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THE USE OF COMPUTERIZED THERMODYNAMICS TOOLS IN FIRE/EXPLOSION INVESTIGATION

by

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SUMMARY

Several thermodynamics computer codes have been shown to be useful in fire/explosion investigations, particularly in reconstruction analysis involving chemical mixtures. These include CHETAH (ASTM), CECTRP (NASA-Lewis), BLAKE (DoD) and TIGER (DoE/DoD). Applications include the estimation of basic fuel material properties (e.g., heat of formation, heat capacity, and entropy) and hazard properties such as heat of reaction, sensitivity, flame temperature, reaction product compositions, explosion pressure and Chapman-Jouguet detonation parameters.

INTRODUCTION

Most fire/explosion accidents are easily explainable in terms of a fuel, oxidant and ignition source. An automobile crash resulting in burning gasoline is one example. A house explosion and subsequent fire resulting from a natural gas piping leak is another. However, some accidents are quite unexpected from knowledge available at the time. The Texas City explosion (1947) involving bulk ammonium nitrate is one example. Two tank car accidents involving the detonation of nitromethane (1958) and the more recent Pepcon plant explosion (1988) involving bulk ammonium perchlorate in its particular form are further examples. Numerous examples involving chemical mixtures are listed in Reference 1. With an ever-increasing use of new chemicals or chemicals in new forms and applications, more unexpected scenarios are sure to come. More tools and techniques are needed to analyze the circumstances of such events and to prevent future accidents.

A number of thermodynamics tools that are not necessarily familiar to fire protection engineers have been found to be useful for these purposes. These tools are computer programs which take the drudgery out of tedious thermodynamics calculations. Typical applications include the estimation of basic thermodynamic properties (e.g., heat of formation, heat capacity, and entropy) and hazard properties such as heat of reaction, heat of combustion, material sensitivity, flame temperature, reaction product compositions, explosion pressure and Chapman-Jouguet (C-J) detonation parameters. Many of these properties are not tabulated in any handbooks.

A knowledge of these tools and their limitations may be invaluable in some investigations, particularly where there is no other recourse aside from expensive tests.

These tools can help in answering investigative questions involving chemical mixtures, such as:

What reaction could have caused the fire/explosion?

Could an improper mixture of chemicals or contamination be responsible for the accident?

Could a particular chemical or chemical mixture overheat?

Was there a human procedural error or an equipment/system failure (i.e., regarding the mix of chemicals) and what was it?

Was the fire hot enough to cause ignition of a specific target item by radiation?

Could the explosion pressure caused by a particular chemical(s) be sufficient to cause the damage?

What toxic products of combustion might have been generated in the fire?

DESCRIPTION OF CODES

Codes found to be useful are described below.

CECTRP

CECTRP (Chemical Equilibrium Compositions and Transport Properties) was developed by NASA-Lewis[2] and it was originally devised to compute the theoretical performance of rocket propellants. The ideal gas equation of state is utilized. Thus, the range of applicability of the code is limited to the range of the ideal gas equation of state, though small amounts of condensed species are allowed in products without significant error. Code calculations include equilibrium composition, theoretical rocket performance, shock tube parameters and Chapman-Jouguet detonations. The code has recently been modified to compute transport properties (viscosity and thermal conductivity) of gaseous mixtures as well. Thermodynamic data for more than 400 species (including gases, solids and ions) are provided for program input in a temperature range of 300-5000 K, extracted from JANAF (Joint Army Navy Air Force) data[3]. CECTRP, written in Fortran, is available for mainframe applications from the Computer Software Management and Information Center at the University of Georgia, Athens, Georgia.

Figure 1 shows a partial output from a CECTRP calculation for a constant pressure (1 atm) combustion of kerosene in air. Actually, this is one of several calculations conducted to study the variation of adiabatic flame temperature and product species with equivalence ratio (i.e., fuel air ratio/stoichiometric fuel air ratio). For these calculations, kerosene was approximated as an "averaged" hydrocarbon having a chemical formula of $C_{10}H_{20}$ with an enthalpy of formation (at 298 K) of -55 kcal/mole. Input data are on the top lines following the words, "fuel" and "oxidant." The fuel and oxidant are input with their appropriate elemental and compound mole ratios, as well as corresponding heats of formation. Output data for the calculated equilibrium mixture are listed under subheadings such as thermodynamic properties, mole fractions, and species considered.

