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A Comparison of CEA and HSC Software for Oxidant Safety Thermo/Equilibrium Analysis [2]

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ABSTRACT: NASA CEA (ne Gordon-McBride code) and Outokumpu HSC software codes are overviewed and compared for weaknesses and strengths. Various techniques are reviewed that allow similar results from either code that may yield important insight into oxidant safety. Thermo portraits for iron, aluminum and carbon are compared. A collaborative approach to validating such theoretical data is recommended.

KEY WORDS: thermochemistry, thermo portrait, iron combustion, aluminum combustion, carbon combustion, CEA, Gordon-McBride, Coefficients and Properties (CAP), Outokumpu HSC, EQS4WIN, Cequel.

The fire safety of oxidant handling systems has been predominantly addressed with coarse conservative and largely elementary techniques. Estimates of thermodynamic and explosive effects have typically assumed a material's full heat of combustion would be transferred (released as explosive energy), even though complete combustion (especially in the instant of an explosion) is a rarity. Similarly, ideal gas behavior has been typically assumed even though few gases are perfectly ideal. However, today powerful and "convenient" software allows both real-gas and equilibrium effects to be considered in some cases with much less effort than in the past and by a wider audience. Such mathematical techniques and related software were first developed and are most mature and robust for doing uniformly mixed gas phase combustion analysis, but today can go further than that.

The writer has recently published his first analysis of the thermo/equilibrium behavior of iron in ideal oxygen and was so impressed with the results, even if flawed, that he feels similar analysis would be worthwhile and that it would be desirable to have similar thermo/equilibrium portraits available for many other materials as well.

With substantial difficulty, the writer used the free NASA software: Chemical Equilibrium with Applications (CEA — the former versions often called Gordon/McBride code, or CAP [Coefficients and Properties] among other titles). However, despite its power and comparative convenience (compared to manual calculations) this software was still far from

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easy to use and often failed to converge to a result amongst numerous other problems encountered. Extracting results for the theoretical equilibrium states of iron and oxygen was still a considerable labor. In a follow-up effort to examine aluminum and oxygen, it became virtually impossible for this analyst to tease desired results from the software. In an effort to find a more robust alternative, the writer considered other software codes: Outukumpu HSC (a rather pricey package more so since its most recent expansion into much more involved process-stream analysis), EQS4WIN (a much older apparently Visual Basic program of more moderate price), and several others of a still more pricey nature.

Clearly the open source NASA software enjoys the best prospect of widespread use in the oxygen safety community, if for no other reason than its free access to everyone. However, it is also a time honored program. It began decades ago.

This effort is principally intended to compare the CEA and HSC codes for one type of analysis only: namely for generating extremum themochemical “portraits” of materials and oxidants in combustion. The strengths and weaknesses of each for the new user or users (like the writer) with less than advanced degrees in thermochemical methods were of main interest. A competitive copy of the EQS4WIN code could not be obtained for unknown reasons, but a free demonstration copy of limited capabilities was available and some limited comparison to it will also be possible.

Both codes address multiple types of calculations, but this comparison considers only chemical equilibria and thermodynamics important to worst-case combustion processes.

Tactics prescribed for use with HSC were found to also facilitate much more compliant behavior from the CEA code though both still have their quirks and operate quite differently. Data related to very similar calculations were very similar for both codes. Each software package had its own strengths and weaknesses. However, overall, the promise of this theory and software is both impressive and compelling, and the writer hopes and recommends that a much greater and even major role be played by these data and analysis in the future. This paper focuses on the relative merits of HSC and CEA, but further papers are planned to promote, expand, and defend their use and this recommendation.

CEA (Gordon/McBride) Code

The NASA CEA code is a Fortran IV command-line program available free from the NASA Glenn (formerly NASA Lewis) website as a download. It is apparently (although the writer has not been able to verify this) open source, hence the actual source code may be available so that users can modify it if so inclined. Versions for both Windows and Unix/ Linux are available. However, the download also contains a compiled version of the code ready to run after extracting several support files. The writer has yet to explore the Linux version (but is marginally Linux-able and may do so in the future). The Windows version does not “install” and thus there are no modifications made to the Windows Registry and so it should be relatively robust for operation in the various versions of Windows out there and could probably even be run off a disk, cdrom or USB key and conveniently transported from system to system, a significant benefit.

CEA will perform chemical equilibria calculations based on ideal gases behavior and the user can specify temperature and pressure (TP mode), enthalpy and pressure (HP mode), entropy and pressure (SP mode), volume and temperature (VT mode), volume and internal energy (VE mode), entropy and volume (SV mode), or alternatively, rocket chamber combustion conditions, combustion in incident or reflected shock waves, or combustion in Chapman-Jouguet detonations can be explored. Most of the computation modes could be of interest to assorted oxygen system safety analysis, however this analysis will focus only on equilibria of materials (mostly the metals, iron and aluminum, but also carbon) in oxygen for which the enthalpy, ambient initial pressure, temperature, and composition are known (this is the enthalpy/pressure, or HP, mode in CEA). However, since adiabatic combustion temperatures are typically estimated by assuming the heat of combustion is transferred into known or assumed combustion products, one can, with possible apparent exceptions, sometimes work backwards with this mode by "declaring" the products are the initial condition and then adding heat to them.

The principal resource for use of the CEA code is the *NASA Reference Publication 1311, Computer Program for Calculations of Complex Chemical Equilibrium Compositions and Applications, Part I. Analysis* (October 1994) and *Part II. Users Manual and Program Description* (June 1996) [***1,2***][2]. Both are available as free portable document format downloads from the NASA web site.

The writer is aware of only a few papers published in the ASTM G4 collegium employing the CEA code or its predecessors [***3-6***]. All have typically also employed the HP (specified enthalpy and pressure) or rarely the TP (specified temperature and pressure) facilities, but there may have been some misinterpretation of the output results [***7***].

Appendix 1 exhibits the specific steps that were used with the software to generate equilibria for metal element reactions with supplemental heat or heat losses. CEA seems quite powerful for this purpose.

HSC for Windows 3.0

Outokumpu HSC Chemistry for Windows 3.0 (this is the 3.0 version of HSC not the version for Windows 3.0) is chemical reaction and equilibrium software from Outokumpu Research Oy. This program carries copyrights as early as 1974, but it apparently first became available for PC/Windows use in the early 1990s (likely when Microsoft introduced its Visual Basic Windows programming language). HSC Version 3.0 was introduced in the later 1990s (the manual carries a April 30, 1997 date) and, although this is the writer's speculation, may be written in Microsoft Visual Basic, perhaps VB 4.0, the first 32 bit Visual Basic version.

HSC 3.0 will calculate reaction equations, heat and material balances, equilibrium compositions, electrochemical cell equilibria, formula weights, phase stability diagrams, and Eh-pH diagrams. Hence it has some worthwhile capabilities that CEA lacks and lacks other capabilities that CEA provides. Hence they are not fully interchangeable. Combustion and thermo data of interest to this paper are obtained with the equilibrium-composition facility. This facility appears to be equivalent to the CEA TP mode of calculation (adiabatic reaction temperature is specified rather than added-heat as in the CEA HP mode), but no effort was made to directly compare the two TP modes, since the HP mode offered other benefits that were desired.

The principal reference for HSC is the users manual (April 30 1997) [***8***] . Within the writer's knowledge only a few papers have appeared in the ASTM G4 collegium that em-

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

ployed this software or an earlier version 2.0 [***9,10***] but none of them addressed equilibrium issues.

Currently (2010) Outokumpu is marketing Version 6.0 of this software which is a major (and expensive) revision targeted for chemical process use in which the user can specify a chemical reaction and then alter the parameters of the reactants and automatically pass the data from the first calculation into a second third and forth reaction step to simulate the behavior of a complex plant as the process streams move from reactor to reactor. Although analogous multiple-step combustion is also a distinct possibility (and the writer attempted a very humble first step in his earlier effort), this approach has clearly not been employed in oxidant system safety analysis literature to any great extent to date. At present, HSC is priced at about $2000 dollars (US), and is apparently about three times the cost of its earlier versions which, unfortunately, are no longer available.

HSC Version 3.0 does a full windows install with all the complexities and conflicts that that can entail due to modifications to the Windows Registry and the placement of support files in various scattered directories of the computer. The writer used a copy installed without problem on a Windows XP system, but is aware that other XP systems have been incompatible with this version of HSC, and this is a serious shortcoming in the software from the writer's perspective. If HSC is indeed a VB program, there are known potential conflicts that can occur with Visual Basic programs (and presumably other programming languages also) and at least some depend upon the base of installed support files in a computer. However, at least some (maybe all) VB programs can be written that do not "install" (as is the case for the ASTM Committee G4 computational utility "G4Math12.exe" which is a VB Version 3.0 program) and could have far better compatibility among the various generations of Windows Operating systems. However, the full install procedure does tend to restrict the use of the software to a single machine and may be considered an important commercial aid to license enforcement by the author.

Appendix 2 exhibits the steps that were used with the software to generate the promised thermal portraits for metal element reactions with supplemental heat or heat losses. The writer finds HSC to be less powerful for this specific purpose than CEA in some key regards and more powerful in other regards, however, it did prove more robust in generating most results.

Other Software Options

EQS4WIN

A paper dealing with gas phase fire limits [***11***] reports data generated with the thermochemical program EQS4WIN from Mathtrek. The writer sought to obtain a copy of this program for comparison. He was not successful. Mathtrek does have a web site, and on it they have a free demonstration Version 1.0 that is limited in what it can do to reactions involving up to five species (several short of what Fe/O_2 combustion would apparently involve).

The Version 1.0 appears to be a Visual Basic 3.0 program. It successfully installed into a Windows XP computer and ran. However, as for HSC, the install is again a disadvantage. This program employs a different approach to presenting the data, however, the Version 1.0 could not accommodate sufficient numbers of species to perform an analysis for iron and oxygen combustion.

Factsage

Factsage is code that can be found with an Internet search that is claimed to be more powerful than HSC but may be in the “If you have to ask what it costs?” category.

Cequel

This program is described by Kuo [***12***] as a modified version of CEA but with facilities to adjust for certain real gas behavior and to aid in transfer of results to Excel spreadsheet use. It is currently (2010) listed as a $1200 package on the Software and Engineering Associates, Inc.. web site (www.seainc.com).

Stanjan

Stanjan is a Stanford University program written by William C. Reynolds, and apparently the author has died and the program is no longer being distributed.

Others

Kuo [***12***] also mentions codes named BLAKE and others which are cited with licensing issues but some may also be classified. Indeed, many chemical companies write and maintain their own proprietary thermochemistry software and little information is available for any of them.

Operations and Results for HSC and CEA

Equilibria Calculations

The theory of calculations of equilibrium combustion conditions (as for other chemical reactions) are described in Glassman [***13***] and Kuo [***12***]. Most, but not all, methods involve determining when the Gibbs Free Energy of a system is a minimum (or equivalent criteria), since that is the condition that uniform combustion will theoretically seek. Typically, a large series of nonlinear equations is set up for estimating the Gibbs Free Energy (GFE) of a mixture of potential reactants and products. The number of equations is typically so large and has so many dependent variables interspersed that a closed expression for the GFE (a single equation in which the GFE is not a function of itself) is not possible, hence one can not take a derivative and solve for an extremum condition by simply setting it to zero. Instead numerical methods are used to perform repeated calculations for astute guesses that are then narrowed in (converged) to locate the minimum and therefore the equilibrium. Sometimes the variations used do not lead to a meaningful result (they do not converge), even when there is a valid result possible.

Setting up the pertinent equations requires thermodynamic data for every potential constituent including heat capacity, latent heats (of transformation, melting, boiling, decomposition, etc.) etc. Both CEA and HSC cite large database files containing thousands of thermodynamic property data for potential materials of interest. JANAF data are typically included and are major players. These tables and their accuracy are crucial to the equilibria that are estimated. To make the calculation viable some of the data must be in a compact format and as such are typically curve fitted equations based on either experimental or theoretical data.

Equilibria calculated in this way can yield precise results yet can be grossly inaccurate. The final result is no more valid than the initial speculations as to the potential materials that may be present at the equilibrium point, the property data provided for each, and other unique considerations, and the way the materials behave .

