

## Thermal Decomposition of Energetic Materials

Iowa Army Ammunition Plant  
August 28-29, 2018

William W. Erikson

(with input begged, borrowed, and stolen from many colleagues)

# Introduction / Outline

- Who am I?
- Preliminary considerations
- High-level perspective of Sandia Laboratories
  - Overall view
  - Energetic materials-specific
- Thermal Decomposition Trends and Observations
- Thermal Decomposition Experiments (work of Behrens, Maharrey)
  - STMBMS experiments with RDX & IMX-101
- Thermal Ignition / Cookoff of Energetics (work of Hobbs, Kaneshige)
  - SITI Experimental
  - Engineering Model Development
  - Examples with PBX9501, Composition B
- Conclusions, Future Efforts, Acknowledgements

# Who am I?

- PhD 1999, Brigham Young University
  - Advisor: Merrill Beckstead—well known in solid propellant community
  - Dissertation was on using detailed elementary reaction chemistry to study unsteady combustion phenomena, emphasis on RDX
- 19 years at Sandia Laboratories
  - Energetic materials—thermal analysis, decomposition, thermal ignition (cookoff)
  - Pyrotechnic components modeling/simulation
  - Solid propellant fires
  - Heat transfer modeling/simulation for various applications (satellites, NW components, etc.)
  - Energetic Materials Capability Realization Team (provides models for use in full-system representation of nuclear weapons for safety purposes)
- Joint Army Navy NASA Air Force (JANNAF) involvement
  - Participated in Combustion and Propulsion Systems Hazards meetings since about 1995
  - Current co-chair of “Thermal Decomposition and Cookoff” Mission Area

# What might be important to consider

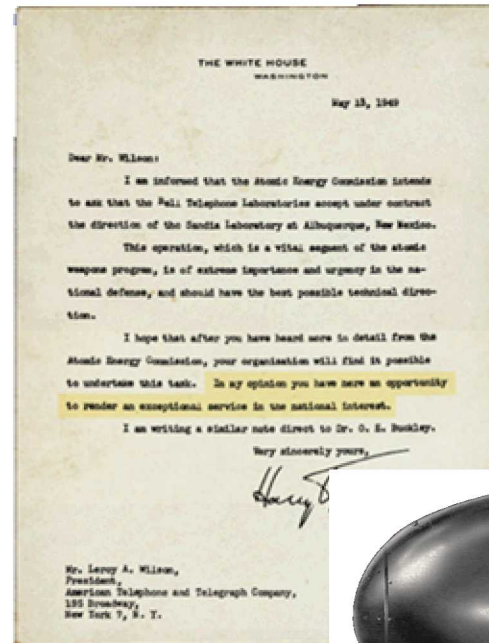
- Preliminary questions, regarding out-of-spec explosive material:
  - Can it be economically retrofitted/reprocessed to fulfil its intended purpose?
  - Is there another use for the excess, out-of-specification material?
    - donor charge for a detonation disposal system?
    - massive experiment for validation? (i.e. a 1 kton non-nuclear shot)
- My background in cookoff, safety analysis makes me think of a few questions for the proposed gasifier disposal method (if you have a hammer, everything looks like a nail):
  - How small do the pieces of explosive need to be so that when a piece explodes / detonates, it won't damage the facility?
  - How dilute does the explosive need to be within the coal/RDX mixture (1%? 10%?) so that explosion of a chunk won't propagate to other explosives in the feed stream?
  - If feed stream is slurry, what chemical reactions might occur within the stream? Any possibilities for self-heating?



# SANDIA'S HISTORY IS TRACED TO THE MANHATTAN PROJECT

*...In my opinion you have here an opportunity to render an exceptional service in the national interest.*

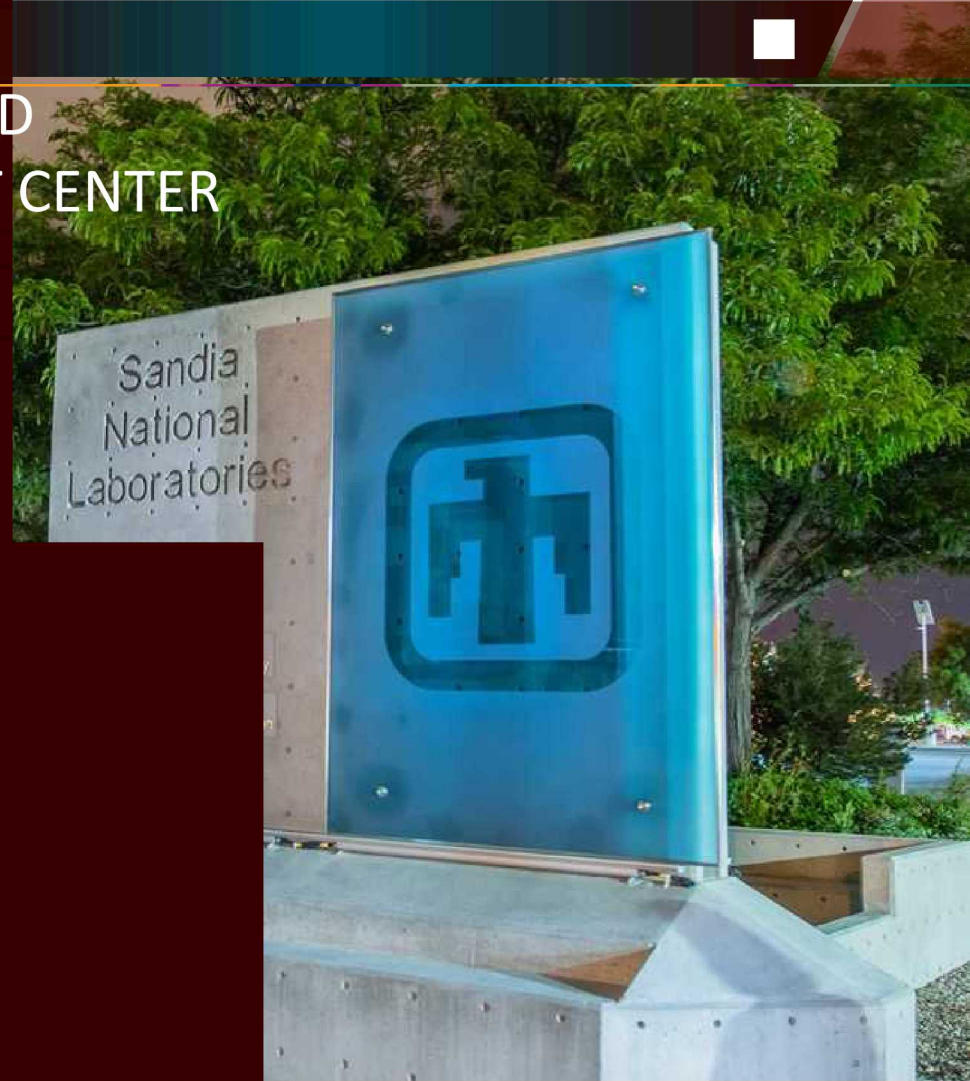
- July 1945  
Los Alamos creates Z Division
- Nonnuclear component engineering
- November 1, 1949  
Sandia Laboratory established
- AT&T: 1949–1993
- Martin Marietta: 1993–1995
- Lockheed Martin: 1995–2017
- Honeywell: 2017–present



SANDIA IS A FEDERALLY FUNDED  
RESEARCH AND DEVELOPMENT CENTER  
MANAGED AND OPERATED BY

National Technology & Engineering  
Solutions of Sandia, LLC, a wholly  
owned subsidiary of Honeywell  
International Inc.: 2017 – present

Government owned, contractor  
operated





# SANDIA HAS FACILITIES ACROSS THE NATION

## Activity locations

- Kauai, Hawaii
- Waste Isolation Pilot Plant, Carlsbad, New Mexico
- Pantex Plant, Amarillo, Texas
- Tonopah, Nevada

## Main sites

- Albuquerque, New Mexico
- Livermore, California



# SANDIA HAS FIVE MAJOR PROGRAM PORTFOLIOS



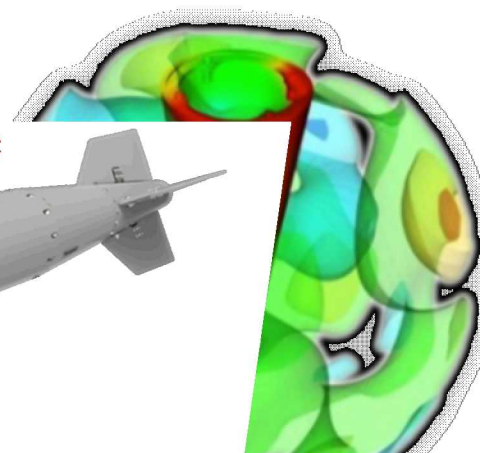


# NUCLEAR DETERRENCE



Responsibilities form a critical mandate

Warhead systems  
engineering &  
integration



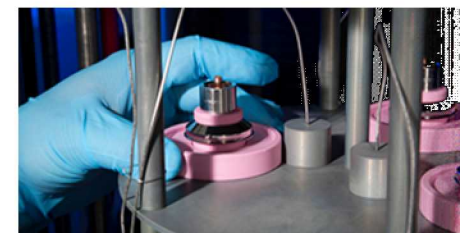
Design agency  
for nonnuclear  
components

- Gas transfer systems
- Radar
- Safety systems
- Arming, fuzing & firing systems
- Neutron generators



Interdisciplinary  
capabilities

Required for design,  
fabrication, production,  
inspection, computation/  
simulation  
Major environmental test  
capabilities & diagnostics  
Materials sciences  
Piggyback-initiated high explosives  
Computational analytics



Production agency

- Neutron generators
- Sandia external production
- Microelectronics
- Thermal battery backup

# Drivers for Energetics Work at SNL

- Sandia is responsible non-nuclear portions of weapons. These components includes a variety of energetic materials (explosives, propellants, pyrotechnics) which produce a variety of functions (detonators, ignitors, timers, actuators, etc.)
- Sandia is also responsible for overall system safety
- Much of our work on energetic materials focuses on the **Always / Never** concept:
  - **The nuclear weapon should ALWAYS function when given the Presidential directive for use.**  
(deterrence depends on reliability; system must have long shelf life and still be reliable, etc.)
  - **The nuclear weapon should NEVER function any other time.**  
(system should not function in spite of mishaps, accidents, an adversary's interventions, etc.)
- We want to understand how energetic materials within a system might behave in a possible accident scenario (e.g. weapon in a fire), so we do experiments and modeling/simulation to allow for safety assessments to be made. Focus is on energetic materials within nuclear weapons.
- In addition to our primary responsibility for nuclear weapons applications, we collaborate with others (e.g. DoD under Joint Munitions Program, Joint Insensitive Munitions Technology Program, etc.). These efforts look at other materials (propellants, explosives) that may have broader applicability.
- We develop tests and experiments as well as computational models that can be used by others.