Figure 2 illustrates results of these calculations for an equivalence ratio of 0.5 to 4.0, corresponding to the expected range of flammability in air, 0.7 - 5.3%. Results indicate a peak temperature of 2321 K at an equivalence ratio just slightly rich of stoichiometric (i.e., equivalence ratio = 1.0), corresponding to a fuel concentration of about 1.5%. A limiting flame temperature of 1554 K is noted at the lower flammable limit. Variation of significant product species is also shown. Carbon monoxide formation is shown to increase significantly as the mixture becomes fuel rich. Hydrogen formation is shown to form as the mixture approaches the upper flammable limit. This example illustrates the diagnostic value of such calculations.

TIGER

TIGER was developed by the United States Army Material Command Explosive Research Program to calculate the detonation parameters of condensed explosions. The emphasis in this program is in the hydrodynamics calculation of Chapman-Jouguet detonation wave parameters. Special equations of state, such as the BKW-R and JCZ, are built-in to handle the enormous reaction pressures [i.e., >7000 MPa (>1,000,000 psi)] possible from condensed explosives. Written in Fortran, TIGER for the IBM PC[4] is available from the Lawrence Livermore National Laboratory through a limited distribution to Department of Defense and Department of Energy contractors only.

Figure 3 shows partial output from a TIGER calculation for a detonation of TNT. Input data is listed to the right of the word "TNT" under the composition heading. Output data follows for the calculated equilibrium mixture, including equation of state constants, C-J parameters, thermodynamic properties and composition. Results indicate a detonation pressure of 196,880 atm and a detonation temperature of 2688 K. Frozen product species include several ions, caused by high temperature disassociation. The detonation velocity of 6958 m/sec is the sum of the sound speed and the particle velocity. This is in good agreement with a value of 6825 m/sec for large experimental charges[5]. TIGER cannot definitely predict whether detonation can occur, but provides several indicators of its likelihood. For example, a material with a relatively low calculated detonation velocity or

THERMODYNAMIC EQUILIBRIUM COMBUSTION PROPERTIES AT ASSIGNED PRESSURES

CASE NO. 1

	CHEMICAL FORMULA	MOLES	ENERGY	STATE	TEMP	DENSITY
FUEL	C 10.00000 H 20.00000	3.00000	−55.000	G	298.15	0.0049
OXIDANT	N 1.58000 O 0.42000	71.429	0.000	G	298.15	0.0012

O/F = 4.8971 PERCENT FUEL = 16.9576 EQUIVALENCE RATIO = 3.0000 REACTANT DENSITY = 0.0014

THERMODYNAMIC PROPERTIES

P, ATM	1.0000
T, DEG K	1230
RHO, G/CC	2.1178−4
H, CAL/G	−0.1
S, CAL/(G) (K)	2.5674
M, MOL WT	21.376
(DLV/DLT)P	−1.00285
(DLV/DLT)P	1.0368
CP, CAL/(G) (K)	0.4200
GAMMA (S)	1.3074
SON VEL,M/SEC	790.9

MOLE FRACTIONS

C(S)	0.00120
CH_4	0.0082
CO	0.25521
CO_2	0.00083
HCN	0.00004
H_2	0.25519
H_2O	0.00123
NH_3	0.00002
N_2	0.48546

ADDITIONAL PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MOLE FRACTIONS WERE LESS THAN 0.50000E−05 FOR ALL ASSIGNED CONDITIONS

C	CH	CH_2	CH_2O	CH_3	CN	CNN	CN_2	C_2	C_2H
C_2H_2	C_2H_4	C_2H_6	C_2N	C_2N_2	C_2O	C_3	C_3O_2	C_4	C_4N_2
C5	H	HCO	HNCO	HNO	HNO_2	HNO_3	HO_2	H_2N_2	H_2O(S)
H2O(L)	H_2O_2	N	NCO	NH	NH_2	NO	NO_2	NO_3	N_2H_4
N2O	N_2O_4	N_2O_5	N_3	O	OH	O_2	O_3		

REACTANTS

C 10.0000	H 20.0000	0.0000	0.0000	0.0000	4.0000	M	−55.00	G 298.150	F 0.00486
N 1.5800	O 0.4200	0.0000	0.0000	0.0000	71.4290	M	0.00	G 298.150	O 0.00118