Kinetics (the speed with which compounds form and modify) can be critical. In some cases equilibia can take long periods of time to obtain, and in real world combustion reactions (which are often fast) the time may not be available. And in some practical systems, the kinetics can even express in a way to effectively thwart combustion. For example there are industry practices [***14, 15***] for employing the low-level dilution (literally near trace levels) of oxygen with argon to provide a kinetic barrier against combustion and allow the safe use of aluminum in applications where the basic thermochemistry would incorrectly suggest the hazard could be extreme. Indeed as will be reviewed in more detail later, often a small amount of argon is needed in the equations to facilitate calculations when, in fact, in real systems, the same low-level presence of argon might fully thwart combustion in a real system. Hence, when thermochemical calculations predict combustion, they may be in complete error, however, when they predict combustion is not possible, they may be much more reliable.

Similarly, equilibria once established in a real combusting system can be slow to adjust to changing conditions such as heat loss and cooling. In this case, “frozen” equilibra can obtain. A classic combustion example of this is in the formation of nitric oxide in internal combustion engines. Nitric oxide is quick to form at high temperatures but comparatively slow to decompose or react during cool down. Hence, in an engine in which the expanding piston quickly and adiabatically cools the combustion products, nitric oxide is often trapped (quenched) at its high temperature equilibrium concentrations. Hence low temperature equilibria calculations that seek to reflect combustion during cool down will be in error and the writer (who is still on a learning curve) has not yet found a simple way (if one exists) to “freeze” or lock-in a fixed amount of a product in either the HSC or the CEA software.

The same effect is common in metal equilibria testing. Many metal equilibrium concentrations are measured by soaking the metals and/or their oxides in oxygen for long periods then quickly cooling, quenching, them to trap the equilibrium composition and allow later chemical analysis. In the case of iron combustion, it is relatively easy to burn iron to produce a high temperature $Fe_{0.947}O$ (wustite, a eutectic composition) product and then cool it to produce room temperature wustite even though wustite is *not* the equilibrium composition at room temperature, nor does it revert at much less than glacial speed.

As a result both CEA and HSC begin by searching their data libraries for every potential compound that could be formed. This tends to be every constituent atom as well as every binary, ternary, quaternary and so forth permutations that could conceivably form if the molecule were separated into its most basic atomic constituents and then reformed in every potential random way. For example, carbon dioxide would be taken as one carbon atom and two oxygen atoms that might form carbon, atomic oxygen, diatomic oxygen, carbon monoxide or carbon dioxide. However, if there were many carbon dioxide molecules present, one could also speculate on the formation of molecules such as C_2, C_3, C_4, C_5, C_6, O_3, O_4, O_5, O_6, CO_3, CO_4, CO_5, and C_2O, C_3O, C_4O, etc. And if one were to list such molecules whether they existed or not into the thermo libraries, these programs would estimate how much of them would be present at equilibrium, *as if they existed whether they do or not*.

For example solid carbon is often a product of combustion and is known to exist in several allotropic forms: diamond, graphite, and "fullerenes" of which "bucky balls" (spherical molecules of structure similar to soccer balls that would correspond to the molecular designation C_{60}, and which have been found in the fuel-rich combustion of organic materials, the latter molecules of which were not discovered until the 1980s). It does not appear any of the programs take these latter variations into consideration as yet, and, indeed, their thermodynamic differences may not be known nor significant. However, HSC does report testing for C_2, C_3, C_4, and C_5.

Furthermore, there can be isomeric possibilities for a given stoichiometry (e.g. ortho- and para–hydrogen) and fractional stoichiometries (e.g. $Fe_{0.947}O$, $FeO_{1.056}$) that might be significant.

In some cases, extraneous possibilities are no concern because the thermo data would result in a calculation of a negligible presence of them at equilibrium (no harm, no foul), but depending upon the specific thermo data, the results could also be thrown way off.

Furthermore, earlier examination of CEA results for iron by the writer [7], infers that transient combustion can be sustained in a way that may produce an apparent (but false) elevation of the heat of combustion, in the form of an elevated preheated *in-situ* heat of combustion. This too can affect results.

Both programs assume the largest possible number of potential participants, and as a result both programs require the user to provide the final say. The user can add data to the libraries, or during the actual calculation the user can select species to exclude from the calculation or to add to the calculation. If the user gets the list of potential materials correct, the results are thought to be fairly valid, if approximate. If not, the results can be a pure fiction.

For these reasons, the writer feels that within the oxidant safety community, these calculations are perhaps best done collaboratively to prepare discrete portraits of the materials and that then the portraits should be assessed, validated ("peer reviewed") and revised for likely use by others and they should weight and flag any missing or fictitious or kinetic or frozen equilibia problems or otherwise problematic aspects.

Iron Combustion

Example Fictitious Results for Iron

The thermo library for the HSC program that was examined is significantly larger than for the CEA program. For example when specifying the combustion of iron in oxygen, Table 1 exhibits the product materials that might be present according to both programs (and EQS4WIN Version 1.0). The list for HSC is larger, and this apparently gives HSC more flexibility, however, not all of these are meaningful. HSC lists data extracted from numerous sources, and as such, in some cases the results may not always be reported as precisely as needed and there may be errors in the properties. The table displays only three potential phases (g,l,s) for EQS4WIN but multiple solution phases are also possible for this software and for HSC.

For example, HSC tabulates $Fe_{0.947}O$ and its chemical equivalent $FeO_{1.056}$, apparently because there are data in the literature reported for both of these. These are not isomers, they

TABLE 1—*Iron/Oxygen Species in CEA, HSC, and EQS4WIN Thermo Tables (Ignoring ionization)*

	CEA	**HSC**	**EQ4WIN**
Gases:			
	Fe	Fe	Fe
	FeO	FeO	FeO
	O	O	O
	O_2	O_2	O_2
	O_3	O_3	O_3
Liquids:			
	Fe(l)	Fe	Fe(l)
	$Fe_{0.947}O$(l)	$Fe_{0.947}O$	$Fe_{0.947}O$
	—	FeO	FeO
	—	$FeO_{1.056}$	—
	—	$FeO_{1.5}$ (W)	—
	Fe_3O_4	Fe_3O_4	?
	—	Fe_3O_4 (H)	—
Solids:			
	Fe(a)	Fe	Fe, α
	Fe(b)	Fe	Fe, β
	Fe(d)	Fe	Fe, δ
	—	$Fe_{0.945}O$	—
	$Fe_{0.947}O$ (cr)	$Fe_{0.947}O$	$Fe_{0.947}O$
	—	FeO	FeO
	—	$FeO_{1.056}$	—
	—	$FeO_{1.5}$ (W)	—
	Fe_2O_3 (cr)	Fe_2O_3	Fe_2O_3
	—	Fe_2O_3 (H)	—
	Fe_3O_4 (cr)	Fe_3O_4	Fe_3O_4
	—	Fe_3O_4 (H)	—

1

are merely slightly different amounts of the exact same material (1.056 moles of $Fe_{0.947}O$ is theoretically identical to one mole of $FeO_{1.056}$, just as 0.947 moles of $FeO_{1.056}$ is identical to one mole of $Fe_{0.947}O$). However, the properties listed in the tables, as for many other chemi-

TABLE 2—*Iron/Oxygen Combustion Calculations from CEA, HSC*[a]*.*
(Including fictitious oxide products)

	A	**B**	**C**	**D**	**E**	**F**	**G**
	CEA[a]	**CEA**[a]	**HSC 3.0**[a]	**HSC 3.0**[a]	**HSC 3.0**[a]	**HSC 3.0**[a]	**HSC 3.0**[a]
ACT[b]**—K**	3389.73	3440.68	3420.89	3469.79	3420.89	3416.52	3538.52
Mole Fractions:							
Fe (g)[c]	0.04668[e]	0.05309[e]	0.04722	0.05381	0.04722	0.05126	0.03957
O (g)[c]	0.01597[e]	0.01827[e]	0.01697	0.01942	0.01697	0.01666	0.01759
O_2 (g)[c]	0.01862[e]	0.02033[e]	0.01837	0.02014	0.01837	0.01747	0.1370
FeO (g)[c]	0.01899[e]	excluded	0.01818	excluded	0.01818	0.01905	0.01174
$Fe_{0.947}O$ (l)[c]	0.89974[e]	0.90830[e]	0.89926	0.90662	excluded	excluded	0.45852
$Fe_{0.94701}O$ (l)[c]	N/A[f]	N/A[f]	excluded	excluded	0.89926	excluded	0.45852
$FeO_{1.05601}$ (l)[c]	N/A[f]	N/A[f]	excluded	excluded	excluded	0.89556	excluded
Moles:							
Fe (g)[d]	0.04803	0.05489	0.04862[g]	0.05669[g]	0.04862[g]	0.05026[g]	0.04062[g]
O (g)[d]	0.01643	0.01889	0.01747[g]	0.02010[g]	0.01747[g]	0.01633[g]	0.01843[g]
O_2 (g)[d]	0.01916	0.02102	0.1892[g]	0.02084[g]	0.01892[g]	0.01713[g]	0.01406[g]
FeO (g)[d]	0.01954	excluded	0.1872[g]	excluded	0.01872[g]	0.01868[g]	0.01205[g]
$Fe_{0.947}O$ (l)[d]	0.92572	0.93907	0.92597[g]	0.93822[g]	excluded	excluded	0.47070[g]
$Fe_{0.94701}O$ (l)[d]	N/A[f]	N/A[f]	excluded	excluded	0.92597[g]	excluded	0.47070[g]
$FeO_{1.05601}$ (l)[d]	N/A[f]	N/A[f]	excluded	excluded	excluded	0.87806[g]	excluded

[a] All results for rxn of 0.947 moles Fe with 0.5 moles O_2 (stoichiometric for 1.0 moles $Fe_{0.947}O$, 0.947 moles $FeO_{1.056}$).
[b] ACT– Adiabatic Combustion Temperature.
[c] All results are relative mole fractions of combined gas, liquid and solid products.
[d] All results are relative moles of combined gas, liquid and solid products.
[e] Raw result from CEA software
[f] N/A—Not an available product in CEA software
[g] Raw result from HSC software.

cally identical pairs, are not necessarily consistent with identical materials, because the experimental errors of different experimentalists often produce different results. Table 2 exhibits equilibria results from CEA and HSC for a series of contrived calculations, including chemically identical pairs of products.

For the calculations of Table 2, two fictitious oxides were added to the HSC user tables. One was a wustite, called $Fe_{0.94701}O$, with a trivial difference in stoichiometry (for identification purposes only), but with the identical properties of the existing $Fe_{0.947}O$ entry copied and pasted from the HSC tables. The other was a corresponding fictitious identical oxide, $FeO_{1.05601}$ with properties "corresponding" to $Fe_{0.947}O$, namely, since one mole of $FeO_{1.05601}$ is chemically identical to both 1.056 moles of $Fe_{0.947}O$ as well as 1.056 moles of the fictitious $Fe_{0.94701}O$, the intensive properties were kept the same (so the oxide would have the correct phase change points) and the extensive properties were multiplied by 1.056 (so the slightly greater amount of oxide would have the correct heat capacity).

In Table 2, Column A is for the stoichiometric combustion of iron with oxygen to produce wustite as predicted by CEA by default. Column B is the same calculation with gaseous FeO product excluded from the calculation, as though it does not exist as a gas. Column C is for a calculation by HSC that duplicates and is limited to the potential product list of Column A but at the slightly higher final adiabatic combustion temperature that is predicted by HSC. Column D is analogous to Column B, in that it duplicates Column C but with gaseous FeO excluded as a potential product. Column E is a duplicate of Column C but with the fictitious oxide $Fe_{0.94701}O$ that has identical properties to $Fe_{0.947}O$ replacing the latter as a potential product. Column F is a duplicate of both Column C and Column E but with the fictitious oxide $FeO_{1.05601}$ allowed instead of $Fe_{0.947}O$ or $Fe_{0.94701}O$, respectively. Column G is a duplicate of Column C but with both $Fe_{0.947}O$ and $Fe_{0.94701}O$ allowed as potentially chemically different products.

In other words, Table 2 contains seven different ways to calculate the combustion of the exact same reactants and reports them in two ways. And the results are illuminating.

