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from: Hobbs ML (1516, MS0836)

subject: Implementation of a PETN failure model using ARIA's general chemistry framework

Summary

We previously developed a PETN thermal decomposition model that accurately predicts thermal ignition and detonator failure [1]. This model was originally developed for CALORE [2] and required several complex user subroutines. Recently, a simplified version of the PETN decomposition model was implemented into ARIA [3] using a general chemistry framework without need for user subroutines. Detonator failure was also predicted with this new model using ENCORE. The model was simplified by 1) basing the model on moles rather than mass, 2) simplifying the thermal conductivity model, and 3) implementing ARIA's new phase change model. This memo briefly describes the model, implementation, and validation.

Model

Table 1 shows the conservation equations, chemical mechanism, and rate equations used in the decomposition model. Table 2 gives the auxiliary equations used to calculate the pressure. Table 3 presents the nomenclature and model parameters. The one-step mechanism shows PETN going directly to equilibrium products calculated with TIGER [4] at atmospheric pressure and 400 K. The product hierarchy did not vary much from this composition as long as the temperature was above the boiling point of water. The thermal conductivity was determined by matching the finite element predictions of the center temperature to the measured temperature during the initial transient ramp experiment #103.

Predicted ignition times

Figure 1 shows good agreement between the predicted and measured internal temperatures and pressure for SITI experiment #103. Figure 1 demonstrates the model ability to replicate details from a single experiment. Figure 2 shows a comparison for predicted and measured ignition times for a large number of the SITI and ODTX experiments [1]. The solid lines are predictions using the new implementation of the PETN model into ARIA. The dashed lines are the predictions using the older implementation of the PETN model using CALORE. Both models give acceptable predictions with the SITI predictions being quite similar. The ODTX predictions using the CALORE model seem to match the data better for faster cookoff scenarios. The newer model did not use the ODTX data for calibration, only the SITI data. The ODTX data could be made to fit better and is suggested in the Future Work Section. The interested reader can find more detail about the experiment specifics in reference [1].

Predicted detonator failure

Figure 3 shows the predicted failure of a detonator using several different models described in [1]. The cyan line was predicted with the original CALORE model using a 2D model. The new ARIA model is shown in red using

the same mesh. Two other threshold predictions are shown in Fig. 3 using an pseudo 3D model and a 3D model with the actual geometry. The failure criterion (referred to as crit4) for the new model was changed from 6×10^{-4} to 4×10^{-4} with this new ARIA model. This new value is expected to perform as well as the older CALORE model.

Future Work

We have made several improvements in the SITI apparatus. We suggest that additional PETN experiments be performed with PETN at various densities and ullages. SITI experiments should be performed to determine if PETN decomposition is pressure dependent. We also believe that PETN with various binders should be investigated to determine cookoff characteristics. Also, we believe detonation failure should be studied further. Perhaps we could investigate the propagation of a detonation wave unto a booster to determine a failure criterion for systems where a PETN detonator is used with a booster charge.

Summary and Conclusions

We have implemented a simple PETN ignition model into ARIA using the new general chemistry framework. This model was implemented in a timely fashion (in under 1 week) including fitting of new parameters for a mole based chemistry model with melt acceleration. The thermal conductivity was determined by comparisons of ARIA predictions of the initial temperature ramp in SITI experiment #103. The ignition times were determined using SITI ignition data. The ODTX data was not used in the fitting procedure. However, better agreement could be obtained by using this data to set the melt acceleration factor.

We used the model to predict the failure of a detonator. We used the same form of the failure criterion as documented in Ref. [1]. We had to change the critical failure criterion from 6×10^{-4} to 4×10^{-4} to get similar results. This new threshold value should be used with the current implementation of the PETN model.

We have shown in previous work that nitramine explosives such as TATB, HMX, and RDX are pressure dependent. We believe that PETN might also be pressure dependent, but we currently do not have experimental evidence supporting this hypothesis for PETN. We propose that further experiments and modeling be performed on PETN and PETN bonded with various binders.