# Explosives Components Facility

**Sandia's 111,000 sq. ft. Explosive Components Facility (ECF) is a state-of-the-art facility that provides a full-range of chemical, material, and performance analysis capabilities for energetic materials and explosive components:**

- advanced design of energetic devices and subsystems
- optical ordnance
- energetic materials processing, synthesis, and formulation
- rapid prototyping of energetic components and test articles
- additive manufacturing and micro-energetic materials
- testing of explosives and explosive components and subsystems
- advanced explosives diagnostics
- reliability analyses
- failure modes evaluation
- safety evaluation

The ECF has the full-range of capabilities necessary to support the understanding of energetic materials and components:

## Characterization Laboratories

- thermal properties
- gas analyses
- powder characterization
- microscopy, micro CT-scan
- spectroscopy
- aging and compatibility
- triaxial mechanical testing

### User liaison

Leanna Minier (505) 844-2352

[lminier@sandia.gov](mailto:lminier@sandia.gov)

## Performance Test Facilities

- firing pads (to 1 kg)
- instrumentation (temperature, pressure, strain, displacement)
- high-speed camera systems
- high-speed data acquisition systems
- single-stage light gas gun facility
- high and low-pressure combustion chambers
- optical and semiconductor bridge (SCB) initiation laboratories

## Diagnostic Capabilities

- piezoelectric gauges
- VISAR (Velocity Interferometer System for Any Reflector)
- flash x-ray
- electrostatic discharge tester (ESD)
- electro-thermal response tester (ETR)

## Remote Sites support ECF missions

- Explosives Machining
- Terminal Ballistics
- Light-Initiated High Explosives



# Energetic Material Thermal Decomposition Trends

- Energetic materials often exhibit “sigmoidal” decomposition behavior. There is an induction period with slow reaction rate which then accelerates to a peak rate which then tapers off.

(Example 1. with AP)

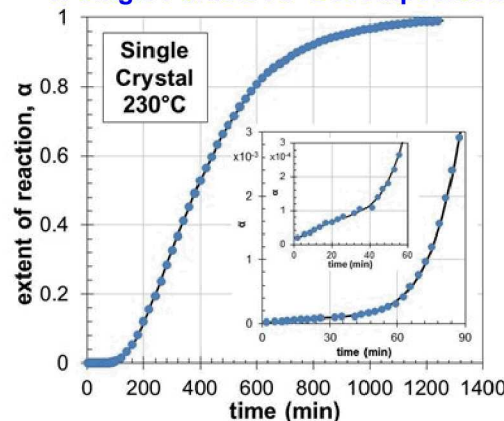
- Many energetic materials have pressure-dependent decomposition behavior (react faster when confined or in a closed vessel, compared with open). Similarly, high density (say pressed) will react faster than ones at low density (e.g. prills).

(Example 2. with PBX 9502)

- Many energetic materials react more quickly in liquid state (melt / dissolved) as compared to solid state.

(Example 3. with RDX)

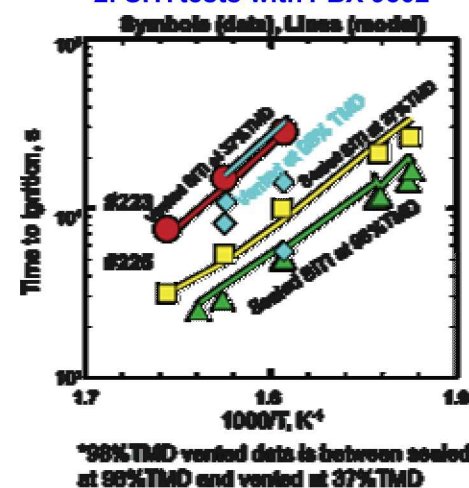
## 1. Single Particle AP Decomposition



P. W. M. Jacobs and W. L. Ng, “A Study of the Thermal Decomposition of Ammonium Perchlorate Using Computer Modelling,” *Reactivity of Solids, Proceedings of 7th International Symposium on the Reactivity of Solids*, Bristol, England, July 1972, J. S. Anderson, M. W. Roberts, and F. S. Stone, eds., (1972) pp. 398-410.

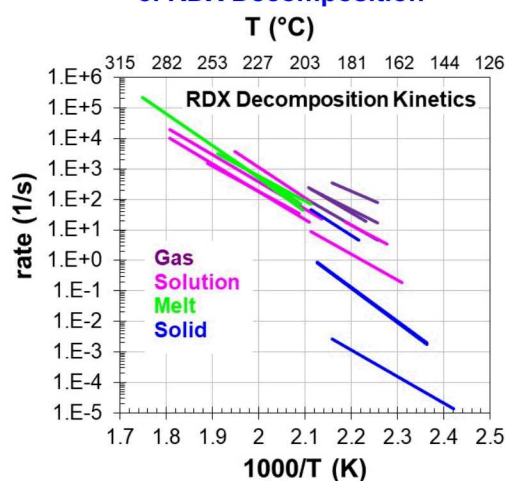
M.L. Hobbs and M.J. Kaneshige, “Ignition Experiments and Models of a Plastic Bonded Explosive (PBX 9502)”, *J. Chem. Phys.*, 140, 124203 (2014).

## 2. SITI tests with PBX 9502

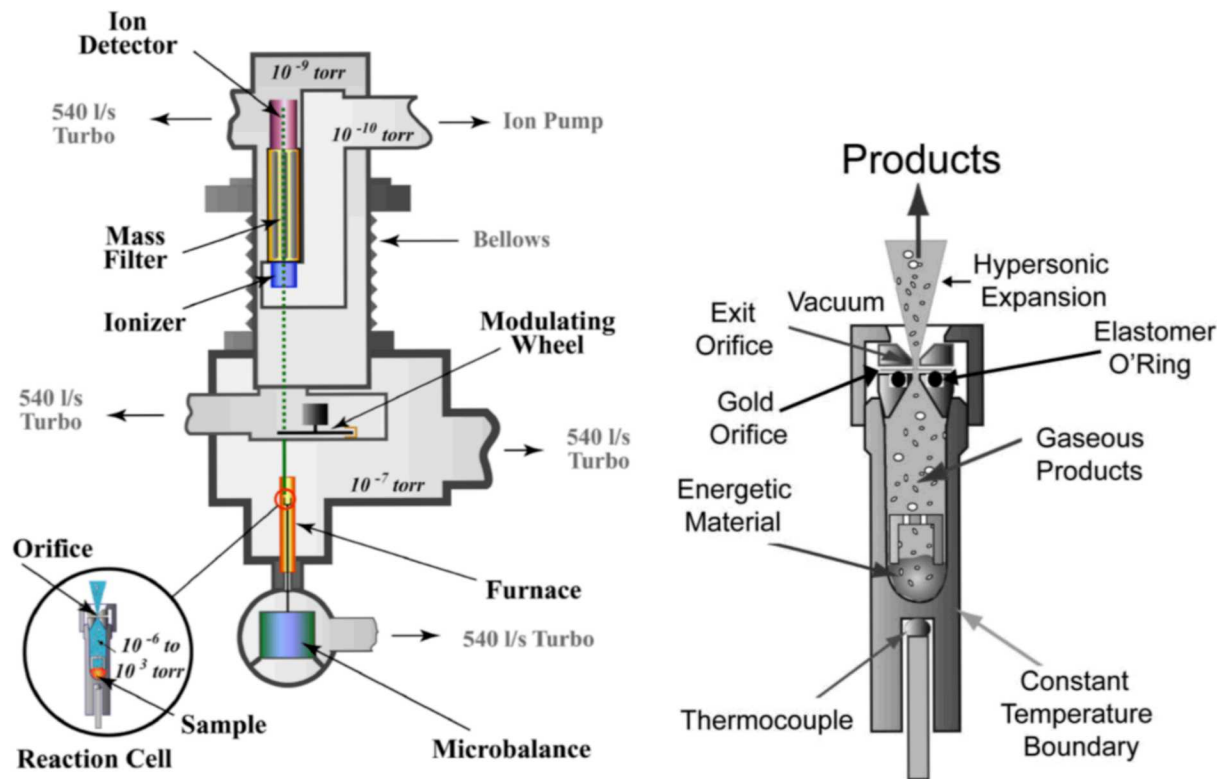


G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov and V. A. Strunin, *Thermal Decomposition and Combustion of Explosives and Propellants*, Taylor and Francis, London, 2003.