Since CEA reports results as either overall mole fractions or overall mass fractions, the raw results are the mole fraction results in the upper section. Since HSC apparently reports either moles or mole fractions *in each phase (but apparently not the overall composite),* the raw results are the moles in the lower section. In each case the writer has manually done the conversions to allow inter-comparisons of both the mole and mole fraction results (in conversion from mole fractions to moles, balancing the oxygen was used since it appeared to give better results than balancing the iron).

Observe that Columns A and C compare the results of CEA and HSC for the exact same calculation (HSC constrained to match the products of CEA) and the results are fairly comparable. HSC yields a slightly higher (by only ~1%) adiabatic combustion temperature and slightly different amounts of gaseous products (all within 5% of each other) but the relative amounts of liquid oxide were extremely close.

If the presence of FeO gas is disallowed as in comparable Columns B and D, respectively, again the results are similar. Both codes produce a higher prediction of adiabatic combustion temperature than their corresponding result (by about 1.5%) and both increase the amounts of all remaining species present by corresponding amounts (roughly an increase of 1.5% in liquid oxide and about 10-15% increase in respective gaseous products).

If the fictitious unique product oxide $Fe_{0.94701}O$ with identical thermo properties to $Fe_{0.947}O$ is substituted for $Fe_{0.947}O$ as in Columns C and E, the results are identical as they should be.

If the fictitious yet identical product oxide $FeO_{1.05601}$ is substituted for $Fe_{0.947}O$ of Column C or $Fe_{0.94701}O$ of Column E as is shown in Column F, the adiabatic combustion temperature should be exactly the same and is only 0.1% lower. The gaseous products (as moles) should be exactly the same, but they vary somewhat surprisingly by as much as much as 10%. However, the moles of liquid oxide are in excellent agreement with there being ~5.5% more $Fe_{0.947}O$ than $FeO_{1.05601}$ and this is nearly exact (since there are 1.056 moles, or 5.6% more, of

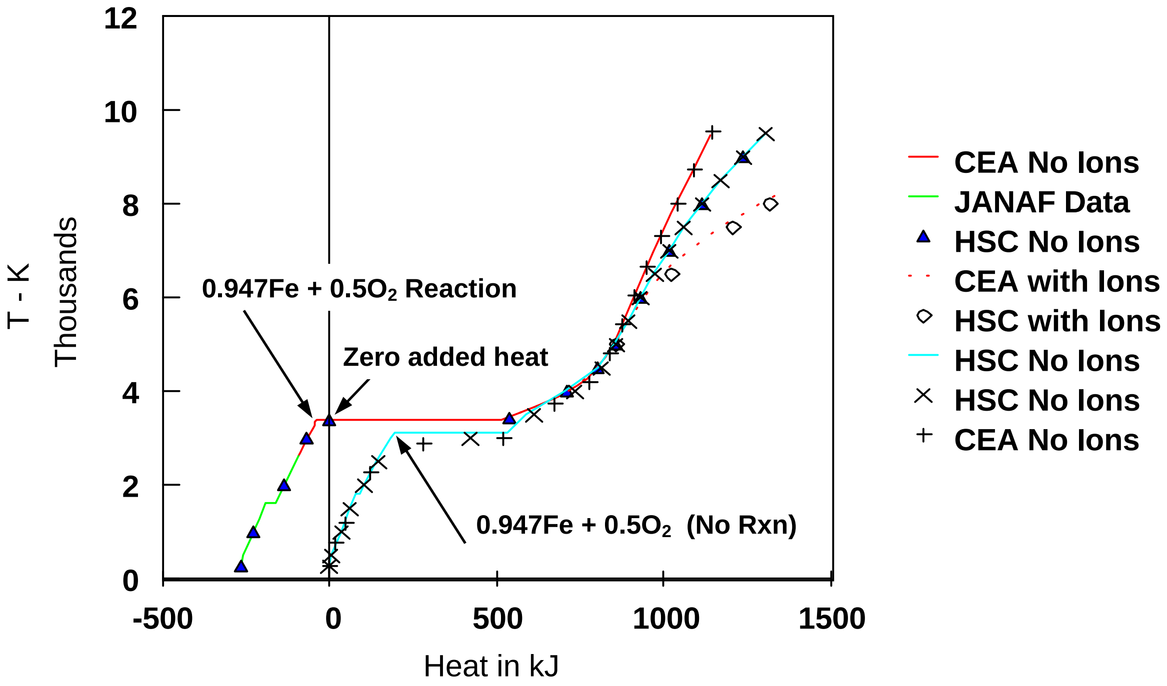

FIG. 1—*Thermochemical portrait of the combustion of 0.947Fe and 0.5*O_2 *to form* $Fe_{0.947}O$ *wustite.*

$Fe_{0.947}O$ to a mole of $FeO_{1.05601}$).

Finally, if $Fe_{0.947}O$ and $Fe_{0.94701}O$ are both allowed to be present in a calculation as in Column G, then a fictitious (clearly bogus) result obtains. A significantly but very importantly not hugely (about 3.5%) higher adiabatic combustion temperature is calculated. The individual gaseous products differ and by about up to nearly 50% in some cases. Since both liquid oxides are identical, the sum of their results should be identical to those of Column C but instead the sum is about 1.6% percent higher. This bogus result would be valid if indeed the two materials were chemically different, despite their identical thermo properties, and would therefore change the entropy of the combination, but as handled here, the entropy would not change and therefore this result is in error, but again not hugely so, except in the gaseous products. Nonetheless, it exhibits why the user must be precise in specifying the calculation to be made correctly, and that is not at all trivial nor obvious to do.

Figure 1 depicts and exhibits a thermo "portrait" like that used in the writer's earlier effort [*7*] to examine and understand iron combustion. Data like these were found to be very informative. The solid red line is extracted from CEA for a reaction of 0.947 moles of iron with 0.5 moles of diatomic oxygen (without "ions"). This is the precise stoichiometry for combustion constrained to yield a pure $Fe_{0.947}O$ product, and the adiabatic combustion temperature (ACT) and equilibrium results of Table 2, Column A would apply to the zero-added heat point as indicated on the solid red curve. The resulting curve which results from the addition or removal of heat in the calculation, is extended at high temperature up to 9500K at which point the constituents are predicted as fully dissociated gases of Fe gas and monatomic oxygen, O, gas. At the lower temperature extreme the curve extends down only as far as 2626 K at which point CEA predicts it will be virtually pure $Fe_{0.947}O$. Below 2626 K, CEA failed to converge to a solution.

As a result, the green curve was added and exhibits JANAF data for $Fe_{0.947}O$ down to room temperature. However, this is a fortuitous yet artificial constraint that is applied. At room temperature, the equilibrium product is not necessarily $Fe_{0.947}O$, and indeed, Darken and Gurry [***16***] indicate that pure $Fe_{0.947}O$ is not present in the equilibrium composition at room temperature at oxygen concentrations up to at least 30%. Nonetheless, in the real-world combustion of iron, in which quenching effects often can and typically do freeze equilibria and trap the products present at higher temperature equilibrium values, one might and can actually find this result to obtain, and the writer has observed this approximate result in some of his own real-world tests. Wustite equilibria are very easy to freeze. But under some real-world conditions, one might also find the presence of pure iron and higher oxides and mixtures of oxides, as well, in equilibrium, and real-world combustion results like this with higher oxides present have been reported also.

In order to further compare the HSC and CEA software, points have been added to Figure 1 as solid blue triangles that were generated with HSC 3.0 for identically constrained systems (again without “ions”) . Here again as was noticed before, the results are quite similar and an excellent fit to the CEA results up to about 5000 K. Above 5000 K, the two sets of results diverge with the HSC results being more endothermic (requiring more added energy to achieve similar temperature rise). In addition, HSC is somewhat more compliant than CEA and allows for points to be generated that extend to lower temperatures than those below which CEA failed to converge. And these lower temperature results nicely fit the JANAF thermo data for $Fe_{0.947}O$.

The source of the difference between the two sets of results at high temperature is of interest. It is known that at high temperatures, thermodynamic data are very difficult to obtain with precision and differing assumed heat capacity data may be the cause. However, at high temperatures, additional endothermic processes become significant. At about 5000 K, the software predicts ionization of the products (forming plasmas of mixed ionic and neutral material) will begin to develop. CEA allows one to include ionic species in the results, and the dotted red curve on Fig 1 exhibits the results when CEA includes ionic species. These results lie to the right of the nonionic CEA results because ionization is an endothermic process.

When CEA includes ionic species, it specifically cites the presence of gaseous electrons, plus gaseous ions of Fe (Fe^+, Fe^-) and oxygen (O^+ and O^-). Table 3 exhibits results from CEA at 5000 K and 8000 K as Columns A, B, E, and F. In addition, when these same ions that were predicted by CEA are allowed in the HSC code results for the corresponding conditions, the results yield Columns C, D, G and H of Table 3 and these are among the open circle data points on Fig 1. However, HSC allows for still higher (2^+ and 3^+ or 2^- and 3^-) ions of Fe and O that do not appear to be included in the CEA code and were not included here.

Since the ionic results from HSC fit the corresponding curve from CEA in Fig. 1 so well, and the mole fractions are in such good agreement across the board in Table 3, it is perhaps likely that the disparity between the nonionic results is, indeed, due to significantly different heat capacity data for the monatomic gas species in the two sets of software tables. Fig 2 exhibits data from both codes for the principle nonionic constituents (Fe and O) at 5000 K and 8000 K. And indeed, the data points for the heating of the radical, O, as determined by both codes, lie upon one another (green curve and triangle points), but the curves for heating of the Fe gas (red and blue curves) differ. At 8000 K, there is about a 70 kJ difference between the codes and this is approximately the difference between the nonionic HSC and CEA curves of Figure 1 at 8000 K.

Fortunately for this combustion scenario, the discrepancies between the codes above

TABLE 3—*How the formation of plasma (ionic mixtures) alters equilibrium results for wustite oxide at 5000 K and 8000 K. (0.947Fe and 0.5O_2 to form $Fe_{0.947}O$ wustite).*

	A	B	C	D	E	F	G	H
	CEA[a]	**CEA**[a]	**HSC 3.0**[a]	**HSC 3.0**[a]	**CEA**[a]	**CEA**[a]	**HSC 3.0**[a]	**HSC 3.0**[a]
ACT[b]**—K**	5000	5000	5000	5000	8000	8000	8000	8000
Mole Fractions:								
Fe (g)[c]	0.48686[e]	0.48266[e]	0.4869[e]	0.4822[e]	0.48639[e]	0.29953[e]	0.4864[e]	0.3145[e]
O (g)[c]	0.50397[e]	0.50242[e]	0.5037[e]	0.5021[e]	0.51351[e]	0.44890[e]	0.5135[e]	0.4541[e]
O_2 (g)[c]	0.00518[e]	0.00515[e]	0.005371[e]	0.005337[e]	0.00005[e]	4x10^{-5}[e]	0.0000518[e]	4.0x10^{-5}[e]
FeO (g)[c]	0.00398[e]	0.00394	0.004014[e]	0.003962	0.00006[e]	3x10^{-5}[e]	0.0000442[e]	2.5x10^{-5}[e]
Fe^{+} (g)[c]	excl[f]	0.00312[e]	excl[f]	0.003227[e]	excl[f]	0.12573[e]	excl[f]	0.1156[e]
Fe^{-} (g)[c]	excl[f]	—	excl[f]	<10^{-7}[f]	excl[f]	1x10^{-5}[e]	excl[f]	5.6x10^{-6}[e]
O^{+}(g)[c]	excl[f]	—	excl[f]	<10^{-8}[f]	excl[f]	2x10^{-5}[e]	excl[f]	1.8x10^{-5}[e]
O^{-} (g)[c]	excl[f]	3.x10^{-5}[e]	excl[f]	2.7x10^{-5}[f]	excl[f]	8x10^{-5}[e]	excl[f]	7.4x10^{-5}[e]
e^{-} (g)[c]	excl[f]	0.00309[e]	excl[f]	0.003196	excl[f]	0.12566[e]	excl[f]	0.1155[e]

[a] All results for rxn of 0.947 moles Fe with 0.5 moles O_2 (stoichiometric for 1.0 moles $Fe_{0.947}O$, 0.947 moles $FeO_{1.056}$).

[b] ACT– Adiabatic Combustion Temperature.

[c] All results are relative mole fractions of combined gas, liquid and solid products.

[d] All results are relative moles of combined gas, liquid and solid products. Not used.