TABLE 1. PETN ignition model[a]

Energy conservation	$\rho_b C_b \frac{\partial T}{\partial t} = \nabla\cdot\left(k\nabla T\right) + rh_r$	(1)
Mechanism	$\mathrm{PETN}\ (C_5H_8N_4O_{12}) \rightarrow 4.12CO_2 + 3.76H_2O + 2N_2 + 0.12CH_4 + 0.76C$	(2)
	or	
	$\mathrm{PETN} \rightarrow 10\mathrm{Gas} + 0.76\mathrm{C}$	(3)
Rates	$r = A\xi\exp\left(\frac{-E+\zeta\sigma}{RT}\right)[\mathrm{PETN}]$	(4)
Species conservation	$\frac{d[\mathrm{PETN}]}{dt} = -r\ ;\ \frac{d[\mathrm{Gas}]}{dt} = +10r\ ;\ \frac{d[C]}{dt} = +0.76r$	(5)
Distribution parameter,[b]	$\zeta = \mathrm{norminv}\left(\frac{[\mathrm{PETN}]}{\rho_{b,o}/Mw_{PETN}}\right)$	(6)

[a]Nomenclature and model parameters are given in Table 3.
[b] "norminv" is the inverse of the standard normal cumulative distribution function that has a mean of 0 and a standard deviation of 1.

TABLE 2. Auxiliary equations used to calculate the thermodynamic pressure[a]

Pressure	$P = \frac{nRT_{ave}}{V_g}$	(7)
Gas moles	$n = \int_V [Gas]\, dV$	(8)
Ave. gas temperature	$T_{ave} = \frac{\int_V \rho C T\, dV}{\int_V \rho C\, dV}$	(9)
Gas volume	$V_g = \int_V \phi\, dV$	(10)
Gas volume fraction	$\phi = 1 - \frac{S_f \rho_{c,o}(1-\phi_o)}{\rho_c}$	(11)
Reacted solid fraction	$S_f = \left([\mathrm{PETN}] Mw_{\mathrm{PETN}} + [\mathrm{C}] Mw_{\mathrm{C}}\right) / \rho_{bo}$	(12)
Condensed density	$\rho_c = \rho_{c,o}\left[1 - 0.000275\left(T - T_o\right)\right]$	(13)

[a]Nomenclature and model parameters are given in Table 3.

TABLE 3. Nomenclature and model parameters

Symbols	Description	Value	Units
Ln(A)	Logarithm of pre-exponential factor	35	$Ln(s^{-1}K^{-n})$
C_b	Bulk specific heat	below 250 K: 1090 above 623 K: 1760 250 to 623 K: linear interpolation	$Jkg^{-1}K^{-1}$
[C]	Carbon concentration	Initially 0	$kgmol/m^3$
E/R	Activation energies divided by R	16120	K
ϕ	Gas volume fraction	Field variable	m^3/m^3
ϕ_o	Initial gas volume fraction	$1-\rho_{bo}/\rho_{co}$	m^3/m^3
[Gas]	Product gas concentration	Initially 0	$kgmol/m^3$
$h_{f,i}$ where i= PETN, gas, carbon	Heat of formation of species	-593.0×10^6, -253.8×10^6, 0	$Jkgmol^{-1}$
h_{latent}	Latent enthalpy (melting)	1.77×10^5	$J\ kg^{-1}$
k	Thermal conductivity	below 413 K: 0.24 above 419 K: 0.02 413 to 419 K: linear interpolation	$Wm^{-1}K^{-1}$
$M_{w,i}$, where i= PETN, Gas, C	Molecular weight of species	316.1, 30.7, 12.0	kg/kgmol
n	Moles of gas	Field variable	kgmol
normsinv	Inverse of the standard normal distribution	function	none
P	Pressure	Initially 0	MPa (psig)
P_o	Initial pressure	0.08 (12.1) SITI, 0.1 (14.7) ODTX	MPa (psia)

[PETN]	PETN concentration	Initially $\rho_{bo}/M_{w,PETN}$	kgmol/m^3
ρ	Bulk density	Field variable	kgm^{-3}
$\rho_{b,o}$	Initial bulk density	Detonator: 890 ODTX: 1682 SITI: 1682	kgm^{-3}
ρ_c	Condensed density	Field variable	kgm^{-3}
$\rho_{c,o}$	Initial condensed density (TMD)	1780	kgm^{-3}
R	Gas constant	0.08206	m^{3}atm kgmol^{-1} K^{-1}
R	Gas constant	8314	J kgmol^{-1}K^{-1}
σ/R	Distribution parameters divided by R	-1350	K
S_f	Reacted solid fraction	Field variable	kg/kg
T	Temperature	Field variable	K
T_{ave}	Average gas temperature	Global variables	K
T_{melt}	Melting point	416 (normal distribution over 413-419)	K
T_o	Initial temperature	300 K	K
V_g	Gas volume	Global variable from Eqn. 11	m^3
ζ	normsinv	Field variable	none
ξ	Melt rate acceleration factor	1+0.5*(1+tanh[(T-416)/3])*4	none