NAMELISTS – NO INPT2 VALUE GIVEN FOR OF, EGRAT, FA OR FPCT

SPECIES BEING CONSIDERED IN THIS SYSTEM

J 3/78	C(S)	J 3/78	C	J12/67	CH	J12/72	CH_2	J 3/61	CH_2O
J 6/69	CH_3	J 3/61	CH_4	J 6/69	CN	J 6/66	CNN	J12/70	CN_2
J 9/65	CO	J 9/65	CO_2	J12/69	C_2	J 3/67	C_2H	J 3/61	C_2H_2
L 4/80	C_2H_4	L 2/80	C_2H_6	J 3/67	C_2N	J 3/61	C_2N_2	J 9/66	C_2O
J12/69	C_3	J 6/68	C_3O_2	J12/69	C_4	J 3/61	C_4N_2	J12/69	C_5
J 3/77	H	L12/69	HCN	J12/70	HCO	J12/70	HNCO	J 3/63	HNO
J 6/63	HNO_2	J 6/63	HNO_3	J 9/78	HO_2	J 3/77	H_2	J12/65	H_2N_2
L11/65	H_2O(S)	L11/65	H_2O(L)	J 3/61	H_2O	L 2/69	H_2O_2	J 3/77	N
J12/70	NCO	J 6/77	NH	J 6/77	NH_2	J 6/77	NH_3	J 6/63	NO
J 9/64	NO_2	J12/64	NO_3	J 3/77	N_2	J12/65	N_2H_4	J12/64	N_2O
J 9/64	N2O4	J12/64	N2O5	J12/70	N3	J 3/77	O	J 6/77	OH
J 3/77	O2	J 6/61	O3						

OF = 3.672805

Figure 1. Partial output from CECTRP calculation; combustion of kerosene; equivalence ratio = 3.0.

equilibrium temperature may be considered suspect, having little chance of being detonable.

BLAKE

BLAKE is a general thermodynamic code derived from the TIGER code at the United States Army Ballistic Research Laboratory[6]. It is intended primarily for gun propellant applications, where gun chamber temperatures may range from 1500-4000 K and pressures may range up to 700 MPa (~100,000 psi). The unique feature of the code is that it uses a truncated virial equation of state for the application. Also, it has a library of input data containing ingredients found in most gun propellants. Written in Fortran, its availability is limited to Department of Defense contractors.

Sample output is not shown for BLAKE since it has a similar format as TIGER.

CHETAH

CHETAH (Chemical Thermodynamic and Energy Release Evaluation Program) provides predictions of the potential maximum reaction energy and a measure of the relative sensitivity of chemical compounds. It was developed by the ASTM Committee E-27 on Hazard Potential of Chemicals. The program also provides excellent estimates of enthalpy, entropy and heat capacities from 300 to 1500 K for an unlimited number of organic and organometallic compounds. It also computes the net change in enthalpy, entropy and free energy for balanced chemical equations. CHETAH version 4.4 for PC applications has recently become available from ASTM[7-11]. It is written in BASIC. A preprocessor is given in this version, which greatly simplifies input, particularly for complex chemical structures. Version 6.x is reported to be the next planned release, which will include all elements and allow solid/liquid products (the present version includes 22 elements).

Figure 4 shows the input and output from a CHETAH calculation to determine the energy release potential for TNT. Note that the input is actually a structural representation of the TNT, pieced together from structural chemical building blocks listed in the CHETAH manual. The