[e] Raw result from software

[f] excl—Excluded from calculation

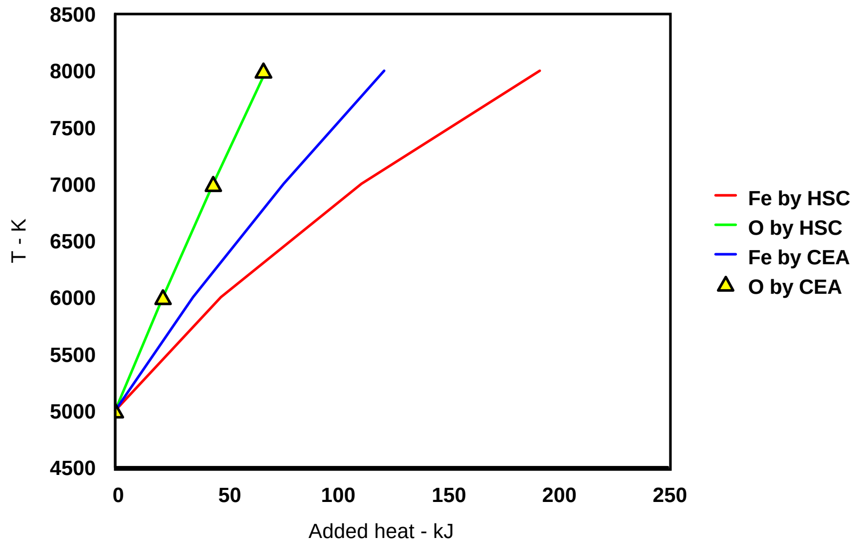

FIG. 2—*Heat capacity of nonionic Fe and O gas species of Figure 1 between 5000 K and 8000 K.*

5000 K, should have little impact on oxygen safety analyses since routine combustion temperatures for Fe above this level are unlikely to obtain. At these temperatures, Fe is not flammable in oxygen, because the oxide "heat of formation" or "heat of reaction" (what the writer prefers to call the *in-situ* "heat of combustion") is near zero.

Fig. 1 also exhibits data for the sum of thermo behaviors of the unmixed reactants (0.947Fe and $0.5O_2$) as the light blue curve obtained using HSC code and shows how this same result obtains if one applies the codes to a corresponding mixture of the reactants but does not allow them to react. Reaction is excluded in the HSC code by not listing any cross species, yielding the "x" points which lie on the same curve as for the summation of the unreacted reactants below 5000K, and, above 5000K, the reacted result indicated by the blue triangles. Reaction is excluded in CEA by "omitting" any cross species before doing the calculation and these data appear on Fig. 1 as the "+" points which lie on the summation curve below 5000K and lie on the CEA reacted result (red) curve above 5000 K.

Teasing Cooperation From the Codes

When learning to use the CEA code, the writer, as for others, found it downright recalcitrant at times when it came to performing numerous desired analysis. The CEA manuals did not seem to help. However, the HSC User's Manual mentions HSC can present similar problems and suggests that the user avoid perfectly stoichiometric reactants (like those of Table 2 and the curves of Fig. 1, that can theoretically completely react away gases) as well as other systems that can be completely absent any gas species. Indeed, HSC recommends a trace of argon gas be added to every problem, and *it prompts you to do this if you forget*. Following repeated failed efforts with CEA to run equilibria for stoichiometric aluminum reaction with oxygen (to yield Al_2O_3), the writer tried both of these suggestions and, *Lo!*, both proved useful individually and in combination (but not every time and they did not resolve every last issue). HSC similarly choked at times on this Al/O_2 submission and both techniques worked there also, as advertised.

Fig. 3 presents the key portions of the iron/oxygen thermo portrait of Figure 1 (nonionic case) and exhibits the effects of added trace extraneous argon. The solid curves present the prior basic data from CEA and JANAF. The cross, circle and square data points depict data which included respectively: 0.00001, 0.0001, and 0.001 moles of argon. All of these data points fit the curve nicely with only the lowest temperature cross point being shifted a small amount.

Although CEA would not converge at temperatures below about 2626 K, the addition of argon (and in some cases with needed tinkering) enabled convergence of the CEA software without too much hassle at temperatures down to ~600 K, which is well below the melting point of $Fe_{0.947}O$. At the lowest temperatures, sometimes the same set of conditions might not converge twice in a row or might yield differing equilibrium compositions, but the portrait thermo data were consistent for all. This overlaps a large portion of the green portion of the curve that represents JANAF data for $Fe_{0.947}O$.

In these lower temperature data from CEA, the code is predicting an equilibrium that is largely liquid or solid $Fe_{0.947}O$. However, a small error in stoichiometry appeared between 2626 K and 600 K, and although the thermodynamics (the temperature/heat data) still fit the JANAF data of Fig 3, formation of a small amount (a few tenths of a percent) of Fe_3O_4 (magnetite) was predicted at temperatures above 1000 K. And this formation is not stoichiometric in that although the reactants submitted to the code were $0.947Fe + 0.5O_2$ (stoichiometric to the eutectic $Fe_{0.947}O$) plus a trace of argon, the stochiometry of the combined products output is shifted slightly to an approximate overall $0.950Fe + 0.5O_2$ (plus trace argon) proportion. This may sug-

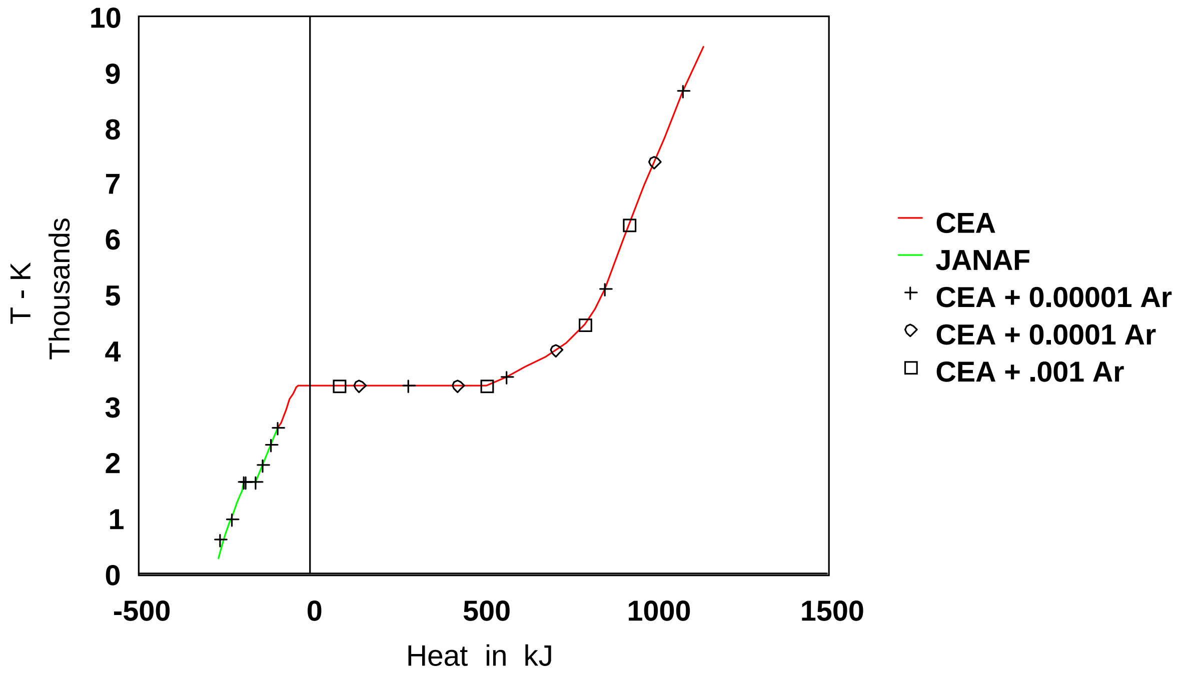

FIG. 3—*The effect of trace argon and slightly off-stoichiometric reactants on the thermochemical portrait of Fig. 1 (0.947Fe and 0.5O_2 to form $Fe_{0.947}O$ wustite).*

gest a rounding error or error in stoichiometric coefficients is present in the CEA code. However, if one then specifies $0.95Fe+0.5O_2$ as the reactant set, the code often converges to predict 0.99999 mole fraction $Fe_{0.947}O$.

Between 600 K and 1000 K, CEA predicted an equilibrium that shifts away from $Fe_{0.947}O$ to roughly 44% Fe (α) and 56% Fe_3O_4. This agrees with the equilibria presented by Darken and Gurry [***16***].

Below 2626 K, the shifting of the stoichiometry away from the input (0.947 Fe + 0.5 O_2 plus trace argon) for this example did not improve convergence of the code. Slight shifting to increase the oxygen (in an effort to produce excess oxygen so as to allow for gaseous products) does not in fact yield a prediction of increased gaseous products. Instead, the predicted equilibrium shifts to increased Fe_3O_4, and the minimum stoichiometry that allowed convergence at 2626 K, was 0.947 Fe + 0.5741 O_2, at which point 29% Fe_3O_4, 70% $Fe_{0.947}O$ is predicted along with about 2% O_2. At 2397 K, the minimum stoichiometry that allowed convergence was 0.947 Fe + 0.65781 O_2 , which converged to about 92% Fe_3O_4 and about 8% O_2. Convergence did not occur for either offset stoichiometry below 2625 K and 2397 K respectively. Nor did convergence occur for offsets of stoichiometry to increase the iron fraction.

Although CEA predicts shifts among the known oxides present as the temperature and stoichiometry change even at low temperatures where liquids and solids would be present (and indeed were in general agreement with the results in Darken and Gurry [***16***] for the conditions above), some have indicated CEA "does not handle multiphase systems well" [***6***]. In comparison, the mathematical routines for HSC previously appeared to be more robust at convergence than for CEA and indeed, HSC even boasts an ability for generating phase diagrams for materials. Fig. 4 again presents the basic data of Fig. 1 using HSC for nonionic cases, and in this case the full range of known oxides ($Fe_{0.947}O$, Fe_3O_4 and Fe_2O_3) were allowed to be present in the

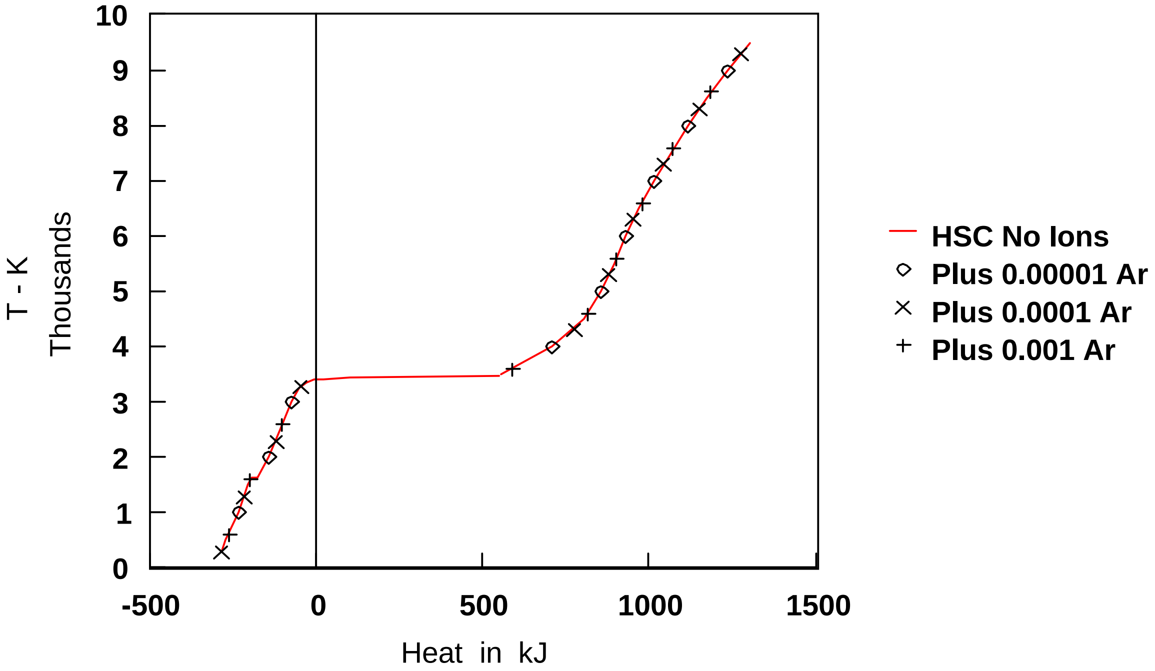

FIG. 4—*The effect of trace argon on the thermochemical portrait of Fig. 1 using HSC. (0.947Fe and 0.5O_2 to form $Fe_{0.947}O$ wustite).*

calculation and are shown as a solid red curve.