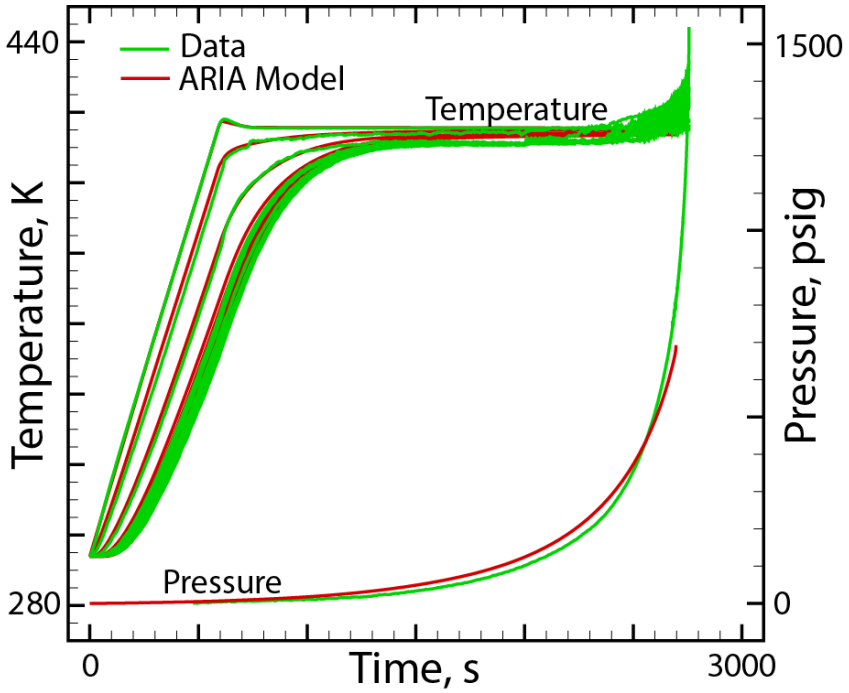

Figure 1. Predicted (red lines) and measure (green lines) temperature and pressure from SITI run #103