## 3. RDX Decomposition



# Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS) Apparatus\*



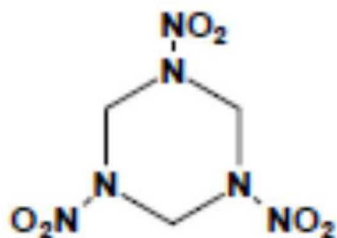
- Apparatus is located in SNL-CA, designed by Rich Behrens (now retired). Several researchers worked with Rich over the past 30+ years. Current P.O.C. is Leanna Minier (SNL-NM).
- Goal is to understand thermal decomposition mechanisms by determining when various product species are evolved from the parent material.
- Various energetic materials have been studied using the apparatus.

\*S. P. Maharrey, D. Wiese-Smith, A. M. Highley, R. Behrens and J. J. Kay, "Interactions Between Ingredients in IMX-101: Reactive Chemical Processes Control Insensitive Munitions Properties," Sandia National Laboratories, SAND2014-2012, March, 2014.



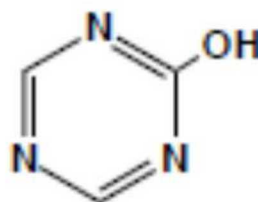
# Maharrey et al. 2002 RDX Decomposition Work\*

cyclotrimethylenetrinitramine  
(1,3,5-trinitrohexahydro-s-triazine, RDX)



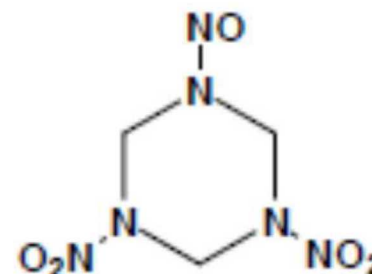
RDX (I)

oxy-s-triazine  
(OST)



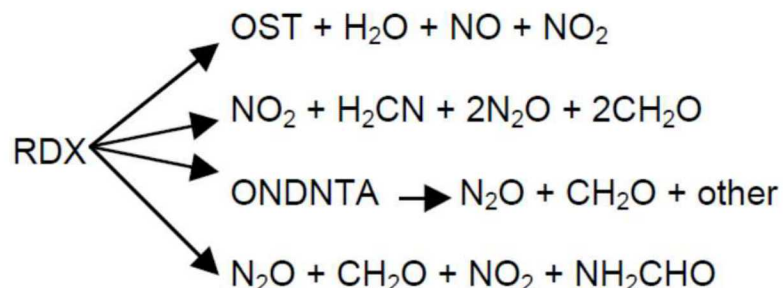
OST

1-nitroso-3,5-dinitrohexahydro-s-triazine  
(ONDNTA, mononitroso RDX analogue)



ONDNTA

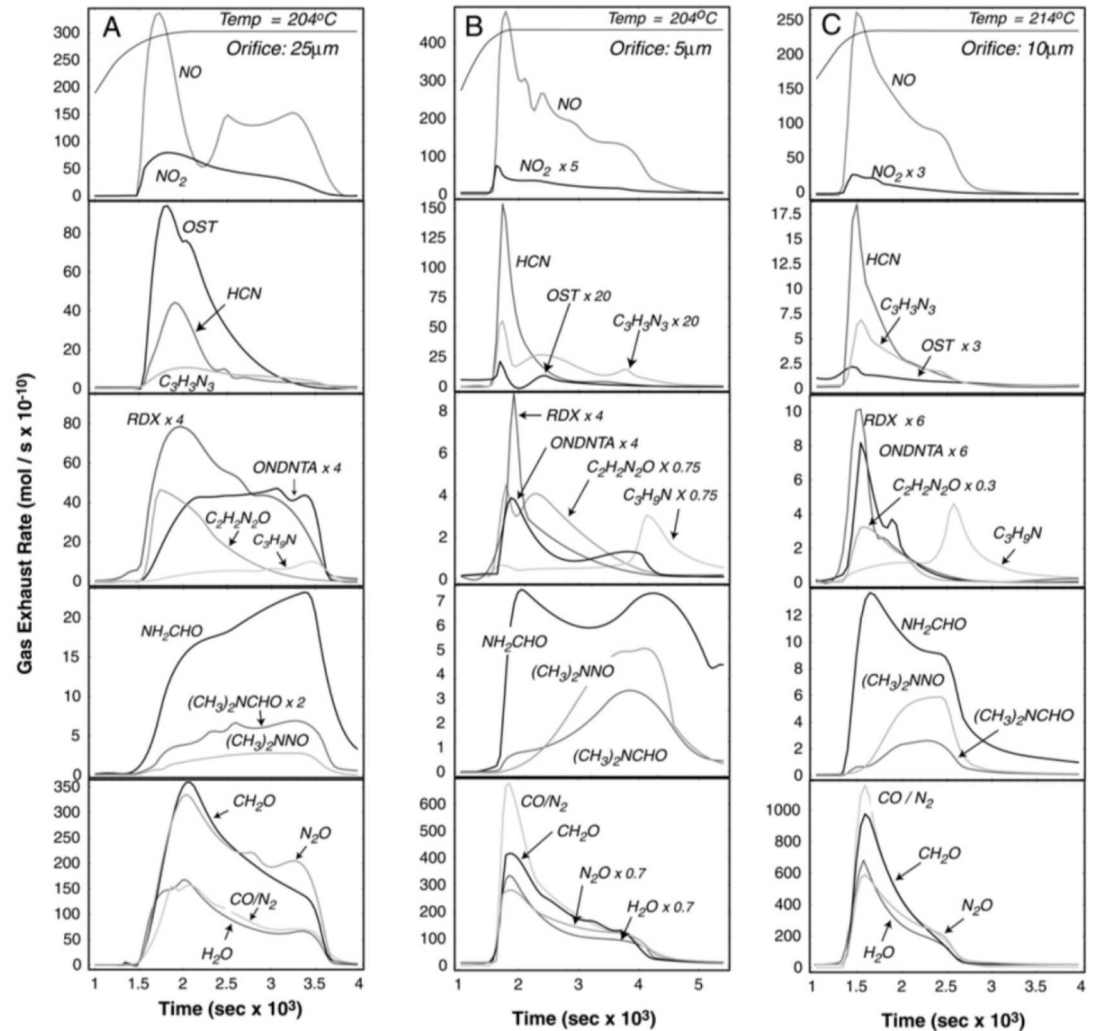
1-nitroso-3,5-dinitrohexahydro-s-triazine  
(ONDNTA, mononitroso RDX analogue)



\*S. P. Maharrey, D. Wiese-Smith, and R. Behrens, "Development of a Physicochemical Model for the Thermal Decomposition of RDX," 38th JANNAF Combustion Subcommittee Meeting, 8-12 April 2002, Destin, FL. Vol I (2002-0458), pp. 373-386.

# Behrens, Maharrey RDX Decomposition

- STMBMS tests with RDX
- Varied the orifice diameter and temperature (in this study, RDX was in the liquid phase; others test conducted at lower temperatures)
- Looked at gas evolution rates of a number of different species.
- Used the data to develop complex reaction pathway scheme (next viewgraph)



R. Behrens and S. Maharrey, "Reaction Kinetics of RDX in the Condensed Phase," JANNAF 39th Combustion Subcommittee Meeting, 1-5 Dec. 2003, Colorado Springs, CO.

# Behrens, Maharrey RDX Decomposition

- Complex reaction cycles
- Different chemistry is activated depending on heating conditions
- Numbered trajectories in chart characteristic of:

- ① TGA/DSC tests
- ② Flash Heating
- ③ Slow Heating

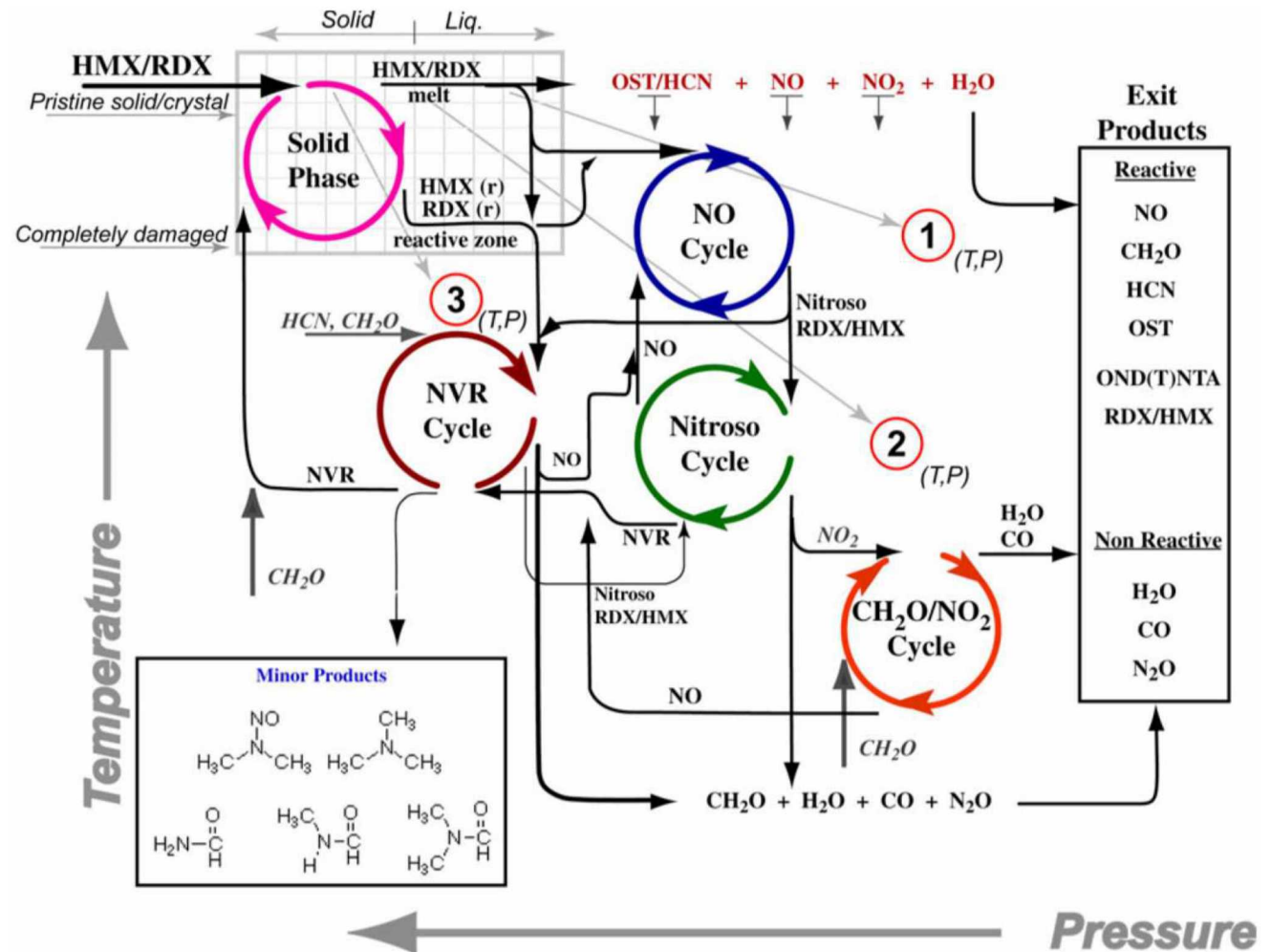


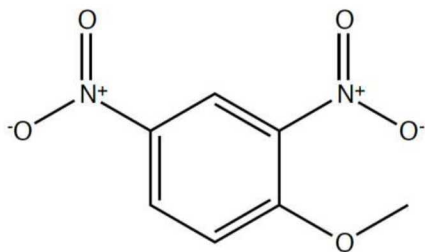
Figure 1. Reaction scheme representing the processes that can control the decomposition of RDX and HMX over a range of conditions. The temperature and pressure coordinates provide a notional view of which reactions will contribute most significantly under different sets of pressure and temperature conditions.

R. Behrens and S. Maharrey, "Reaction Kinetics of RDX in the Condensed Phase," JANNAF 39th Combustion Subcommittee Meeting, 1-5 Dec. 2003, Colorado Springs, CO.



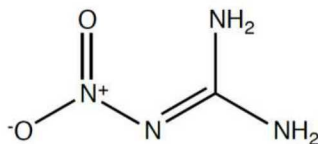
# IMX-101\*

- IMX-101 is a melt-castable insensitive replacement for Comp B (RDX/TNT).
- Contains 3 ingredients (DNAN, NQ, NTO) with formulas below.
- DNAN (2,4 dinitroanisole, aka 1-methoxy-2,4-dinitrobenzene) melts at ~95 °C, processable using steam
- Formulation passed all six IM compliance tests of NATO STANAG 4439.  
(Fast Cookoff, Slow Cookoff, Bullet Impact, Fragment Impact, Sympathetic Detonation, Shaped Charge Jet)
- A study was initiated at SNL to determine if there are chemistry reasons for the insensitivity studied individual ingredients as well as combination using:
  - Tests with STMBMS apparatus
  - Separate tests using FTICR (Fourier Transform Ion Cyclotron Resonance) mass spectrometer



1-methoxy-2,4-dinitrobenzene  
(DNAN)

35 – 45%



2-nitroguanidine  
(NQ)

35 – 45%

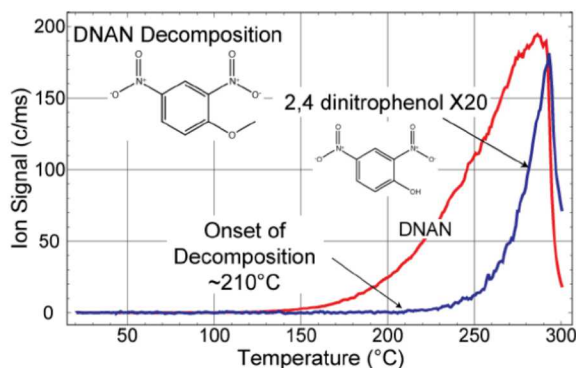


1,2-dihydro-5-nitro-1,2,4-triazol-3-one  
(NTO)

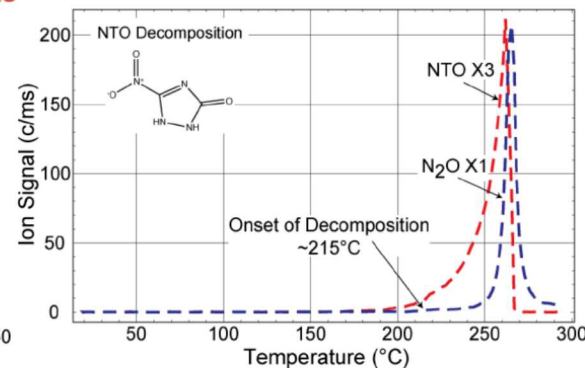
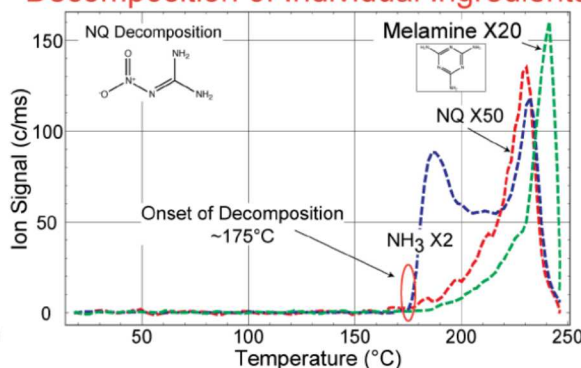
15– 25%

\*S. P. Maharrey, D. Wiese-Smith, A. M. Highley, R. Behrens and J. J. Kay, "Interactions Between Ingredients in IMX-101: Reactive Chemical Processes Control Insensitive Munitions Properties," Sandia National Laboratories, SAND2014-2012, March, 2014.

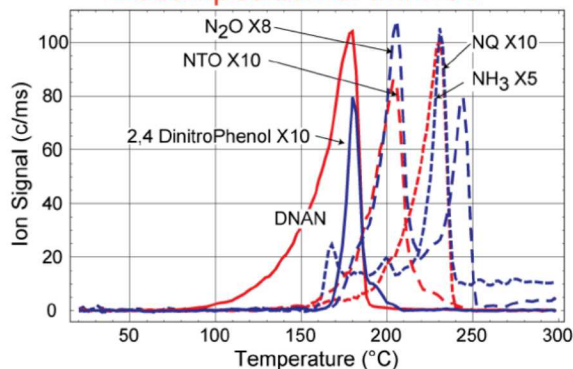
# IMX-101 Decomposition Chemistry from STMBMS\*



## Decomposition of Individual Ingredients



## Decomposition of IMX101



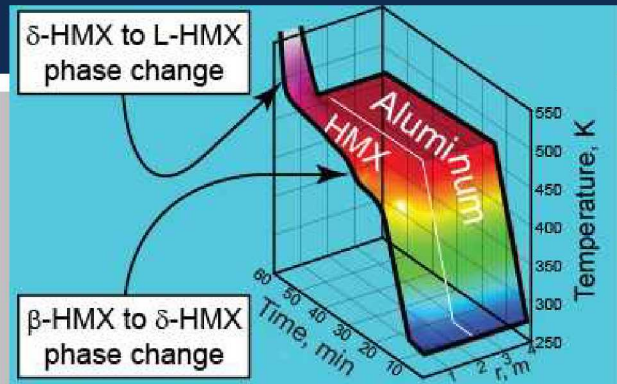
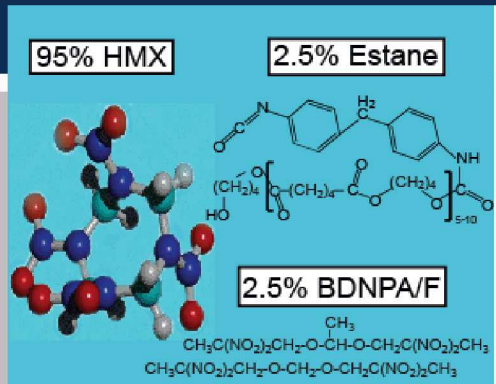
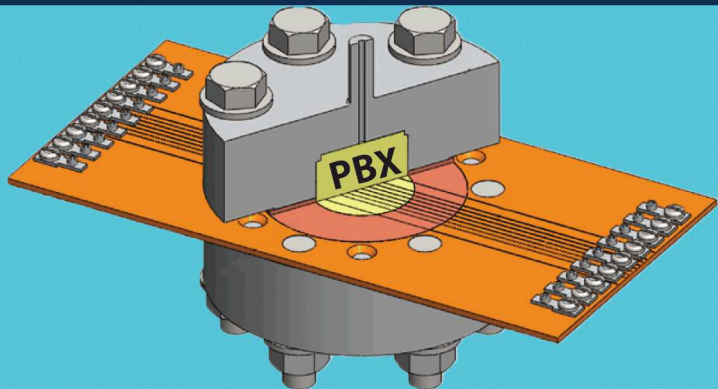
## Summary Table of Results

Material	Decomposition Onset (°C)	Decomposition Range (°C)	Peak Decomposition (°C)	Decrease in Onset (°C)	Residue (% Sample)
DNAN	210	210 - 300	260	-	0
NQ	175	175 - 250	240 (Decomposition), 250 (Polymerization)	-	~33
NTO	215	215 - 280	265	-	~7
IMX-101	160 (DNAN), 145 (NQ), 165 (NTO)	160 - 210 (DNAN), 145 - 240 (NQ), 165 - 225 (NTO)	180 (DNAN), 230 (NQ Decomposition), 205 (NTO)	50 (DNAN), 30 (NQ), 50 (NTO)	16 - 34 <sup>a</sup>