HSC had no difficulty converging at the lowest temperatures examined of 300 K. Fig. 4 also exhibits data from HSC with addition of trace argon to the reactants of 0.00001 mole (cross points), .0001 moles (circle points) and 0.001 moles (square points). And all of these data from HSC are generally good fits to the red curve.

Very interestingly, although CEA and HSC predict significantly different equilibria at the lower temperatures, the effect on the thermo portrait (heat/temperature curve) at temperatures of most interest to Oxygen Safety Practitioners was small.

A Quick Look at Aluminum/Oxygen Combustion

Aluminum combustion in oxygen has been important in several practical and academic ways. Aluminum is a very useful and desirable material, but it has been involved in a number of extremely serious incidents and has produced much more explosive (very rapid) and much more destructive consequences than iron combustion. Aluminum has often been assigned an adiabatic combustion temperature at the vaporization point (~4000 K) of its most stable oxide (Al_2O_3), alumina, on the basis that this oxide dissociates at its phase transition (often called "boiling point" with some controversy) and, as for FeO dissociation, that such alumina dissociation would absorb energy through reversal of the reaction (or some sub step) and prevent any further temperature rise. However, the product oxide is at such a high temperature and transfers so much heat of reaction (*in-situ* heat of combustion) that extensive vaporization of the base aluminum (boiling point of ~2800 K) is expected (and apparently occurs). This leads to a common model of combustion in which vaporized aluminum gas evolves and mixes with and reacts with oxygen (perhaps as a gaseous diffusion flame) and burns (at least in large part) to form a cloud of liquid Al_2O_3 droplets that condense some distance (potentially very small) from the aluminum surface. This view is that the gaseous aluminum and oxygen come together to form a hot liquid aerosol product. And indeed in aluminum combustion there tends to be large quantities of aluminum oxide dust formed that squares with at least partial burning in the gas phase to form such small droplets (literally powders of micron-scale size). Such small droplets might also result from formation of a gaseous oxide and later condensation but the predicate has always surmised that aluminum oxide does not congruently vaporize.

In comparison, iron in combustion at the temperatures predicted by Fig 1, transfers much less heat and the differential temperatures between the oxide vaporization temperature and the boiling point of Fe (~3400 K versus ~3300 K) are much smaller so the prospect of a gaseous cloud of iron gas evolving and mixing with a gaseous oxygen is much less plausible, or is at least likely on a much smaller scale. And such analysis has been used to ague (and explain why) iron is much less destructive in combustion.

This is why even small amounts of argon in the oxygen are believed to so effectively inhibit combustion of aluminum mechanically because as the oxygen is consumed to form liquid oxide of negligible volume, it leaves the argon gas behind to accumulate in the thin flame zone to dilute and interfere with combustion. And experimental results are consistent with this description. Argon is a potent inhibitor in this case.

Table 4 lists basic equilibria for aluminum/oxygen combustion that CEA and HSC predict and are related to select data from Table 2. In this case neither CEA nor HSC converged when one mole of aluminum was input for reaction with 0.75 moles of O_2. However, when 0.00001 moles of Argon were added to the calculation, the cited results obtained. In this case, CEA predicts that if all the gaseous oxides of aluminum are excluded from the calculation except for gaseous Al_2O_3, the results differ surprisingly little (and there is very little gaseous Al_2O_3 that forms in the vapor).

Table 4 shows adiabatic combustion temperatures by HSC in columns “D” and “F” but does not list composition data. This is because the latent heat plateau for aluminum combustion is at a rather constant temperature and the ACT lies within that plateau. When one asks the HSC software to produce composition data within the latent plateau its resolution is not adequately precise to discriminate the various points. In the case of some metals, the latent plateau exhibits some incline and that allows for HSC to resolve results but this is not the case for aluminum. This is a serious shortcoming in the HSC software (and would apparently be present with CEA if used in the similar TP mode). However, CEA has little difficulty generating corresponding composition data (Columns “A”, and “B” in Table 4) at points along the plateau since position is nearly (if not exactly) linear in added heat. HSC is able to resolve composition data in columns “C” and “E” because these data allow the presence of AlO liquid and this adds enough incline to the plateau that HSC can resolve the compositions fairly well.

Figure 5 exhibits the individual thermodynamic equilibria of aluminum and oxygen. The green curve depicts one mole of aluminum that is heated to the melting point then to the boiling point and beyond until at 9500 K a monatomic gas is predicted. The red curve is for three quarters mole of diatomic oxygen (stoichiometric with one mole of aluminum to form Al_2O_3) that heats until it dissociates and by 9500 K is also a monatomic gas. The black curve is the sum of these two curves to represent the heating required to bring these two unmixed materials through the range of temperatures.

However, both CEA and HSC are able to calculate how these two materials would behave if they were mixed and were in equilibrium, but if they were not allowed to cross react. In

TABLE 4—*Aluminum/Oxygen Combustion Calculations from CEA, HSC*[a]*.*

	A **CEA**[a]	**B** **CEA**[a]	**C** **HSC 3.0**[a]	**D** **HSC 3.0**[a]	**E** **HSC 3.0**[a]	**F** **HSC 3.0**[a]
ACT[b]**—K**	3965.66	4117.65	~4000	~3974	~4111	~4105
Mole Fractions:	**Normal CEA Comb.**	**Only oxide Gas is Al_2O_3 (g)**	**Normal HSC Comb. w/ AlO (l)**	**no ALO (l)**	**No oxide gases w/AlO (l)**	**No oxide gases no AlO (l)**
Al (g)[c]	0.10213[e]	0.31813[e]	~0.06861	N/A[i]	~0.04411	N/A[i]
O (g)[c]	0.31419[e]	0.37070[e]	~0.25990	N/A[i]	~0.21794	N/A[i]
O_2 (g)[c]	0.06337[e]	0.06337[e]	~0.05330	N/A[i]	~0.04739	N/A[i]
O_3 (g)[c]	—	—	Negl.[g]	N/A[i]	Negl.[g]	N/A[i]
AlO (g)[c]	0.20529[e]	excluded	~0.14787	N/A[i]	excluded	excluded
AlO_2 (g)[c]	0.00739[e]	excluded	~0.02089	N/A[i]	excluded	excluded
Al_2 (g)[c]	0.00003[e]	0.00028[e]	~0.00001	N/A[i]	~0.00001	N/A[i]
Al_2O (g)[c]	0.07649[e]	excluded	~0.00370	N/A[i]	excluded	excluded
Al_2O_2 (g)[c]	0.03570[e]	excluded	~0.00600	N/A[i]	excluded	excluded
Al_2O_3 (g)[c]	0.00037[e]	0.00092[e]	N/A[h]	N/A[h]	N/A[h]	N/A[h]
Ar (g)[c]	0.00001[e]	0.00001[e]	~0.00001	N/A[i]	~0.00001	N/A[i]
Al_2O_3 (l)[c]	0.19502[e]	0.25630[e]	~0.19959	N/A[i]	~0.19753	N/A[i]
ALO (l)[c]	N/A[f]	N/A[f]	~0.24012	excluded	~0.49298	excluded

[a] All results for rxn of 1.0 moles Al with 0.75 moles O_2 (stoichiometric for 1.0 moles Al_2O_3).
[b] ACT– Adiabatic Combustion Temperature.
[c] All results are relative mole fractions of combined gas, liquid and solid products.
[d] All results are relative moles of combined gas, liquid and solid products. Not used.
[e] Raw result from CEA software
[f] N/A—Not an available product in CEA software
[g] Negl.—Negligible.
[h] N/A—Not an available product in HSC software
[i] NA¯HSC software can not resolve some values on the latent plateau precisely

CEA one merely “omits” any cross products from the calculation, and in HSC one deletes any cross products from the assorted phase listings. In this case, combining them might release heat of mixing and entropy may also change. However, in Figure 5, the open-circle points were generated this way with HSC, and the cross data points were generated with CEA and both sets exhibit only small departures from the unmixed summation which does not factor in entropy, heat of mixing or other factors.

Figure 6 exhibits thermo portraits for aluminum combustion relating to those for iron in Figure 1 and includes the black curve for unmixed reactants from Figure 5. The red curve is

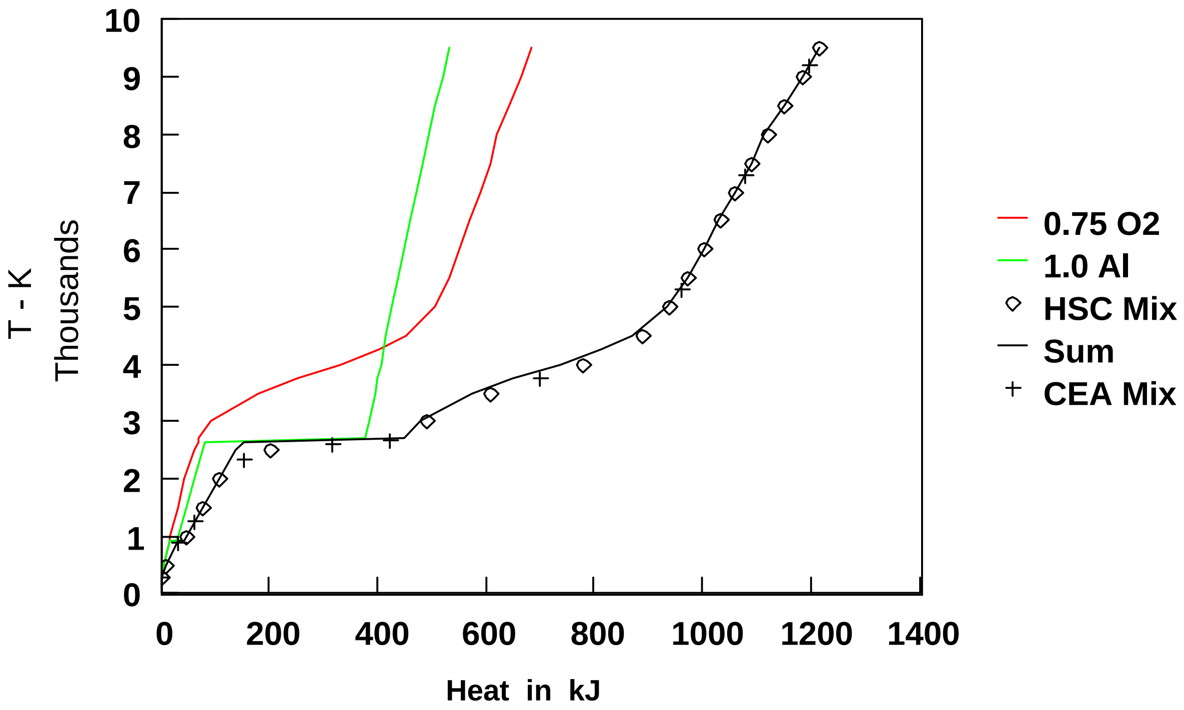

FIG. 5—*Thermo Portrait for Combustion of Aluminum by CEA and HSC.*
(1.0 mole Al with 0.75 Mole O_2 , trace Argon).

from CEA (and the ACT and composition data from Table 4, Column A apply to the zero added-heat point), but for this plot the combustion is with a trace of argon (such argon of which again might well interfere with real combustion even though it facilitates and can actually be required for the calculation). The green curve is a default calculation from HSC (the ACT and composition data from Table 4, Column C, apply to the zero added heat point) . The two are fairly similar and the biggest difference is a more rounded appearance for HSC data at the vaporization point onset. Among the differences between the equilibria predicted for these two curves (as is seen in Table 4 also) are the following: There is a presence of liquid AlO allowed in the results for HSC (there are no data for liquid AlO in the CEA tables), as well as for several solid forms of Al_2O_3 (versus just one available in CEA). There is also the presence of gaseous Al_2O_3 in some cases for the results from CEA (while HSC contains no data for this gas in its tables).