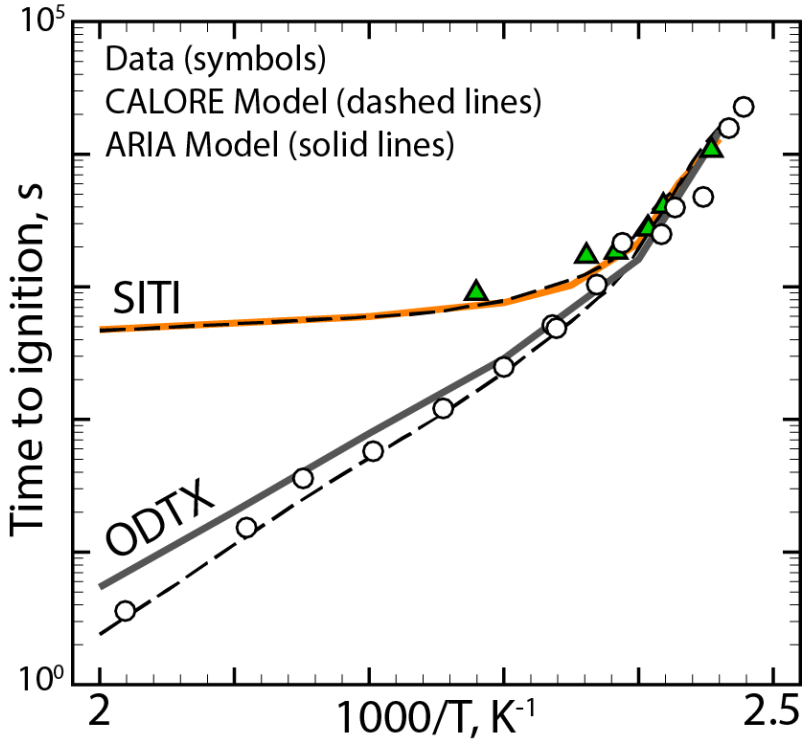

Fig. 2 Predicted (lines) and measured (symbols) ignition times from

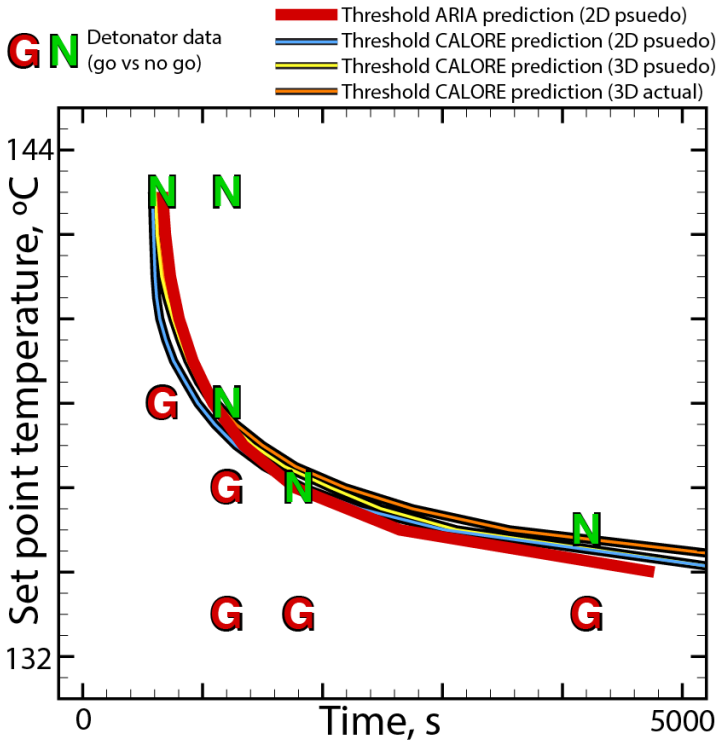

Fig. 3. Failure plot for detonator. The detonator was ramped to the set point temperature in 10 minutes and held at the set point. The device was then given the design electrical signal and the output signal recorded. A fully functional detonator was designated as a "go" and is depicted in the plot as a red "**G**." If the device failed to give the correct output signal, the test was considered a "no go" and is depicted in the plot as a green "**N**."

Sample ARIA Input Deck (EXCERPTS FROM AN ARIA INPUT DECK)

Here is kinetics include file (kinetics.inc)

```
#*********************************************************************
#-Reaction parameters (5-step model)
#*********************************************************************
# sorbed gas
# {e1 = 16120}
# {s1 = -1350}
# {lna1 =  35}
# {zeta =  4} Melt rate acceleration
#
# NOTES:
#*********************************************************************
# Kinetics for 1-step PETN decomposition model
#
# PETN (C5H8N4O12) --> 4.12 CO2 + 3.76 H2O + 2 N2 + 0.12 CH4 + 0.76 C
# PETN --> 10 Gas + 0.76 C
#
#*********************************************************************
```

Here is PETN include file (petn.inc):

```
{ECHO(OFF)}
{include("kinetics.inc")}
#*********************************************************************
# PETN decomposition model
#*********************************************************************
# Initial bulk density, true density, gas vol. frac., and gas mass.
#*********************************************************************
# rbo  = {rbo  = 1682.}  bulk density, kg/m^3
# rco  = {rco  = 1780.}  condensed density, kg/m^3
# to   = {to   = 293.90} temperature, K
# po   = {po   = 12.09}  pressure, psi
# gmwo  = {gmwo  = 27.8}   gas mol. wt., Kg/Kgmol
# rgo  = {rgo  = (101325*po/14.7)*gmwo/to/8314.} gas density, Kg/m^3
# phio  = {phio  = (rco-rbo)/(rco-rgo)}      gas volume fraction
# vem  = {vem  = 12.87e-6} EM volume (does not include ullage), m^3
# gmaso = {gmaso = rgo*phio*vem  }          gas mass in EM block, kg
#*********************************************************************
# Initial compositions, molecular weights, and heat of formations
#*********************************************************************
# reactants/products  kg/kgmol                          J/kgmol
# mw_petn  = {mw_petn  = 316.137} hf_petn  = {hf_petn  = -593.0e6}
# mw_gas   = {mw_gas   = 30.7}    hf_gas   = {hf_gas   = -253.8e6}
# mw_carbon = {mw_carbon = 12.0}    hf_carbon = {hf_carbon =    0    }
# covol    = {covol    = 496.} BKW covolume
#*********************************************************************
# Volume of gaps (vgaps) and initial moles of gas (no)
#*********************************************************************
# Volumes for gas       m^3
# ullage = {ullage = 1.48e-6}     Expansion gaps
# vtube  = {vtube  = 0.08e-6}     Tube to transducer
# vgaps  = {vgaps = ullage+vtube} Volume where gas might flow occupy
# no = {no=po*(phio*vem+vgaps)/1.206282/to} Initial gas moles, kgmol
#*********************************************************************
# beta-delta phase change and melting
#*********************************************************************
# hm  = {hm   =  1.77e5} Enthalpy of melting, J/kg
# tm  = {tm   =     416} Melting point, K
# dtm = {dtm  =       3} Half of the mush zone width for b-to-d, K
# tl  = {tl   =  tm-dtm} Temperature where melting starts, K
# th  = {th   =  tm+dtm} Temperature where melting ends, K
#*********************************************************************
# Thermal conductivity (linear interpolation)
#*********************************************************************
# klot = {klot = 0.24}
# khit = {khit = 0.02}
```