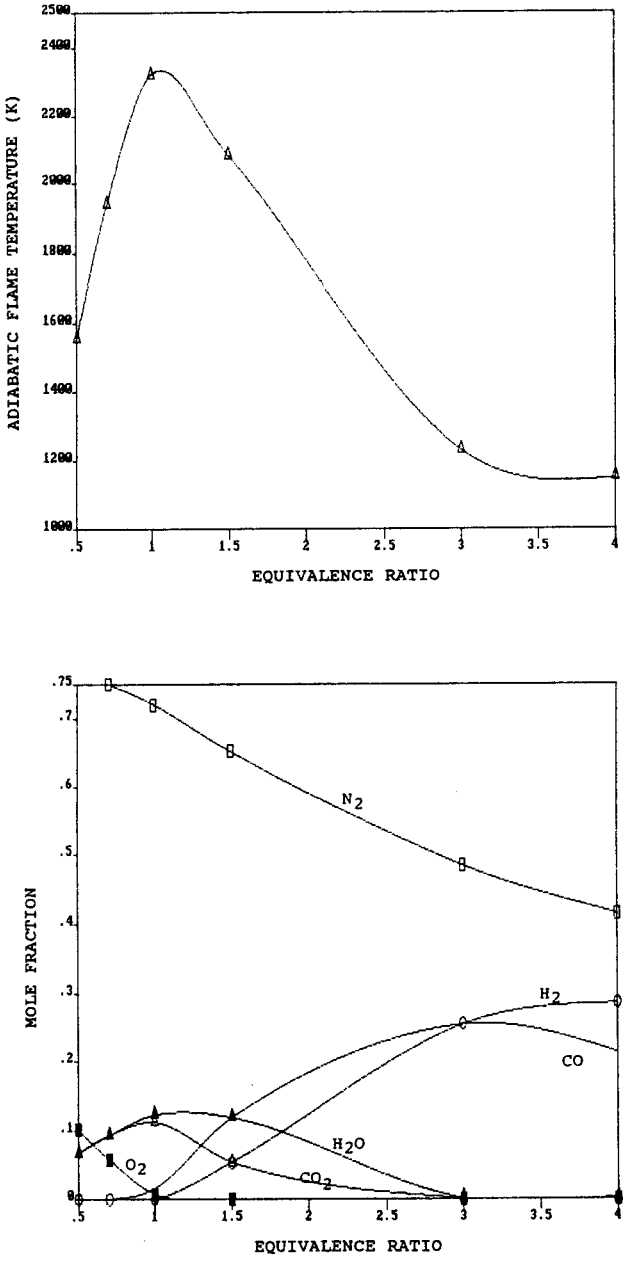


Figure 2. Results of CECTRP calculations; adiabatic flame temperatures and significant product species.

output indicates that TNT is suspected to be a hazardous material, based on four criteria: (1) the maximum heat of reaction exceeds 0.7 kcal/g; (2) the difference between the maximum heat of decomposition and heat of combustion (in excess oxygen) is low, indicating that it has within its own structure sufficient oxygen for decomposition; (3) the oxygen balance of the compound is sufficiently high; and (4) another correlation involving maximum heat of reaction and number of atoms in the compound(s). The

TNT, RHO 1.630, BKWR, AUG-86

THE COMPOSITION IS

name	percent by weight	percent by mole	percent by volume	heat of formation (cal/mole)	standard volume (cc/mole)	standard entropy cal/k/mole	molecular weight	formula
tnt	100.0	100.0	100.0	−16000.00	137.300	0.000	227.13	$c_7h_5n_3o_6$

FOR THE COMPOSITION

the heat of formation is	−70.443001 cal/gm
the standard volume is	0.604489 cc/gm
the standard entropy is	0.000000 cal/k/gm and
the standard energy is	−70.457642 cal/gm

THE ELEMENTS AND PERCENT BY MOLE

c	33.33
h	23.81
n	14.29
o	28.57

THERE ARE 11 GASEOUS CONSTITUENTS SELECTED WITH THEIR CONSTANTS

name	stateg	stater							
1.) n_2	5.21121	−0.13930	0.01627	−0.00051	−1.57152	0.47405	−0.04544	−4203.3	52.0719
bkw covolume	404.0								
jez2 r	0.000	epsilon/k	0.000						
jez3 r	4.050	epsilon/k	120.000						
2.) h_2o	6.85015	0.36037	−0.04975	0.00249	−2.99281	0.96209	−0.09615	−63747.1	49.7736
bkw covolume	270.0								
jcz2 r	0.000	epsilon/k	0.000						
jcz3 r	3.350	epsilon/k	138.000						
3,) co_2	8.81548	−0.29678	0.04112	−0.00144	−2.46420	0.47372	−0.03511	−102412.8	60.4356
bkw covolume	610.0								
jcz2 r	0.000	epsilon/k	0.000						
jcz3 4	4.200	epsilon/k	200.000						

the c–j condition

the shock velocity is	0.6958508E+04 m/s
the particle velocity is	0.1758834E+04 m/s
the sound speed is	0.5199674E+04 m/s

p0 = 1.00 atm v0 = 0.613 cc/gm e0 = −70.46 cal/gm

b.k.w. equation of state – alpha = 0.50 beta = 0.18 theta = 1850.00 kappa = 11.80