The blue curve depicts data from HSC (not exhibited in Table 4) for which all but one solid form of Al_2O_3 have been excluded from the results and the resulting changes are small. However, the circular data points near the vaporization point are for data from HSC (for which the ACT datum from Table 4, Column D, applies to the zero added heat point but for which composition data could not be extracted due to the extreme flatness of the plateau) in which liquid AlO has been excluded from the calculation and these points fall nicely on the CEA curve. Nonetheless, the four sets of data are fairly consistent with each other.

Clearly, Figure 6 exhibits a robust temperature-limiting phase-change mechanism seen as the long constant temperature latent-heat plateau in the curve. In the past, this temperature limit is attributed [***17***] to the phase change (“vaporization”) properties of liquid Al_2O_3. However, Table 4 indicates the vapor phases that CEA and HSC normally predict in equilibrium

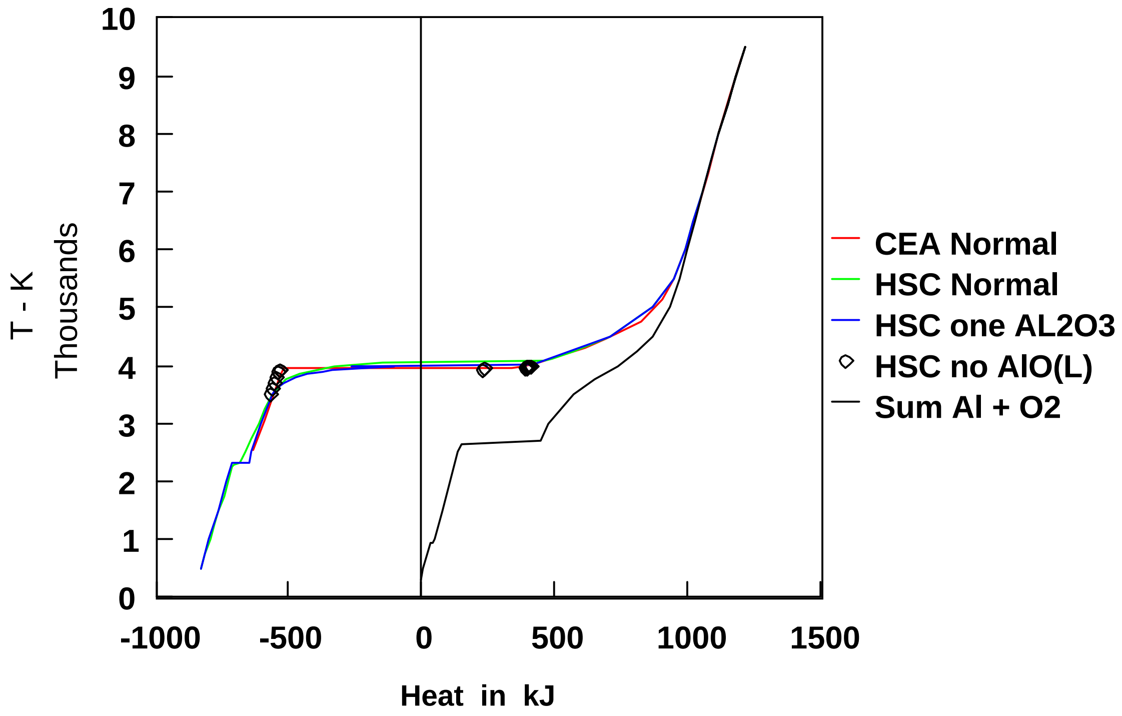

FIG. 6—*Thermo Portrait for Combustion of Aluminum by CEA and HSC.*
(1 mole Al with .75 Mole O_2 ,trace Argon).

with the liquid Al_2O_3 (and AlO in the case of HSC) is not entirely congruent Al_2O_3 (gas of the same molecular formula as for the liquid oxide). However neither is the gas absent any potential oxide, including Al_2O_3 gas in the case of CEA.

Both codes predict that a whole series of gases will form including gaseous Al and O_2 and O, plus AlO, AlO_2, Al_2, Al_2O, Al_2O_2, and (in the case of CEA only) even Al_2O_3. Here again as for iron, the software operator needs to be able to assess whether these are all molecules that can, indeed, form in bulk in the gas phase or whether there are existential or kinetic or other mechanical factors that would prevent any from being present. Here again, evaluation by a Blue Ribbon panel might give these data a fitting perspective relative to oxidant safety.

However, as noted before, both software packages allow one to generate fictitious (“bogus”) results. And the writer did so simply by restricting the potential results. In Table 4, Column B, most gaseous oxide products are excluded. Column B is based on the early model analysis that suggests aluminum oxide ***must*** dissociate completely upon vaporization. In Column B only gaseous Al_2O_3 was allowed in CEA (and very little of it is predicted). Similarly, in Column E, no oxide gases were allowed in HSC. The most interesting aspect of this exercise is that these results are not all that different from the earlier results as to the thermo characteristics that would be of most interest to Oxidant Safety Practitioners.

Figure 7 presents such results over the extended temperature range and all of them are pretty similar. As heat is added to the reaction in the temperature-limited plateau region of Fig. 7, the curve indicates there is a shift away from the liquid Al_2O_3 to greater amounts of gases or liquid aluminum and lower aluminum oxides and gaseous oxygen, or to one or more gaseous lower oxides. So there is both a vaporization and decomposition effect predicted, but gaseous Al_2O_3 is not predicted to any extent.

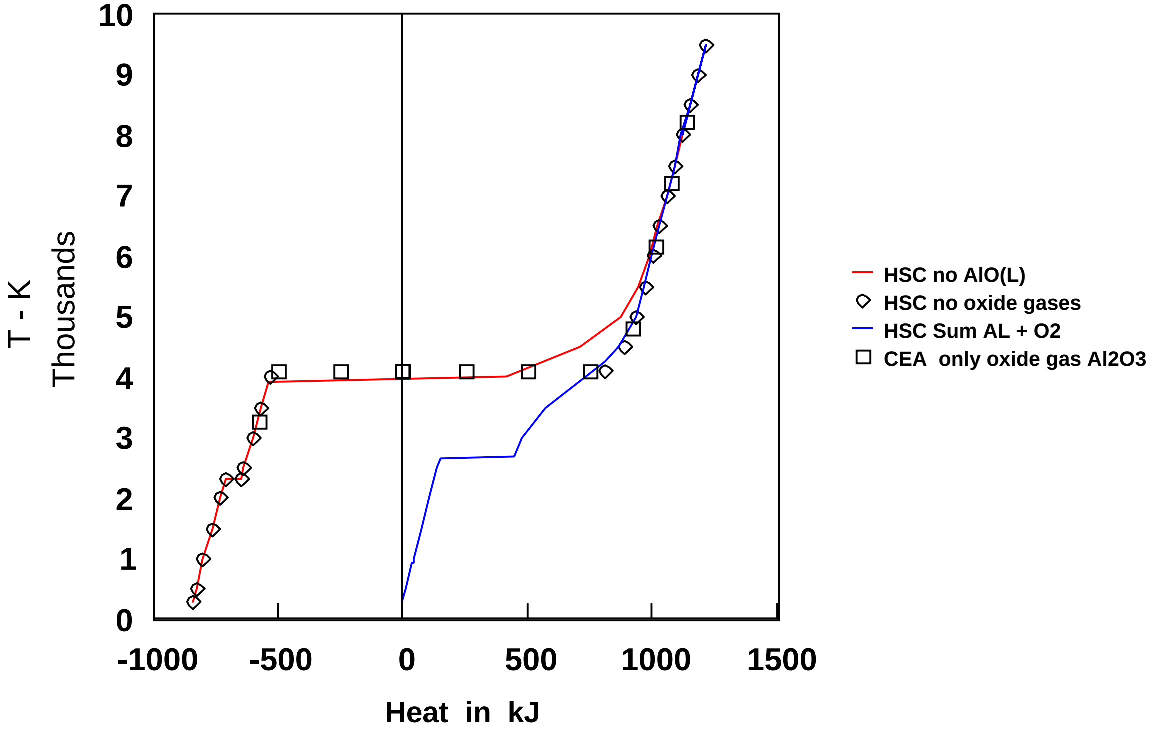

FIG. 7—*Thermo Portrait for Combustion of Aluminum by CEA and HSC.*
(1 mole Al with 0.75 Mole O_2 ,trace Argon).

Indeed, the biggest difference between normal predicted combustion (Red curve) as predicted by either code and calculations which force complete dissociation (open circle and open square data points) upon vaporization is an increase in the latent heat of vaporization. Indeed, in the case of the open square data points, the presence of gaseous Al_2O_3 is allowed but it never appears in the calculations to more than trivial levels (much less than one percent). Indeed both the square points and open circle points extend the latent heat plateau to where it intersects the heating curve for the summation of the individual constituents, as it should. Very significantly, the predicted normal heat of combustion (the heat at the far left end of the curves) is the same for all of these prospects.

Very importantly, regardless of which effect or combination of effects obtains, the gross characteristics of the thermo portraits in Figure 7 are fairly similar. The analysis of any of these curves could lead an Oxidant Safety Practitioner to draw similar conclusions about the thermodynamic possibility of combustion. However, surmise about the speed and hazard of combustion is less clear. Present indications are that vapor burners are faster and more hazardous than liquid burners, and this is an important conclusion to assess.

The agreement between CEA and HSC is again good for these corresponding problems, but here again, there is a need for the available reasoning to suggest what the actual combustion (or a best guess) would produce and an ASTM Subcommittee or Task Group or Users Group to weigh and publish such insight would be desirable.

A Quick Look at Carbon/Oxygen Combustion

Carbon is another interesting material although it is seldom used in oxidant systems but

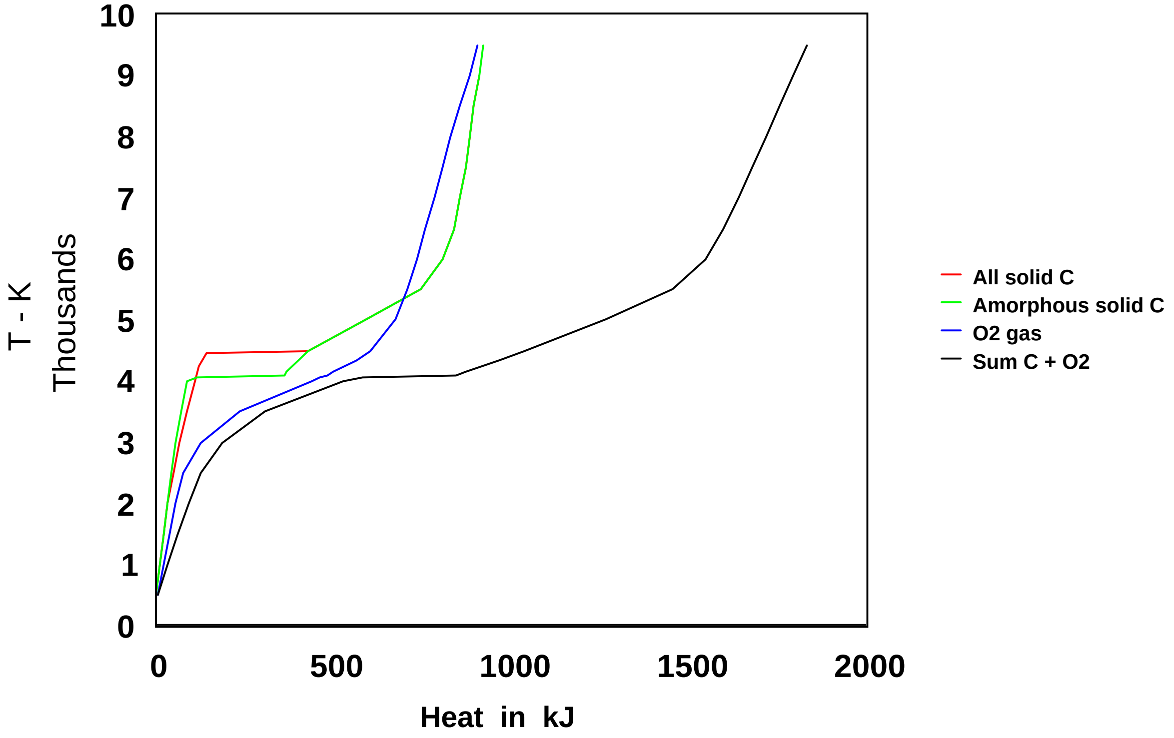

FIG. 8—*Thermo Portrait for Combustion of Carbon by CEA and HSC.*
(1 mole C with 1 Mole O_2 ,trace Argon).

nonetheless has excellent academic value, because its combustion is significantly and necessarily different from the previous examples. Carbon has an extremely low volatility (as is to lesser extent the case with metals). Indeed, at atmospheric pressure, it does not melt nor boil but instead it sublimes at about 4000 K. It has a known stable intermediate product (CO) and very stable gaseous higher oxide product (CO_2) (among many other alternatives that are predicted to form to only trace levels) to which it can combust and both of them are gases at room temperature. As a result, it burns in a number of “normal” scenarios (as it doubtless must) with a unique interfacial combustion mechanism that is relatively rare to see in oxygen (if existent at all) for metals typically used in oxygen. Perhaps, platinum or tungsten with their high phase-change temperatures might be closest. In this aspect carbon might be similar to several metals that burn in other oxidants to produce room temperature gaseous (or even liquid) products (such as tungsten in fluorine to yield gaseous or liquid tungsten hexafluoride) and hence might also exhibit interfacial combustion. It also has interesting properties to the writer as a very informative material with potential to examine gas-phase fire limits in a planned future paper.