Here is the ENCORE include file (encore.inc):

```
{ECHO(OFF)}
{include("petn.inc")}
 ################################################
 ############ ENCORE POSTPROCESSORS ##############
 ################################################

# ... Output File Specifications ...
 Begin Postprocessor Output Control encore_out
   Output Time
   Write To File o_encore.plt
   Floating Point Precision Is 5
   Floating Point Format Is scientific
 End

# ... Create Encore Field Functions ...
 Begin Field Function T_field
  Use Nodal Field solution->Temperature
 End

# ... rhoc [=] kg/m3, condensed-phase density
 Begin String Function rhoc
   Value is "{rco}*(1-0.000275*(Ti-{to}))"
   Use Function solution->Temperature as Ti
 End

# ... sf_e, reacted solid fraction
 Begin String Function sf_e
   Value is "(petn*{mw_petn}+carbon*{mw_carbon})/{rbo}"
   Use Function petn
   Use Function carbon
 End

# ... phi_e [=] m3_gas/m3_mix, encore gas volume fraction
 Begin String Function phi_e
   Value is "1-sf_e*{rco}*(1-{phio})/rhoc"
   Use Function rhoc
   Use Function sf_e
 End

# ... vg_e, Gas volume in energetic material [=] m3
 Begin Integrate Function Postprocessor vg_e
    Use Function phi_e
    Volumes block_10
 end

# ... petn [=] kgmol/m3
 Begin Field Function petn
   Use Nodal Field Solution->Species_petn
 End

# ... gas [=] kgmol/m3
 Begin Field Function gas
   Use Nodal Field Solution->Species_gas
 End

# ... carbon [=] kgmol/m3
 Begin Field Function carbon
   Use Nodal Field Solution->Species_carbon
 End

# ... kgmol_gas_i [=] kgmol/m3, Total kgmol/m3
 Begin String Function kgmolgasi
   Value is "gas"
   Use Function gas
End

# ... n_e, Total moles of Gas [=] kgmol
 Begin Integrate Function Postprocessor n_e
   Use Function kgmolgasi
```

```
  Volumes block_10
 End

# ... Tave, AVERAGE (gas) Temperature ...
 Begin Average Value Postprocessor Tave
  Use Function T_field
  Volumes block_10
 End

# ... x, BKW parameter
 Begin String Function x_e
  Value is "(n_e+{no})*10.5e-3*{covol}/(vg_e+{vgaps})/sqrt(Tave+6620)"
  Use Function n_e
  Use Function vg_e
  Use Function Tave
 End

# ... z, BKW compressibility
 Begin String Function z_e
  Value is "1+x_e*exp(0.298*x_e)"
  Use Function x_e
 End

 Begin String Function psia_e
  Value is "14.7*z_e*(n_e+{no})*0.08206*Tave/(vg_e+{vgaps})"
  Use Function z_e
  Use Function n_e
  Use Function Tave
  Use Function vg_e
 End

 Begin String Function psig_e
  Value is "psia_e-{po}"
  Use Function psia_e
 End

 Begin Evaluate Function Postprocessor p_ave
  Use Function psig_e
  Evaluate value
  Location 0 0 0
 End
```