r = reacnts h(r) = h – (−70.443) e(r) = e – (−70.458) s(r) = s – (0.000)

	p (atm)	v (cc/gm)	t (k)	h(r) (cal/gm)	e(r) (cal/gm)	s(r) (cal/k/gm)	vgs (cc/gm)	cv cal/k/gm)	alpha	beta	adexp
1)	0.19688E+06	0.45843E+00	2688.	2555.55	369.69	−0.13788E+01	0.3745E+00	0.6111E+00	3.700	1.590	2.956

constituent concentrations – moles per kgm of explosive

name		1.)
h_2o	gas	7.1441
co_2	gas	6.8512
n_2	gas	6.2345
hco	gas	2.4814
co	gas	0.6067
nh_3	gas	0.7371
h_2	gas	0.1043
ch_4	gas	0.0856
no	gas	0.0001
c_2	gas	0.0000
hcn	gas	0.0000
*c	solid	20.7939
total	gas	24.2460

Figure 3. Partial output from TIGER calculation; TNT detonation.

THE ASTM CHEMICAL THERMODYNAMICS AND ENERGY RELEASE EVALUATION PROGRAM

JOB ID: TEST 6 **JOB ENERGY RELEASE APPRAISAL**

TITLE: TEST CASE #6 – E.R.E. FOR TNT WITH SOME PRODUCTS SPECIFIED

JOB INPUT DATA — JOB INPUT DATA — JOB INPUT DATA

THE COMPOSITION IS
Temperatures: 25 & 25 Kind: 1 Many: 3

# Mols	R/P	Compound	TSN	OPT	PB	#Rec	Tbl	Grp	No
3.00	R	2,4,6–Trinitrotoluene	48	1	0	4	11	205	1
							11	179	3
							11	180	–3
							12	22	2
1.00	P	Nitric Oxide	1	1	0	1	8	11	1
2.0	P	Carbon Monoxide	1	1	0	1	8	18	1

1 x  TOLUENE (TABLE II, GROUP 25)

\+

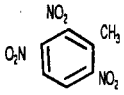
3 x  NITROBENZENE (TABLE 11, GROUP 179)

\+

–3 x  BENZENE (TABLE 11, GROUP 180)

\+

2 x ORTHO INTERACTION BETWEEN ALKANE AND NO2 GROUP ATTACHED TO AROMATIC RING (TABLE 12, GROUP NO. 22)

=  2,4,6 – TRINITROTOLUENE

SCHEME NECESSARY TO APPROXIMATE TNT CHEMICAL STRUCTURE FOR CHETAH INPUT

JOB OUTPUT DATA — JOB OUTPUT DATA — JOB OUTPUT DATA

REACTANT COMPOUND(S)	AMT. (MOLES)	MOL. WT.	ENTHALPY OF FORM.	FORMULA
2,4,6 –TRINITROTOLUENE	3.0	227.1	11.0	$C_7H_5N_3O_6$
PRODUCT COMPOUND(S)				
NITRIC OXIDE	1.0	30.0		
CARBON MONOXIDE	2.00	28.0		
C_1	15.25			
N_2	4.00			
H_2O_1	7.50			
C_1O_2	3.75			

HAZARD EVALUATION

CRITERION NO.	VALUE	RATING
1	–1.25	HIGH
2	–2.34	HIGH
3	–73.97	HIGH
4	168.47	HIGH

THE ENERGY RELEASE POTENTIAL OF THIS MATERIAL (OR MIXTURE) IS << HIGH >>>

Figure 4. Partial output from CHETAH calculation; energy release appraisal for TNT.

computed heat of formation can be used as input to other codes such as BLAKE or TIGER.

OPERATIONAL ASPECTS

Most codes of interest perform either equilibrium or nonequilibrium composition calculations. Equilibrium routines calculate reaction product composition and state, usually based on conservation of mass and energy, and minimization of free energy. Non-equilibrium routines have been devised for special purposes. For example, CHETAH has a non-equilibrium routine which calculates reaction product composition based on maximizing the enthalpy of reaction. This gives a conservative overestimate of energy release, for the purpose of safety evaluation.