Fig 8 exhibits the separate thermo properties for carbon (green curve for amorphous carbon, red curve for carbon composed of equilibrium combinations of amorphous, graphite and diamond forms) and oxygen as the blue curve. The black curve is for combined heats (summation of the blue and green curves) needed to warm unmixed carbon and oxygen with the exact stoichiometry of CO_2 to temperatures up to 9500 K.

Figure 9 duplicates the black curve for unmixed reactants of Fig. 8 and exhibits the results from HSC for normal stoichiometric combustion (green curve), as well as, combustion to yield principally CO with excess oxygen (blue curve) or principally CO_2 (red curve). Finally,

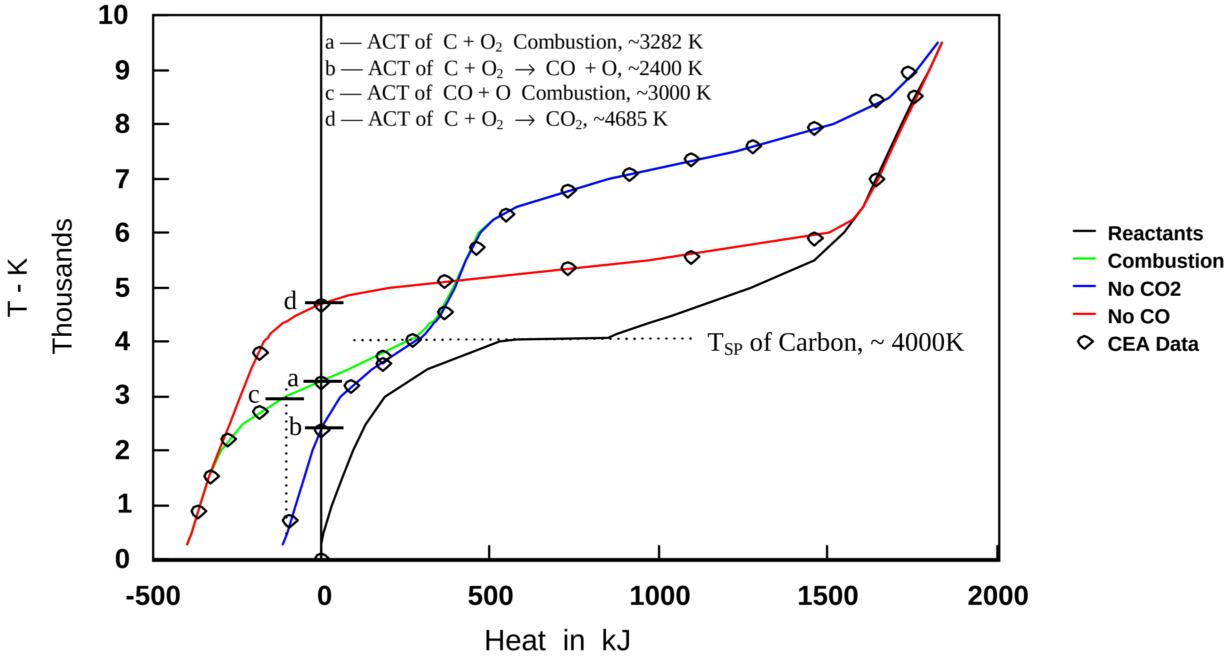

FIG. 9—*Thermo Portrait for C, CO, CO_2 by CEA and HSC.*
(1 mole C with 1 Mole O_2 , trace Argon).

the green curve (which overlays the red and blue curves in regions) exhibits normal combustion of carbon with oxygen relative to the black curve and also of CO with stoichiometric oxygen relative to the blue curve. In this case the software was manipulated only slightly with trace argon added. Although the predicted products of combustion include a myriad of possibilities (Table 7) the green curve for normal combustion coincided with the red “no CO” curve up to about 2000 K, then the CO_2 converts to CO and the curve shifts to coincide with the blue “no CO_2” curve for temperatures above roughly 4500 K. Table 7 also exhibits how even at 2400-4700 K, there are only small amounts of all of these gases present save for CO or CO_2. To produce the blue curve for CO, CO_2 was excluded from the calculation.

Fig 9 also flags some key parameters: the sublimation-point temperature (T_{SP}) of carbon and the plateau for its temperature limiting phase-change region on the black curve which lies above the ACT for both CO_2 and CO. Also indicated is the ACT for the normal combustion of gaseous CO with stoichiometric oxygen at point “c”.

When CEA was used to generate similar data for carbon and oxygen, the agreement was excellent. Open-circle data on Figure 9 indicate how the CEA results compare throughout the range of temperature and enthalpies. CEA data were calculated for one mole of carbon with one mole of oxygen, and CO_2 or CO products were “omitted” from the calculations when needed.

In general, again CEA and HSC each produced reasonably similar results.

Future Work

Although theoretical thermo/equilibrium concepts are clearly pertinent and valuable to any understanding of metal combustion, there is scant thermo/equilibrium commentary and analysis at present in the ASTM Committee G4 collegium or in the related literature known to the writer (specifically the literature cited in the G4 Reference bibliography). Instead, more ele-

TABLE 5—*Carbon/Oxygen Combustion Calculations from CEA, HSC[a].*

	A CEA[a]	B CEA[a]	C CEA[a]	D HSC 3.0[a]	E HSC 3.0[a]	F HSC 3.0[a]
ACT[b]—K	3282.09	4685.39	2400.45	~3292	~4707	~2406
Mole Fractions:						
C (g)[c]	—	0.03838[e]	—	Negligible	0.03742[g]	Negligible
O (g)[c]	0.11562[e]	0.16187[e]	0.00499[e]	0.1164[g]	0.1734[g]	0.00505[g]
O_2 (g)[c]	0.17789[e]	0.00123[e]	0.33000[e]	0.1769[g]	0.00139[g]	0.3300[g]
O_3 (g)[c]				Negligible	Negligible	Negligible
CO (g)[c]	0.47139[e]	excluded	0.66500[e]	0.4702[g]	excluded	0.6650[g]
CO_2 (g)[c]	0.23509[e]	0.77082[e]	excluded	0.2365[g]	0.7557[g]	excluded
C_2 (g)[c]	—	0.00262[e]	—	Negligible	0.00205[g]	Negligible
C_3 (g)[c]	—	0.00054[e]	—	Negligible	0.00024[g]	Negligible
C_4 (g)[c]	N/A[f]	N/A[f]	N/A[f]	Negligible	0.00001[g]	Negligible
C_5 (g)[c]	N/A[f]	N/A[f]	N/A[f]	Negligible	<0.00001[g]	Negligible
C_2O (g)[c]	—	0.02403[e]	—	Negligible	0.02712[g]	Negligible
C_3O_2 (g)[c]	—	0.00024[e]	—	Negligible	0.00258[g]	Negligible
Ar (g)[c]	<0.00001[e]	<0.00001[e]	<0.00001[e]	<0.00001[g]	<0.00001[g]	<0.00001[g]

[a] All results for rxn of 1.0 moles C with 1.0 moles O_2 (stoichiometric for 1.0 moles CO_2, 1.0 moles CO + 1.0 moles O).
[b] ACT– Adiabatic Combustion Temperature.
[c] All results are relative mole fractions of combined gas, liquid and solid products.
[d] All results are relative moles of combined gas, liquid and solid products. Not used.
[e] Raw result from CEA software
[f] N/A—Not an available product in CEA software
[g] Raw result from HSC software.

mentary and approximate methods (employing coarser parameters like burn ratios [***18***]) are employed to surmise whether specific combustion natures are possible or are more likely and are most importantly excluded. Hence it is desirable to raise the consciousness level of the oxygen safety community by introducing and expanding upon the available material. The writer considers the thermo portraits presented here and in the earlier iron work to be illuminating (even if flawed or in error) and is surprised that these are the first times he has seen these data in this format.

The use and operation of thermochemical software to produce these portraits has revealed a series of nontrivial obstacles, hence a high priority will be to expand the series of plausible material thermo/equilibrium portraits similar to this writer's first efforts here and earlier for iron [7]. However, familiarization of the oxidant safety community with these (and any other) software systems is needed. The NASA software, CEA, is a logical starting point for the reasons cited earlier (it is free).

These thermo portraits are a challenge to produce, but once produced and validated, should be relatively simple to interpret and understand. They doubtless allow and even promote straight forward introduction and illustration of new concepts and parameters such as pass-through energy, *in-situ* heat of combustion, and others that are not presently common concepts in existing practice [7]. In time these might lead to more practical, powerful, and useful evaluation parameters than, for example, burn-ratios. The writer is preparing several proposals in this regard for consideration as potential additions to ASTM Standard G 94 on metals evaluation.

Software willing, the writer hopes to begin a preliminary series of additional metal portraits (perhaps for aluminum, nickel, magnesium, zinc, gold, silver, cobalt, magnesium, titanium, chromium, lithium, carbon and tungsten) in a series of oxidants (perhaps oxygen, fluorine, nitrogen trifluoride and nitrous oxide). And the writer appeals to ASTM G4 in this paper and will appeal in his personal contacts for it to launch a formal Subcommittee or Task Group (a Blue-Ribbon Panel) in this area. Hopefully, ASTM G4 will launch such a effort to evaluate these data for practicality and validity, to generate them and fine tune their content and format, to identify areas in need of work or analysis, to flag unique aspects, to educate Committee G4 through its dialogs, and ultimately submit them for adoption as either (1) adjuncts to G-4's body of standards or (2) as a Committee-adopted Manual, or even (but perhaps less likely) as (3) additions to the standards themselves or (4) as stand-alone standards. These promise to improve the perspective on the nagging question of whether metals have enough energy to burn at all or to burn generally or situationally in various ways (as gases, liquids, fines, solid or otherwise) and to be subject to specific scenarios in which extraordinary (therefore subtle or even insidious) combustion may obtain.

This would be a fitting prelude, a baby step, to the addressing of much more difficult issues in the combustion of alloys from among these same metals. Later, the issues of diluent metals, inhibiting metals, synergistic and real-gas effects might all provide for further insight into the performance of combinations and alloys.

In a less technical vein, the writer foresees a huge practical need for additional tools to facilitate use of these data. Graphical tools to read these data have been cited before [7]. Also, the previously cited glitches and obstinacy of the software may be a large factor in why its use has not become more prevalent thus far. Hopefully the commentary here will alleviate some of the obstacles, but others remain. For example, there are myriad ways in which these data may be portrayed. To wit, CEA reports only overall molar or mass fractions of all combined phases, while HSC reports only molar fractions within phases or further subdivisions thereof. There does not appear to be an algorithm for obtaining common reports and the manual conversion of these data is onerous and prone to error, especially when fractional stoichiometry is involved such as for $Fe_{0.947}O$. Development of a utility or spread sheet for performing these conversions would be very useful, and since CEA may be open source software, there is a chance this feature could be directly added into the software itself, another reason to focus initially on CEA as a "standard".