Here is the PETN material model from the ARIA input deck (siti.apr):

```
 Begin Aria Material petn
  Heat Conduction = Basic
  Density = Constant Rho = {rbo}
  Specific Heat = User_Function X=temperature Name = petn_C
  Thermal Conductivity = User_Function X=Temperature Name = petn_k
  Species Names = petn gas carbon
  Pressure = encore_function Name = psia_e
  Molecular_weight of petn   = constant M= {mw_petn  }
  Molecular_weight of gas    = constant M= {mw_gas   }
  Molecular_weight of carbon = constant M= {mw_carbon }
  Specific Heat of petn   = User_Function X=Temperature NAME = petn_C
  Specific Heat of gas    = User_Function X=Temperature NAME = petn_C
  Specific Heat of carbon = User_Function X=Temperature NAME = petn_C
  Begin general chemistry petn_chem
   Species Names = petn gas carbon
   Species Variable Name = Species # molar-based (Density for mass-based)
   Universal Gas Constant = {rgas} #  8314 J/kgmol-K, unless specified
   Enthalpy of Formation for petn   = {hf_petn  } # J/kgmol
   Enthalpy of Formation for gas    = {hf_gas   } # J/kgmol
   Enthalpy of Formation for carbon = {hf_carbon} # J/kgmol
   Begin Reaction R1
    Reaction is petn -> 10gas + 0.76carbon
    Rate Function = Distributed_Arrhenius A = {exp(lna1)} Ea = {e1} sigma = {s1} y0 = {rbo/mw_petn} ProgressSpecies = petn R = 1
    Concentration Function = Standard  mu = Automatic
    Pressure Function = Exponential P_ref = {po} n = {n1}
    Multiplier function = General Function = (T^{m1})*(1+0.5*(1+tanh((T-{tm})/{dtm}))*{zeta})
   End Reaction R1
```

```
  END general chemistry petn_chem
 End Aria Material petn

 Begin Definition for Function petn_C  # [=] J/kg_K
  Type is Piecewise Linear
  Begin Values
    250.0, {1090}
    298.0, {1090}
    623.0, {1760}
   3000.0, {1760}
  End Values
 End

 Begin Definition for Function petn_k  #
  Type is Piecewise Linear
  Begin Values
     250  {klot}
     298  {klot}
    {tl} {klot}
    {th} {khit}
    3000  {khit}
   End Values
 End
```

Here are Governing equation definitions from the ARIA input deck (siti.apr):

```
    EQ ENERGY for Temperature on explosive using Q1 with Lumped_Mass Diff SRC
    EQ ENERGY for Temperature on inert using Q1 with Lumped_Mass Diff
    Source for Energy on explosive = Chemistry Mechanism = petn_chem
    Source for Energy on explosive = Melting Ts = {tl} Tl = {th} latent_heat = {hm}
#    ... Species Equations
    EQ Species FOR species OF petn   ON explosive using Q1 with Lumped_Mass SRC
    EQ Species FOR species OF gas    ON explosive using Q1 with Lumped_Mass SRC
    EQ Species FOR species OF carbon ON explosive using Q1 with Lumped_Mass SRC
    Source FOR species OF petn   ON explosive = chemistry Mechanism = petn_chem
    Source FOR species OF gas    ON explosive = chemistry Mechanism = petn_chem
    Source FOR species OF carbon ON explosive = chemistry Mechanism = petn_chem
```

References

1. Hobbs ML, Wente WB, Kaneshige MJ. "PETN Ignition Experiments and Models," *J. Phys. Chem. A*, **2010**, *114*, 5306-5319.
2. Bova SW, Copp KD, Newman CK, *Calore: A Computational Hat Transfer Program*, Sandia National Laboratories Report SAND2006-6083P (2006).
3. Development team, *SIERRA Multimechanics Module: Aria User Manual – Version 4.42*, Sandia National Laboratories, http://compsim.sandia.gov/compsim/Docs/Sierra/preRelease/GeneralRelease (downloaded 2016).
4. Hobbs ML, Brundage AL, and Yarrington CD, "JCZS2i: An Improved JCZ Database for EOS Calculations at High temperature and Pressure," 15th International Detonation Symposium, Office of Naval research, Arlington, Virginai, ONR-43-280-15, 804 (2014).

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