The traditional method for calculation of equilibrium composition has utilized equilibrium constants. Such technique involves the breaking down of a chemical equation into lesser equations for which tabulated equilibrium constants (as a function of temperature), defining product composition, can be found resulting in a large system of equations to solve simultaneously. However, more efficient methods for adaptation to computers have been devised which use free energy minimization techniques. Reference 12 gives a good description of and a lesson in the tedious nature of such calculations.

Free energy minimization, as a condition for equilibrium, is derived from the first and second laws of thermodynamics. It can be stated in terms of several thermodynamic functions (i.e., minimization of Gibbs free energy, minimization of Helmholtz free energy or maximization of entropy), using whichever is most convenient. Where a state is characterized by temperature and pressure as in constant pressure combustion applications, Gibbs free energy equation ($G = H - T \cdot S$) is most convenient. From thermodynamic relations,

$$dG = -SdT + Vdp + \Sigma \mu_j \, dn_j, \; \mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n} \quad (1)$$

The subscript j refers to the species.

Where a state is characterized by temperature and volume (or density) as in constant volume explosion applications, then Hemholtz Free Energy (A = U - T*S) is most convenient. From thermodynamic relations,

$$dA = -SdT + pdV + \Sigma \mu_j \, dn_j, \; \mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{T,V,n} \quad (2)$$

Thermodynamic equilibrium is achieved by a reaction when the change in Gibbs free energy, ΔG,

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

reaches an algebraic minimum. For a chemical mixture, Gibbs free energy may be calculated as,

$$G_m = \sum_{j=1}^{N} \mu_j n_j \quad (4)$$

subject to constraints of the mass balance of the chemical reaction. The species chemical potential, j, is calculated as follows.

$$\mu_j = \mu_j^o + RT \ln \left(\frac{n_j}{n}\right) + RT \ln p$$

for ideal gases (5)

$$= \mu_j^o$$

for condensed materials (6)

μ_j° data is available in JANAF tables and is incorporated in codes.

To minimize G_m a mathematical scheme such as the LaGrange Method is employed. Equations required to obtain equilibrium composition are not all linear in composition variables, and therefore an iteration procedure is required. A Newton-Raphson technique is used in the CECTRP code.

Different equations of state are utilized in different codes. The simplest equation of state is, of course, the ideal gas equation, which is usually sufficient where pressures are lower than a few hundred psi and the amount of condensed product species is very low. However, as the need arises for higher pressures, an equation of

state which is appropriate to a particular application must be utilized as described above. Some codes allow the option of switching to different equations of state, as needed.

Typical code inputs vary with the code and may include initial conditions of temperature, pressure, density, reactant species and moles, species chemical structure, reactant enthalpies of formation, etc., as needed. While initial conditions and reactants are chosen by the user, chemical structures and heats of formation are usually obtained from handbooks. Heats of formation can also be calculated by CHETAH.

Typical outputs (depending on the code) may include product species composition, reaction pressure, reaction temperature, mixture thermodynamic properties, heat of reaction, heat of combustion, etc., as called for. Various calculation output options are available depending on the code.

The following have been found to be useful to the author:

Constant Pressure Combustion Equilibrium This option is useful for ordinary atmospheric pressure combustion problems, though any initial pressure condition can be specified. The most useful code for this option is CECTRP. With this option, product species can be estimated, heat of combustion or reaction can be estimated for heat release calculations, and adiabatic flame temperatures can be estimated for heat transfer applications.

An effective flame temperature for use in radiation calculations can be derived from the adiabatic version by derating the heat of combustion by an appropriate amount (i.e., 20-40%[12]), and iteratively summing the enthalpies of product species for a given temperature. When that sum equals the derated heat of reaction, an effective flame temperature is found.

Estimation of product species is useful for determining if specific gases of interest (e.g., toxic gases) were generated in a fire incident. However, care must be exercised in estimating the available air to the fire for which product species are sensitive to. Such estimates can be used as inputs to compartment fire models where applicable experimental data is lacking.

Aside from standard atmospheric pressure, other constant pressure environments can be studied as well. Some environments of interest include hypobaric or hyperbaric chambers and high altitude conditions.

Constant Volume Explosion Equilibruim This option is useful for prediction of maximum gaseous explosion pressure in a closed volume. Though a heterogeneous mixture is assumed by the program, it can also be used to calculate maximum pressure in a volume with certain nonheterogeneous mixtures (see example cases). TIGER, BLAKE and CECTRP have this option available. This option has also been useful for determining whether reactant mixtures can explode or not. TIGER has been most useful in this respect for solid/liquid reactants, while CECTRP is most useful for gaseous reactants.