<sup>a</sup> Depending on experiment conditions

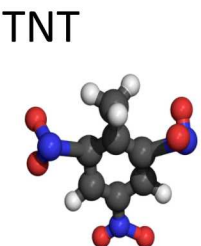
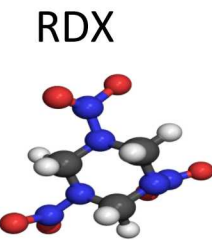
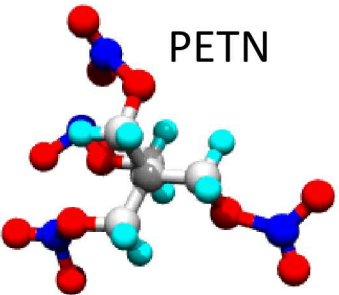
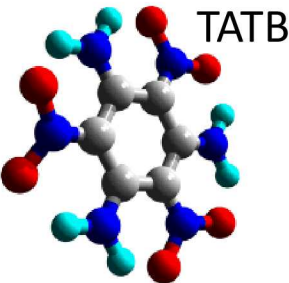
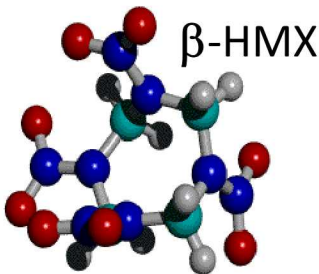
- By itself, DNAN begins to noticeably evaporate at about 130°C; lower in mixture.
- Chemical interactions in the mixture lead to a general (30 to 50°C) decrease in onset temperatures of decomposition reactions. The shift to lower decomposition temperatures may contribute to the insensitive behavior of the IMX-101.
- A multi-step chemical reaction mechanism for IMX-101 is proposed.

\*S. P. Maharrey, D. Wiese-Smith, A. M. Highley, R. Behrens and J. J. Kay, "Interactions Between Ingredients in IMX-101: Reactive Chemical Processes Control Insensitive Munitions Properties," Sandia National Laboratories, SAND2014-2012, March, 2014.



Modeling Ignition and Failure of Explosives:  
PBX 9501, PBX 9502, PETN, Comp-B

Michael L. Hobbs



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the US Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.



# Why model cookoff?

- Need to know behavior in **accidental fires** to assess safety.
- Need to know the **time-to-ignition** for safety timing studies.
- Need to know the **amount of gas produced** to determine if confinement will rupture before ignition.
- Need to know how the damaged state of the material affects the subsequent **burn behavior**.
- Ignition time, gas production, burn behavior are **all affected by confinement** variables such as venting, density, permeability, and ullage.



Carrier	Deaths	Injured	Cost
Oriskany, 1966	44	156	\$63.6M
Forestal, 1967	134	162	\$758M
Enterprise, 1969	28	343	\$554M
Nimitz, 1981	14	48	\$150M
	<b>220</b>	<b>709</b>	<b>\$1525M</b>

Atwood et al, "Experimental Support of a Slow Cookoff Model Validation effort,"  
2004 Insensitive Munitions & Energetic materials Technology Symposium (2004).

***Tremendous cost considering none were under attack!***

# What does PBX 9501 and PBX 9502 look like?

(There are no dyes in these explosives.)

## Pressed PBX 9501

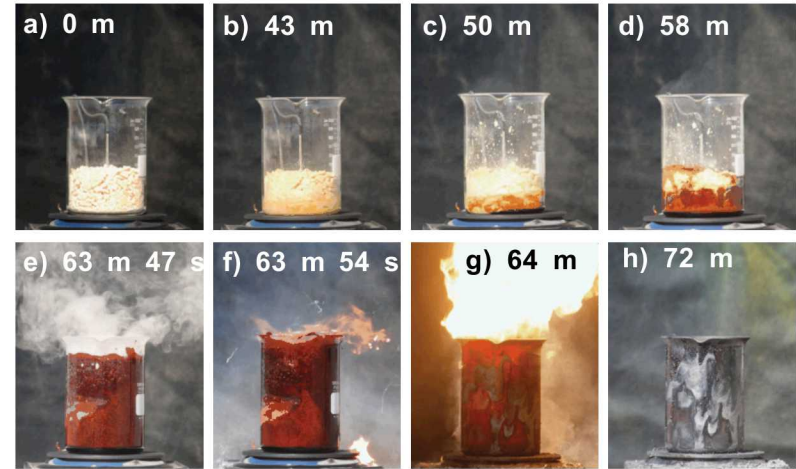
99.7% TMD, 1.84 g/cc,  $\phi = 1.3\%$



## PETN



## Comp-B3 (60% RDX, 40% TNT)



## PBX 9502

Pressed



98.2% TMD, 1.906 g/cc,  $\phi = 1.8\%$

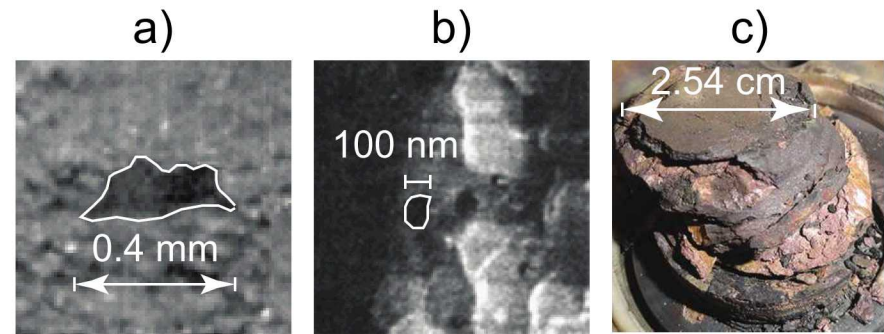
## PBX 9502

Molding powder



38.6% TMD, 0.749 g/cc,  $\phi = 61.4\%$

## Degraded PBX 9502



Macro-pore

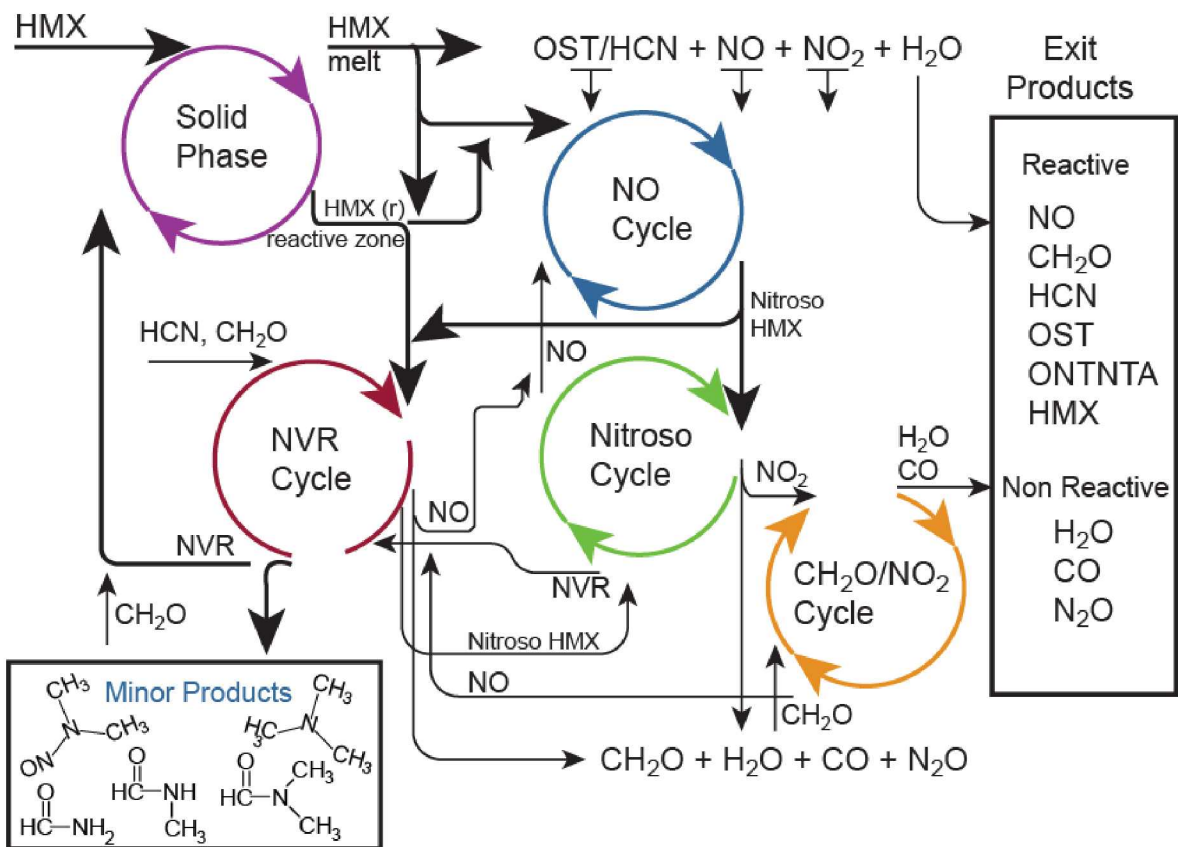
Micro-pore

Swelling

*If porosity is less than about 5%, the pores are not connected.*



# Complex decomposition mechanism



## Highlights

- Reactions occur in gas, solid, and molten phases and depend on physical and morphological changes in the HMX.
- $\beta$  to  $\delta$  phase transition creates grain structure and promotes cracking and nucleation sites.
- Nucleation sites fill with decomposition gases and NVR.
- Controlling mechanisms include unimolecular decomposition and gas phase reactions occurring within a closed pore network.