Conclusions

-Thermo/equilibrium concepts for analyzing chemical reactions are important and are a well established practice (especially for gas phase combustion) of demonstrated value and validity. They have been applied rather extensively to numerous chemical processes and also the combustion of reactive gases and liquid fuels with good success. Their application to the combustion of solids and specifically metals has apparently been much less extensive. This body of technology is not without limits and shortcomings including it predication upon ideal gases in very high temperature conditions for which the assumption of ideality may be significantly flawed.

-The thermo/equilibrium approach to interpreting metals combustion promises new and important insights into the understanding of fire incidents and how to avoid them. The oxidant safety community needs to exploit this approach (regardless of its limitations due to being theoretical and ideal) and that requires its simplification and reduction to practice for the non-thermodynamicist and non-chemist/non-chemical-engineer. The writer stretches the limits of his own abilities here in seeking to open up and simplify the study and implementation of these concepts.

-These analyses are not trivial to do and therefore may be risky if mundanely attempted by tyros and even some more experienced practitioners of the art. However, the writer asserts that material portraits as have been proposed would upon validation and elaboration and prudent annotation be valuable and relatively easily understood tools to teach and exploit many of the critical characteristics needed in the oxidant safety field.

-Chemical thermo/equilibria computer codes are very powerful and provide convenient (if not easy) insight into theoretical processes that otherwise might only be understood in a coarser regard. They provide paths to more sophisticated and likely more pertinent ways to analyze metal (and perhaps other) combustion for oxygen system safety.

-Despite the power of thermo/equilibria codes, they are a challenge to use and a consensus evaluation of the “correct” or “most applicable” results is much needed. The availability of a free open-source NASA program of well established merit makes such an effort not only more realistic but much more compelling.

-The use of chemical thermodynamics programs can be misleading. They produce precise theoretical and ideal results, but the relation of those results to real-gas and real-world combustion are situationally open to question. For this reason, there is merit to a Committee like G4 preparing and tabulating “material portraits” rather than users extracting and evaluating specific results on the fly.

-The HSC and CEA programs appear thus far to produce very similar apples-to-apples results for the combustion properties of interest here, when both are used with similar specifications. The results are plausible and seem to give excellent insight but only time will tell the degree to which they are correct. Each has its own strengths and weaknesses. Both should be employed.

-There are “tricks” needed to improve (and even to gain) cooperation from both software codes, but the benefit of teasing data from these codes outweighs the challenges in coping with them. Indeed, it leads to new concepts and insights that could prove valuable in the future.

-Although the actual equilibria of various combustion schemes can vary and although there have been many debates as the pertinence of many thermodynamic variables in the past, for the materials examined to date the thermodynamic portraits generated have been remarkably consistent and constant, regardless of the products formed and their proportions. Hence the applicability and validity of thermodynamic parameters (such as upgraded burn factors) to assessing and even excluding the prospects of combustion appears to be imperfect but fairly robust and affirmed.

-Due to the complexities of the subject and the software options and their idiosyncrasies, and because CEA is free, simpler to use than HSC, requires less insight than HSC, and may allow for user modification of the code, as well for the near term, CEA should be promoted and employed (adopted) for use as a baby step in this direction and ASTM G4 should launch a thermo/equilibrium task-force/users-group, to begin and promote a dialog in this area, and to both serve as Advocate and Devils Advocate. If CEA is open source, then a Committee-generated portable copy of the software is suggested for development into a convenient adjunct PC utility.

-In general, CEA remains more quirky than HSC for the basic robustness of calculations. It claims to provide other software capabilities to deal with shock waves, detonations, etc., and many in ASTM G4 should begin its learning curve. CEA can generate data as a function of added heat and is therefore very effective at predicting ACT and compositions even in the latent heat regions.

-In general, HSC provides more flexibility and power than CEA, but the richness of its abilities can be overwhelming to its detriment. And because it generates its many results as a function of temperature, when one specifies temperatures in the constant temperature plateaus of phase change (melting, boiling, sublimation points), its results are simply erratic at times (whereas CEA is much more competent in those cases where it does not fail completely to produce any results at all). HSC also has other software abilities of value such as the prediction of phase diagrams. Those who can gain access to this software should begin its learning curve.

-Other software codes may offer specific benefits (such as Cequel for real gas adjustments) and further exploration is also recommended.

Summary

Thermochemical software and the usage of two kinds have been described, key “tricks” needed to obtain compliance from both HSC and CEA software and problems with both have been reviewed, and several results show their basic similarity in these data they produce for several materials. Known strengths and weaknesses of each have been reviewed and the need for clarifying unknown issues has been overviewed. The reasons and need for many more efforts of this kind have been cited.

Further use and extraction of results from these codes are desirable and have been forecast. Because there may be a respected free open source version of this class of software (CEA) available from NASA that can be adopted for the initial baby steps, ASTM G4 has been called upon to establish a group (task force or subcommittee) for incorporating these data into its body of work and teachings and for supporting use of the assorted software.

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Joseph W. Slusser provided crucial software support and commentary in the preparation of this manuscript.

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Appendix A

Use of CEA Software

The precise series of steps needed to obtain results like those reported herein can be difficult to determine. This appendix provides the exact sequence that was used. CEA software is downloaded from the NASA Glenn web site and comes with as series of files which are decompressed and launched in accordance with included instructions. When those steps were complete, a shortcut to the file CEAexec-win.bat places an icon titled "Shortcut to CEA-win" on the Windows XP desktop. For the calculations in this paper the following sequence of steps was employed to extract equilibrium data.

1. Launch CEA with the shortcut titled "Shortcut to CEA-win" icon. A command line window briefly appears then a Window titled "**Chemical Equilibrium with Applications**" appears. It contains a folder with five tabs: Problem, Reactant, Only, Omit, Insert and Output. And the Windows focus is on the Problem tab.
2. In the "**Select ONE Problem Type**" section, click on: "Combustion (Enthalpy and Pressure)—hp".
3. An untitled Window overlays the previous Window. A option "Bar" is preselected for the Pressure Units. Enter 1.0 below on the top line of the "Pressure" list box. Move the focus off the top line and click to register the entry. Enter 3800 and 0, respectively in the "Estimated Temperature: t, k" and "Assigned Enthalpy: h/R" data entry boxes. Click the Save command button at the bottom of the window and it should go away.
4. Back on the opening Window, click on the "Reactant" tab to open it.
5. Click on the first box under "Ident" in the "Reactants Found in the Thermodynamic Library" section. A list box showing "fuel" should appear. Move to the right to the second box and click. A new Window titled "Reactant Selector—Select a Reactant Name from Thermodynamic Library" appears.
6. In the drop down option box just below the tabs, drop it down and click on "moles".
7. In the middle column "Condensed(761)" list, click on the third item shown "AL(cr)". This returns you to the previous Window. Click on the third entry box on the first line and type in "1.0" (for 1.0 moles) of solid or liquid aluminum.
8. In the four entry boxes titled "Temp" type in "300" for an initial temperature of 300 K.
9. On the second line select or enter the following sequence: Select "oxid" for "ident", choose "O2" from "Gases species (1262)", enter "0.5" for amount, and "300" for temp.

10 On the third line select or enter the following sequence: Select "name" for ident., choose "Ar" for name, enter "0.00001" for amount, and enter "300" for temp.

11. Click on an empty temp or amount box to register the last entry, then click on "Save" at the bottom.
12. At the top of the window below the title bar, click on "Activity' then when a menu opens, click on Execute CEA2". You will be presented with a box to name the file that will be created, type in "ALO2.inp".
13. A new window title "File Editor: ALO2".out should open containing a long list of calculations:

    Near the top will be the input data
    Near the bottom will be a section: "Thermodynamic properties" and the second in the list will be the adiabatic combustion temperature.
    The next lower section will be a section titled: "Mole Fractions" and the data in this section should be the same as those in Table 4, column A.

14. A range of differing results can be reported when convergence fails or when changes to the input files are needed.

NOTE: To convert from the standard h/R heat units to kJ, a conversion factor is needed.

$$h/R \text{ (g-mol K/ g-mixture)} \times 0.008314 \text{ kJ/g} \times \text{(mol weight of mixture)}$$

For 1 mol of Fe with stoichiometric oxygen to produce Fe_2O_3:

$$h/R \times 0.008314 \times [(2\times55.859) + (16\times3)]/(2 \text{ mol Fe/mol } Fe_2O_3) = h/R \times 0.6639 \text{ kJ/mol Fe}$$

Appendix B

Use of HSC 3.0 Software

The precise series of steps to obtain results like those reported herein can be difficult to determine. This appendix provides the exact sequence that was used. HSC software was installed into a Windows XP machine using a series of floppy disks. When the installation was complete a shortcut was attached to the file HSC.exe and an icon titled “HSC” appeared on the Windows desktop. For the calculations in this paper the following sequence of steps was employed to extract equilibrium data.

1. Launch HSC by clicking on the icon titled “HSC”.
2. A Window titled HSC Chemistry Ver. 3.02 appears and it exhibits a menu of command buttons. Click on the third button “Equilibrium Compositions”.
3. A new Window “Equilibrium Compositions, Main Menu” appears and is another menu of command buttons.
4. Click on the first button “Create” to start a new file. Later the Edit button can be used to recall this file.
5. A periodic table of the elements appears. Click on the elements Al, O and Ar. Each is listed in the data input window. Then click on the “Ok’ command button to the bottom right.
6. A window opens titled “Delete excessive species”. Hold down the control key and click on the following items AlO(g), AlO2(g), Al2O(g), Al2O2(g), Al2O3 (C), Al2O3 (D), Al2O3 (G), and Al2O3 (K). Then click on the “Delete Selected” Command Button to the right.
7. Click on “Continue” to the bottom right.
8. A new Window opens, titled “Equilibrium Calculations” that lists the materials from the previous Window in three separate categories: “Gases”, “Oxides”, and “Elements”.
9. Click on “Units” on the top line, then click on “K” to convert to Kelvin.
10. Select each entry in the “Temper. K”“ column and change it from “298.15” to “300”.
11. In the “Amount kmol” column, enter “0.75” in the “O2 (g)” row, “0.00001” in the “Ar (g)” row and “1.0” in the “Al” row. The software adds entries into the adjacent column.
12. In the “Step kmol” column enter “0.1” in the “Al” row.
13. Click on the “Options” Tab next to the Species tab near the bottom left of the Window.
14. The window changes to provide you with a, “Equilibrium Calculation Mode” set of options. Enter “40” in the “Number of steps” data box on the first line, then Click on the “Increase temperature” Option box on the second line and then enter “4110” in the “min”. box and “4112” in the “Max” box.. Click outside the box to register the data.
15. Click “Save” at the bottom.
16. Enter a file name such as “AlOx1” to replace the default file name “GibbIn” portion of the dummy file listed.
17. Click ”OK” to the right. This returns you to the previous Window.
18. Click the “Gibb” Command Button to the lower right of the window.
19. A new Window “Calculation of Composition, v. 3.0” opens. Click “Calculate” at the bottom. Then click “Exit” at the bottom.
20. You are returned to the previous window. Click “Exit” at the bottom.
21. You are returned to the “Main Menu”. Click on the “Print” button next to the “Results File” label.
22. A Window titled “Open” appears. Enter your file name (ALOX1) to replace the asterisk in the “File name” data box retaining the remaining characters and the extender “.OGI”.
23. Click “OK” to the upper right.
24. Click “OK’ on the new “HSC” window that opens to query if your points 1-40 should all print.
25. The “SaveAs” window opens and proposes a sequential file name for your “Results” file. Click “OK” to accept the proposal as an .mdi file type.
26. Your “Results file opens (if your system can read .mdi files) with forty sets of calculations shown. The first is for a 4110 K temperature. And three lines below the temperature report is a “Reaction enthalpy” of –2.634 kJ. Scroll down to page ten where the Temperature of 4110.923 K appears and the Reaction enthalpy is shown as -0.01011 kJ (-1.011 E-02) which is near the heat balance point. The next entry down is for 410.974 K and shows a Reaction enthalpy of +0.1351 kJ (1.351E-01). These two records closely bracket the Adiabatic Combustion point. And they are the approximate data that appear in this paper as Table 4, Column E.
27. The composition data shown were converted to composite Mole Fractions for Table 4.