C-J Detonation and Associated Parameters This option predicts C-J parameters (e.g., detonation pressure, temperature, velocity) and is most useful for gaseous or condensed phase detonation problems. TIGER and CECTRP have this option available.

Isentropic Expansion of Reaction Products This option conducted in conjunction with a Constant Volume Explosion or C-J Detonation calculation permits an examination of product species change, temperature, etc., as a specified constant entropy expansion is undertaken. TIGER and BLAKE have this option available. Maximum expansion work can be computed from such a calculation.

Maximum Energy Release and Hazard Potential This CHETAH option allows a quick estimation of the maximum energy release of a material and then uses four combined correlations to suggest a level of sensitivity (or hazard evaluation) for the material. The four correlations are based on heat of reaction, the difference between the heat of combustion and reaction, and oxygen balance of the mixture or chemical.

Thermodynamic Property Estimation This

CHETAH option allows estimation of ideal gas heat capacity, entropy, heat of formation and heat of combustion, at different temperatures. Methods of Benson and others[7] are used to estimate such properties, by summing the individual properties of the material's chemical structural components.

EXAMPLE CASES

A few examples which demonstrate the utility of the codes are described below.

TIGER: Hazard Evaluation of a Complex Mixture

The TIGER code was exercised in support of a recent lawsuit where a type of varnish base mixture used in ink formulations allegedly exploded when overheated, due to a runaway reaction. Several workers were severely burned in the accident. Additional complications included the alleged contamination of one of the solvent ingredients with peroxides. The mixture consisted mainly of various plastic resins, isopropyl alcohol, butyl carbitol acetate, and nitrocellulose. Due to the high nitrocellulose content, the possibility of explosion could not be simply dismissed. Constant volume explosion analysis of several potential recipes including those with peroxide contamination was undertaken. Results indicated that the explosion hazard was negligible for most mixtures (based on heat of reaction and temperature correlations)[13,14]; moderate for a mixture containing 10 peroxides (unlikely composition). It was concluded that the varnish mixture itself did not explode as was alleged, and that the explosion witnessed was that due to solvent vapor from the overheated mixture accumulating in the room and igniting from a number of possible causes. The case was settled quickly for a small fraction of asking settlement.

CHETAH: Problems with Halogenated Agents

Literature (such as case 1465 in Reference 1) indicates that several unexpected explosions and fires have occurred involving the combination of certain metal powders and "safe" halogenated solvents. Drop impact testing has been used to evaluate the sensitivity of several of these combinations. Powdered metals such as Al, Mg, Ti, and Ba and halogenated solvents (e.g., carbon tetrachloride, trichloroethylene, perchloroethylene, and trichloroethane) were tested in combination; some explosions or fires resulted.

The author has conducted a number of CHETAH hazard potential calculations to determine if such results can be predicted. As one example, the computed energy release for one of the more energetic combinations involving aluminum and carbon tetrachloride (CCl_4) is consistent with explosive experimental results.

Similar results were computed by substituting carbon tetrafluoride (CF_4) or bromochlorodifluoromethane ($CBrClF_2$) for carbon tetrachloride, suggesting hazardous combinations. Carbon tetrafluoride is under consideration as a possible substitute for Halon 1301. Bromochlorodifluoromethane is more commonly known as Halon 1211.

NFPA 491M[15] lists an incident involving a violent explosion which occurred when adding bromotrichloromethane ($CBrCl_3$) to ethylene (C_2H_4). CHETAH energy release calculations suggest an extreme hazard at a 0.125/1 mole ratio (i.e. 89% ethylene). Again, an interesting comparison calculation is a substitution of carbon tetrafluoride (CF_4), for bromotrichloromethane. This combination results in a higher level of energy release, suggesting a hazardous combination. Perhaps new halon substitutes should be carefully screened for use with some materials.

Diagnostic Evaluation of Contaminated Ammonium Perchlorate Mixtures

TIGER was exercised in support of a lawsuit involving a large ammonium perchlorate (NH_4ClO_4) plant explosion. Different cases were studied involving the contamination of ammonium perchlorate with polyethylene, asphalt and other materials. Results showed definite enhancement of detonation properties such as detonation pressure, temperature, and C-J velocity when appropriately mixed with these contaminants. Results for uncontaminated

ammonium perchlorate correlated well with experimental values[16]. Also, flame temperatures were estimated for ammonium perchlorate/contaminant mixtures for use in radiation heat transfer calculations.