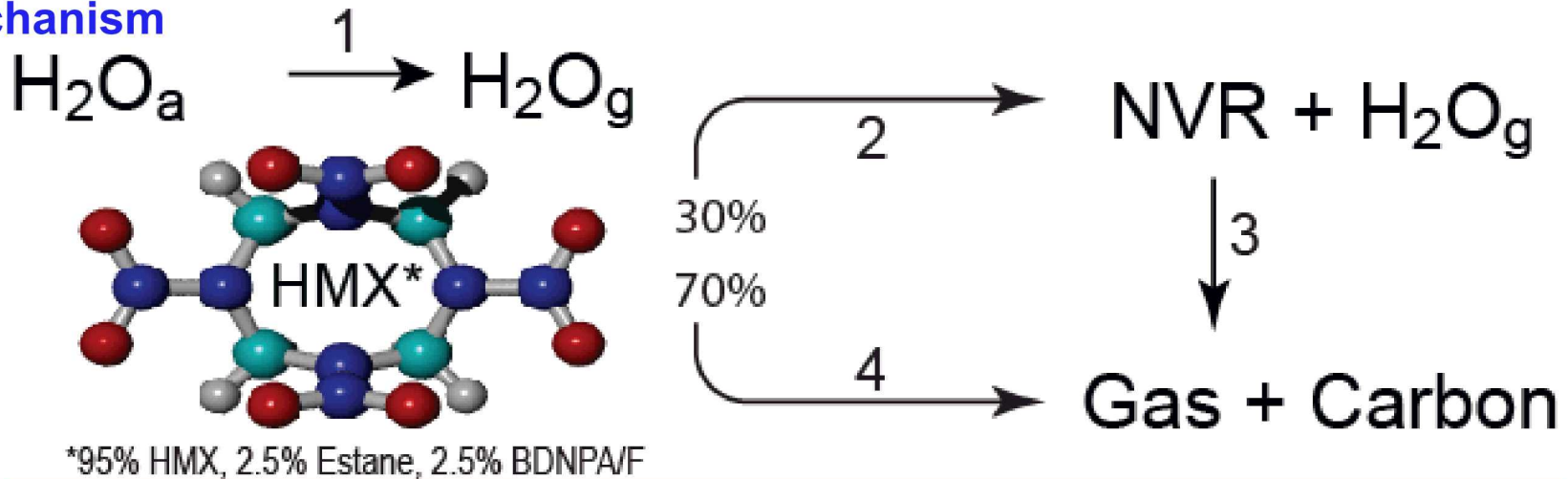
Behrens R., "Thermal Decomposition of HMX: Morphological and Chemical Changes Induced at Slow Decomposition Rates, *Proceedings of the 38<sup>th</sup> JANNAF Combustion Subcommittee Mtg.*, 2002, CPIA Pub. 712, Vol. I: p. 397-408.

***This is for HMX, PBX 9502 also contains 2.5% Estane and 2.5% BDNPA/F***

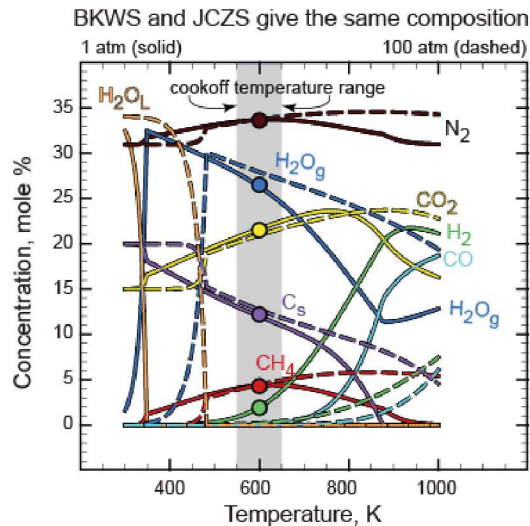


# An engineering based model

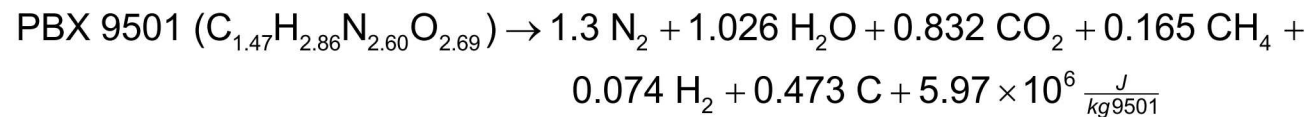
## Mechanism



## Equilibrium compositions



## Reaction products and energies



$$h_{\text{rxn1}} = h_{\text{latent}} = 2.26 \times 10^6 \text{ J / kg}_{\text{H}_2\text{O}} \text{ (endothermic)}$$

$$h_{\text{rxn2}} = 0 \text{ (assumption based on } h_{f,\text{NVR}} = +251.3 \text{ kJ/mol)}$$

# Simple Model Equations for 1-step mechanism

## Solid explosive

### Energy

$$\rho_b C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + r h_{rxn} M_w$$

### Mechanism



### Rates

$$r = \frac{d[\text{Explosive}]}{dt} = A \exp\left(\frac{-E + \zeta \sigma}{RT}\right) [\text{Explosive}]$$

### Species

$$\frac{d[\text{Explosive}]}{dt} = -r \quad \frac{d[\text{Gas}]}{dt} = Ar \quad \frac{d[\text{Condensed}]}{dt} = Br$$

### Momentum

None

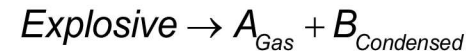
### Distribution parameter, $\zeta$

$$\zeta_i = \text{invsnorm}(x) \quad x = \frac{[\text{Explosive}]}{[\text{Explosive}]_0}$$

Normsinv is the inverse of the standard normal cumulative distribution that has a mean of 0 and standard deviation of 1.

## Explosives that melt/flow

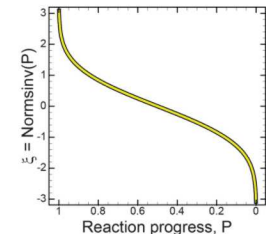
$$\rho_b C_p \frac{\partial T}{\partial t} + \rho_b C_p \vec{v} \cdot \nabla T = \nabla \cdot (k \nabla T) + r h_{rxn} M_w$$



$$r = \frac{d[\text{Explosive}]}{dt} = A \exp\left(\frac{-E + \zeta \sigma}{RT}\right) [\text{Explosive}]$$

$$\frac{\partial [\text{Explosive}]}{\partial t} + \vec{v} \cdot \nabla [\text{Explosive}] = -r$$

$$\rho_b \frac{\partial \vec{v}}{\partial t} + \rho_b (\vec{v} \cdot \nabla) \vec{v} = -\nabla P + \mu \nabla^2 \vec{v} + \rho_b \vec{g}$$

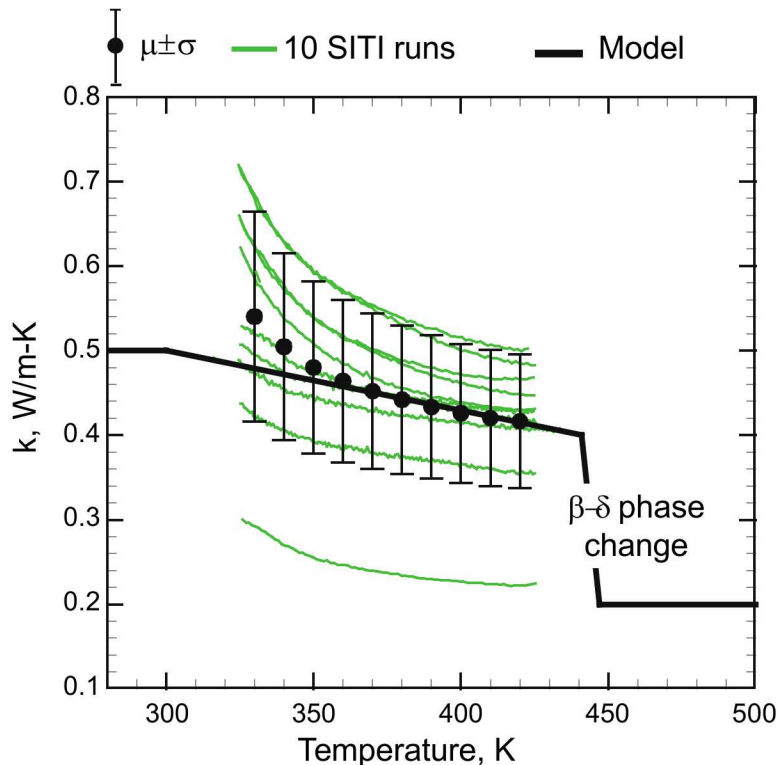


**Engineering model does not 1) track separate gas movement, 2) calculate separate gas and condensed temperatures, and 3) calculate evolving permeability due to reactions or strain. A stress-strain constitutive model for reactive materials is needed.**

