO is not stable and by HSC estimates seeks to reform into Fe and Fe_3O_4 (or even Fe_2O_3) albeit quite slowly, glacially, in many scenarios, may reflect effective equilibrium. In other systems, variations in local properties such as differing temperature pressure, mixture compositions) differing equilibria may be simultaneously present, all of which may be in equilibrium in a local region.

8.9 *Supercritical Fluids*—Supercritical fluid (SCF) can form at elevated pressures whereat neither a traditional gas or liquid is present but rather an intermediate fluid obtains that has some but not all of the properties of both a gas and a liquid. The implications of this form of matter may be substantial, however supercritical regimes are not present in most, oxidant systems with the possible exception of nitrous oxide. Addressing SCF thermo-chemical equilibrium may require definition of new parameters to split the “boiling point” and heat of vaporization with analogs for the transition from liquid to SCF (akin to boiling point and heat of vaporization) with parameters for the temperature transition from liquid to SCF and the presumably latent heat associated with it, as well as, for the transition from SCF to gas (also akin to boiling point and heat of vaporization). And TCE mathematics may then use the specific heats of the SCF and these numbers in its estimates. The ability of current TCE software to cope with supercritical fluids is not clear.

8.10 *Counterintuitive Entropy Effects*—It is known that some materials (hypergolic) will spontaneously react/combust upon contact and that others may do so if inspired with a suitable ignition source, it is also known that the free energy analysis can also produce a spontaneously cooling reaction upon contact when the entropy changes possible are more important than potential heating changes.

9. Practicality and Quality Issues.

9.1 *Practicality*—This proposed draft standard seeks to dissuade casual generation of TCE data but is thoroughly in favor of cautiously vetted, annotated and cataloged thermal profiles. The basis for this is both in practicality and validity. Such data appear to be highly valuable when suitably qualified, verified and tutored. However, errors have proven far too easy to obtain and have resulted from even highly learned early uses of this technology. Furthermore, even the less challenging extraction of parameters from thermal profiles are best implemented with “reader” software that allows a cross-hair to be placed on data points on the profiles and then calculates the desired parameters and reports them. This standard seeks to demonstrate selected practical value to these data. the degree of limitation is undetermined. Similarly the degree of quality will need study in realistic applications. Finally, the authorship of this first draft is by a less than optimally student of the underlying theory and may reveal flaws in future appraisals.

9.2 *Quality*—There has been little to no enthusiasm within the oxidant safety community to employing TCE approaches to estimating fire behaviors. Hence putative "customers" and customer expectations for this approach have been absent. This effort to codify methodology may or may not affect those negative expectations.

10. Precision and Bias—Although there are numerous numerical measures that can be determined with this theory and the resulting software, possible and necessary measures of precision and bias will need to be established by actual usage and so this must be considered a "provisional" draft standard proposal until that is achieved.

11. Correction, Evolution and Revision—As this draft has not been subjected to study, errors have not been identified even if present in large amounts. Similarly its age is too young for evolution and revision to be contemplated.

12. Keywords—TBD

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