CHETAH: Tetrahydrofuran Thermodynamic Properties

The thermodynamic data option was exercised in CHETAH to obtain thermodynamic data for tetrahydrofuran (C_4H_8O) vapor at room temperature and 300 °C. This compound is a solvent used in the synthesis of plasticizers, resins and similar materials. Of particular interest were heat capacity data for use in heat transfer calculations and a quick estimate of heat of combustion for rate of heat release estimates. Such data was not readily available in handbooks.

CECTRP: Gas Mixture Explosion Hazard

A hazard evaluation of a large science laboratory experiment area was undertaken. One hazard to evaluate was a particular scenario involving a mixture of ethane, argon and air within large enclosed experimental vessels. Explosive properties of the mixture were evaluated using constant volume explosion and C-J detonation options of CECTRP. Of particular concern were the maximum pressures which can be developed under certain conditions. Calculated maximum pressures (413 KPa, ~60 psig) were much higher than the design strength of the vessels.

TIGER: Small Bomb in a Room

The maximum pressure possible in a 3 m^3 room with a 0.5 Kg TNT bomb explosion was estimated using TIGER. Input to the code included both air and TNT as reactants. Since TNT is oxygen deficient, additional energy is released during the explosion fireball expansion from reaction with air. A 96 KPa (14 psig) overpressure was calculated. Room walls are expected to yield before reaching this pressure unless they are very strongly reinforced.

CAVEATS

Thermodynamics doesn't indicate anything about the rate of which chemical changes take place or the mechanism of such change. None of the codes described utilize kinetics, which determines the rate of reaction. A reaction which is thermodynamically possible is not necessarily a hazardous reaction, unless its kinetics permit it. Some experience-related Arhenius kinetics can be inferred in these calculations. For example, an equilibrium flame temperature of at least 1400 K (2060 °F) is necessary to achieve a self-sustaining hydrocarbon-air reaction[14]. CHETAH also utilizes experience-related kinetic correlations, providing a measure of hazard potential based on four correlations involving energy release and oxygen balances.

A knowledge of chemical structures is necessary for some calculations (e.g., estimation of heat of formation or thermodynamic properties). Wrong assumptions of chemical structures result in inaccurate results. A chemist should be consulted when unsure.

Only product species present in code libraries can be considered in an equilibrium calculation. New species can usually be inserted into a library, when the data are available. CECTRP has one of the more extensive product libraries.

All mixtures evaluated with the codes are assumed to be heterogeneously mixed. Non-uniform mixtures must be evaluated carefully since results computed may deviate significantly from reality, usually due to an incomplete extent of reaction.

Experience is required for interpretation and manipulation of some calculations. For example, calculations involving the combustion of metals which result in significant amounts of condensed product species (e.g., aluminum oxides) require special interpretation and manipulation to achieve reasonable results with some codes. Sometimes a code such as CECTRP is used as a diagnostic tool for these types of problems before input to such a code as TIGER.

Code results are no substitute for experimental test data, though do provide reasonable estimates in many cases. Tests should be considered (e.g.

ASTM Stability[17], Thermogravimetric Analysis, Differential Scanning Calorimetry, Accelerated Rate Calorimetry, etc.) or experimental test results from literature should be obtained whenever interpretation of results is questionable. Some chemical laboratories routinely use CHETAH for screening new chemical compounds, coupled with a small scale testing program.

Conclusions

Several available thermodynamic computer codes have shown to be useful tools for use in fire/explosion investigation, particularly in reconstruction analysis. The advanced fire protection engineer/investigator should be aware of them and their limitations.

List of Symbols

G = Gibbs free energy, kJ/mole (kcal/mole)
A = Helmholtz free energy, kJ/mole (kcal/mole)
H = enthalpy, kJ/mole (kcal/mole)
S = entropy, kJ/mole (kcal/mole)
U = internal energy, kJ/mole (kcal/mole)
T = temperature, K (R)
P = total pressure, MPa or atmosphere
V = volume, cubic meters (cubic ft)
R = universal gas constant, kJ/mole-K
μ = chemical potential, kJ/mole (kcal/mole)
n = number of moles

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