# Model Parameters

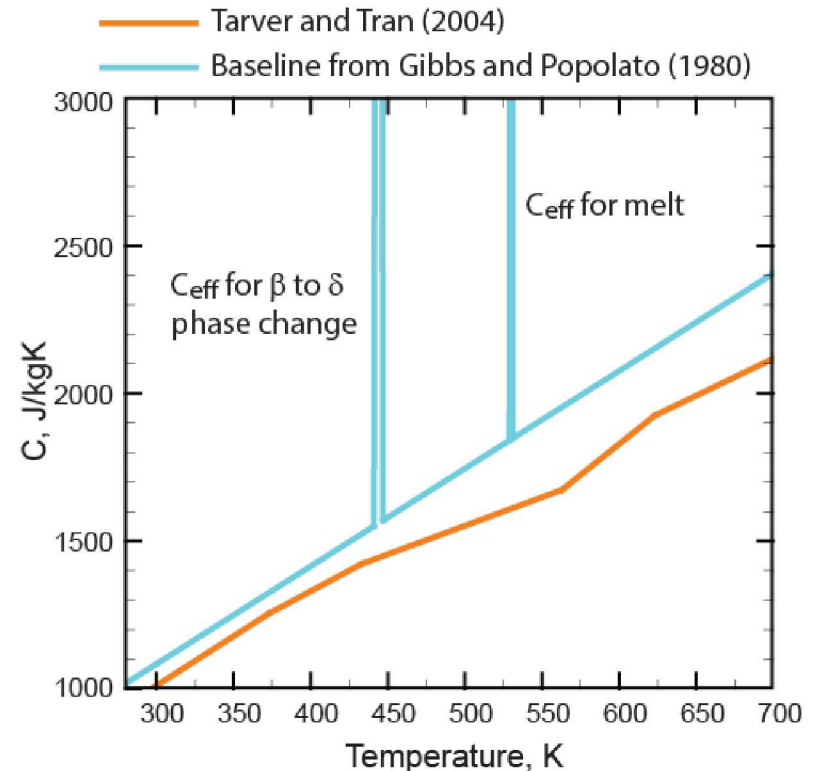
(Key thermophysical properties)

## Thermal Conductivity for PBX 9501\*



\*SIT1 reduction technique from Erikson et al. "Determination of Thermal Diffusivity, Conductivity, and Energy Release from the Internal temperature Profiles of Energetic Materials," *Int. J. of Heat and Mass Transfer*, **79**, 676(2014).

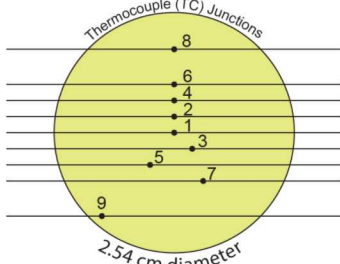
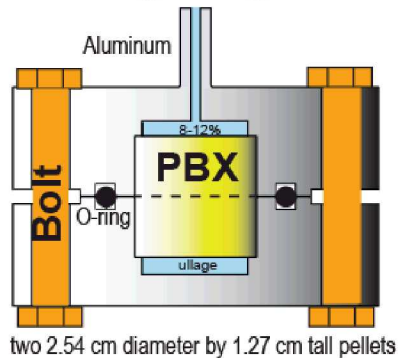
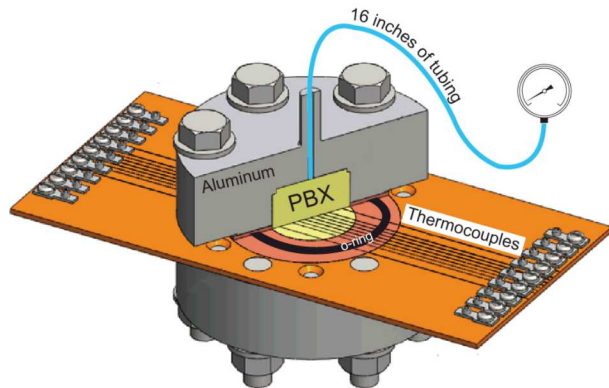
## Specific Heat Capacity for PBX 9501



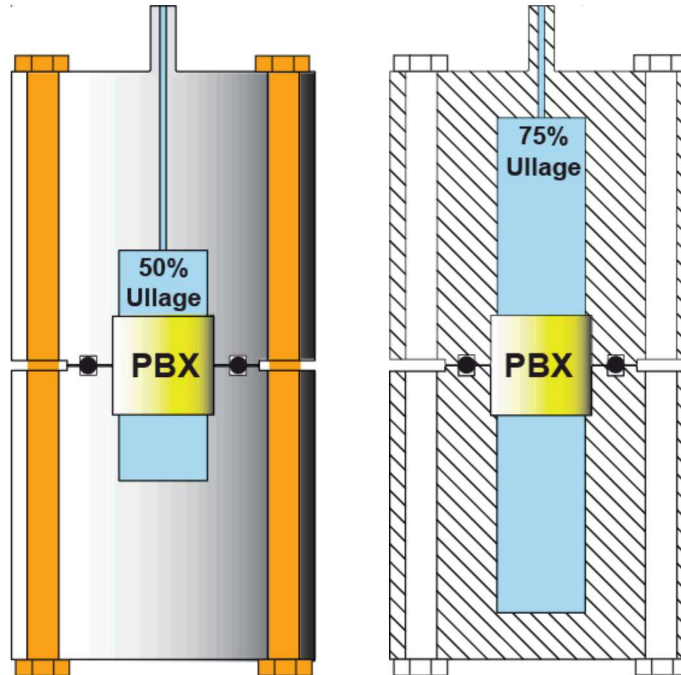
***Runaway is a race between energy generation and energy dissipation.***



# Sandia's Instrumented Thermal Ignition (SITI)



## Large ullage SITI



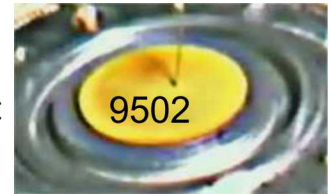
SITI:

$\rho = 1.84 \text{ g/cc}$   
 $453 \text{ K} \leq T_{\text{sp}} \leq 473 \text{ K}$   
28 sealed, 1 vented  
8, 12, 18% ullage (excess gas volume)

Measures: Ignition time, temperature, pressure

## Damage example

onset



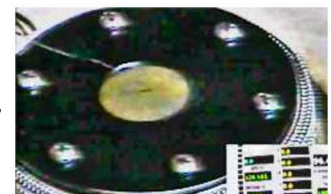
crater



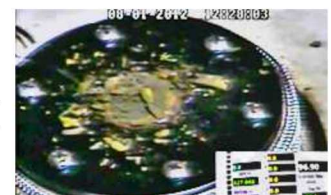
burn



washer

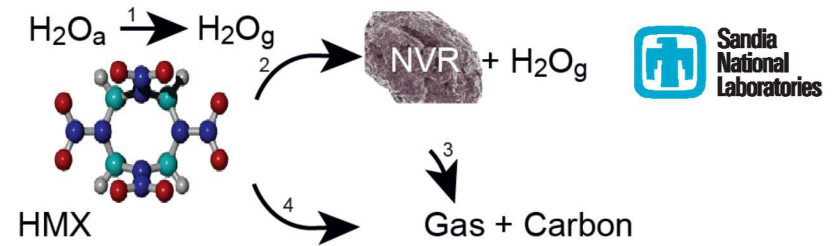


spall

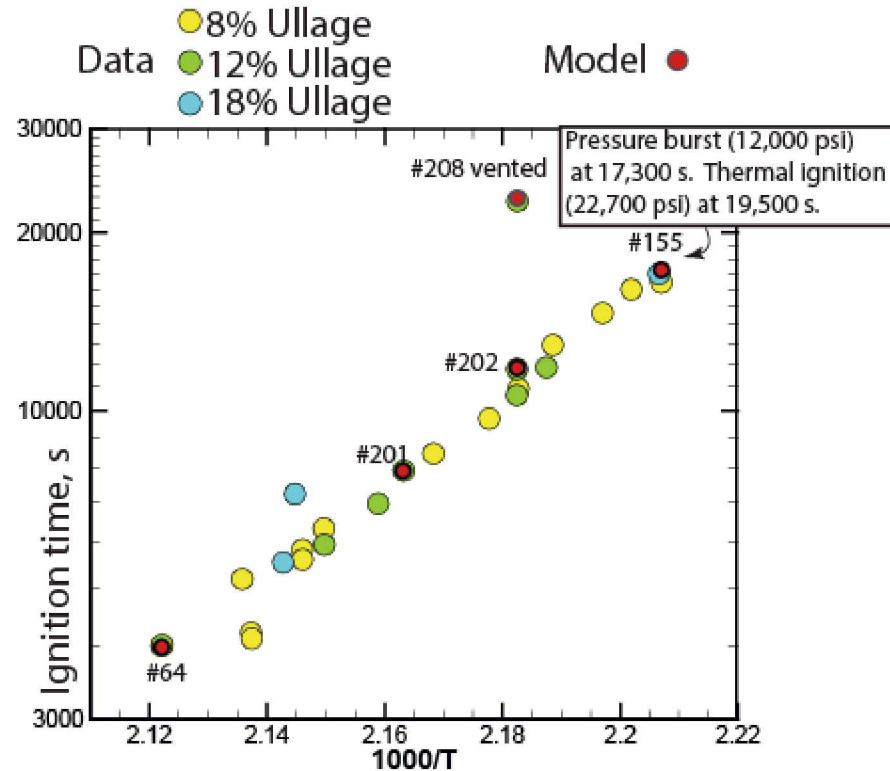
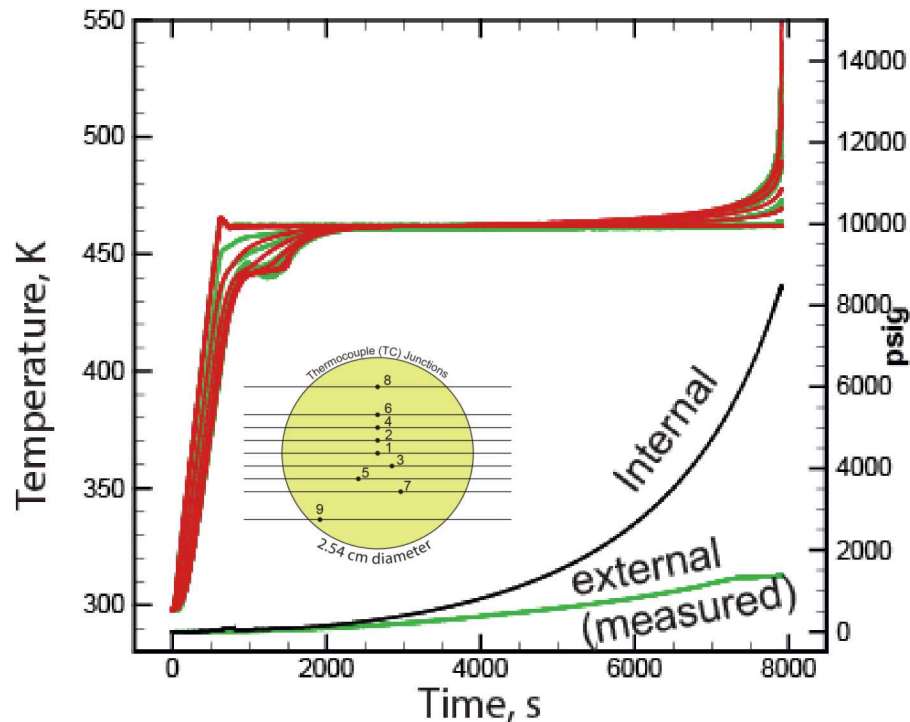


***Incremental bursts heard as audible noises (pop, thud, etc.)***  
***"Couple of popping noises in the video, but no visible smoke." (lab notes)***

# New PBX 9501 model

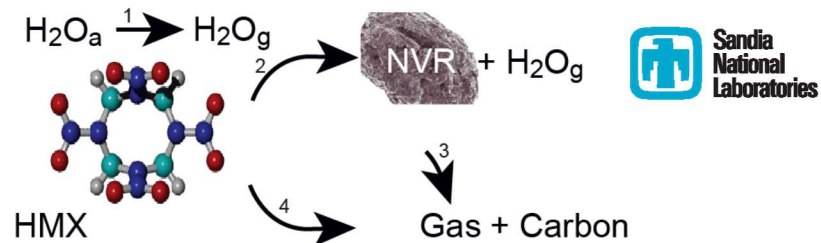


Run #201 (red is model green is data)

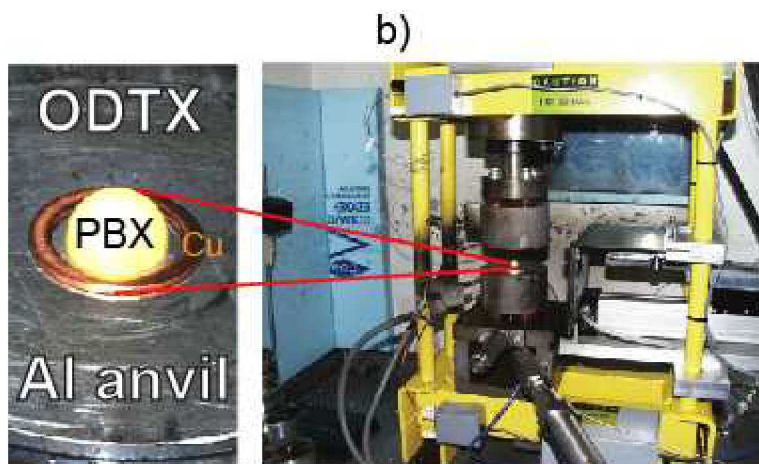
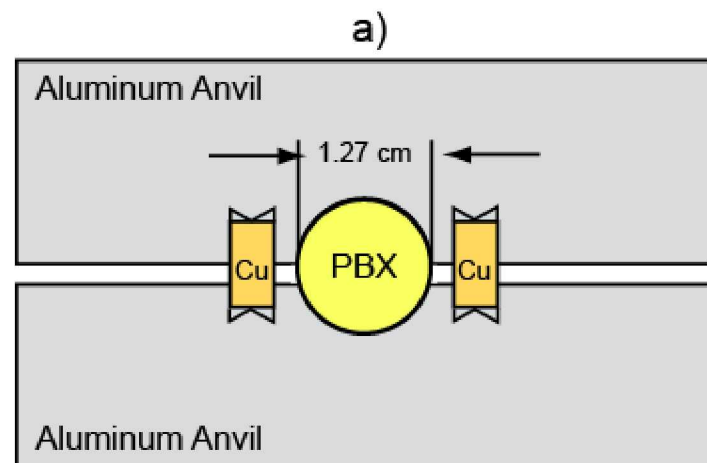


***Model fits data; however we need more vented data***

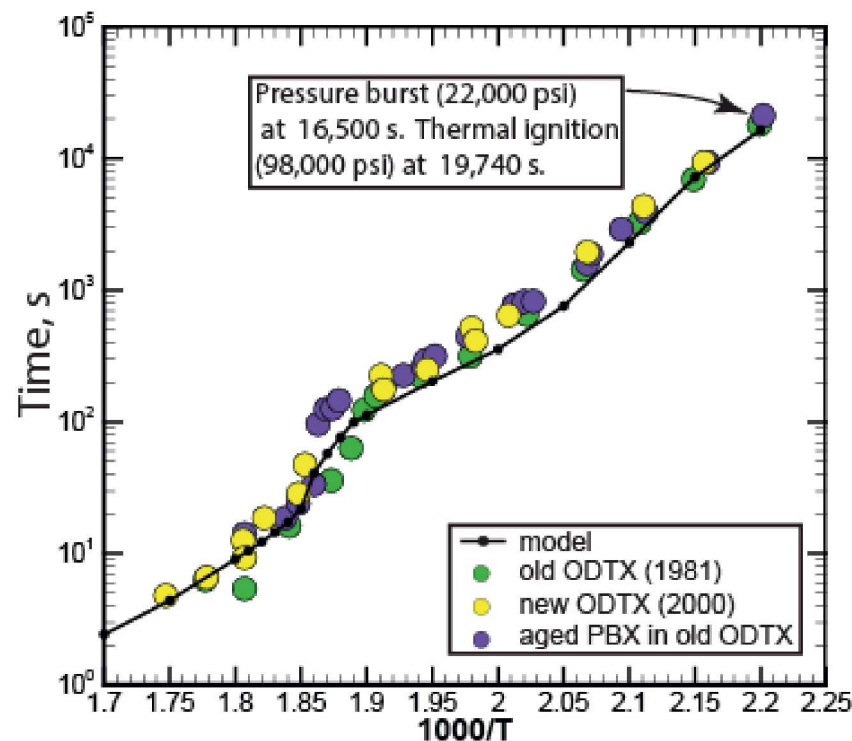
# New PBX 9501 model



## LLNL's ODTX experiment



## Measured/Predicted Ignition time

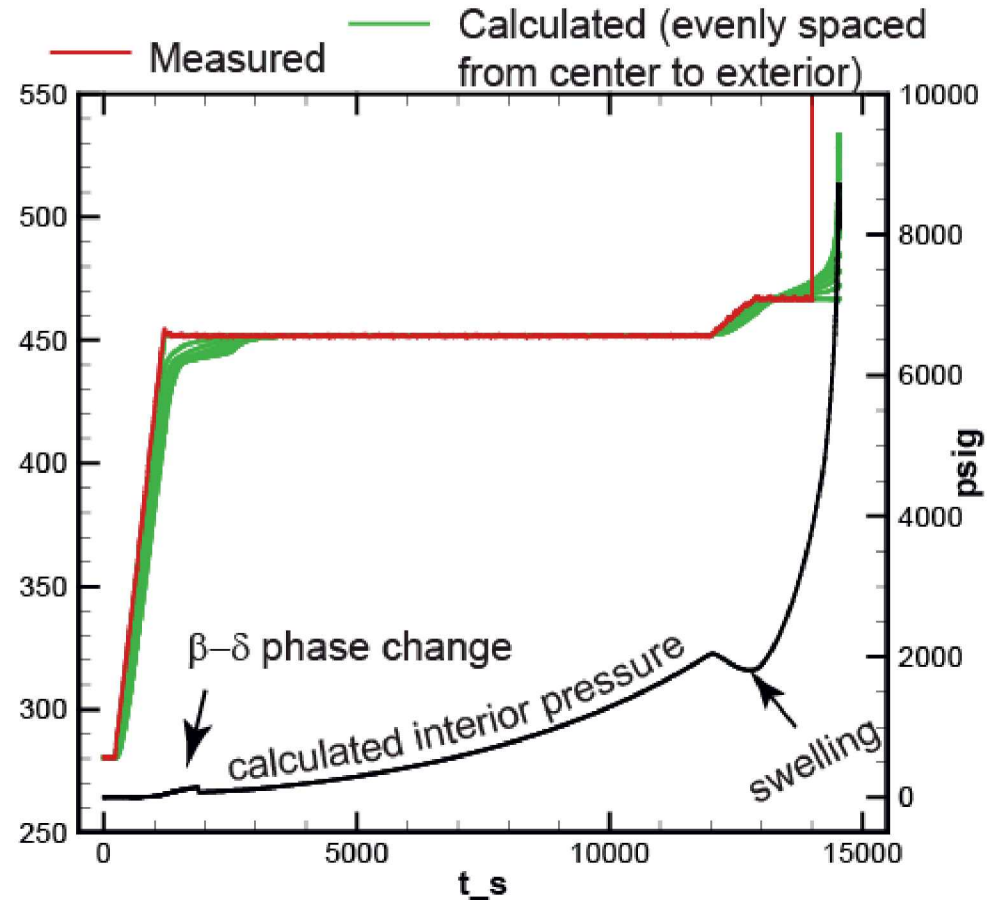
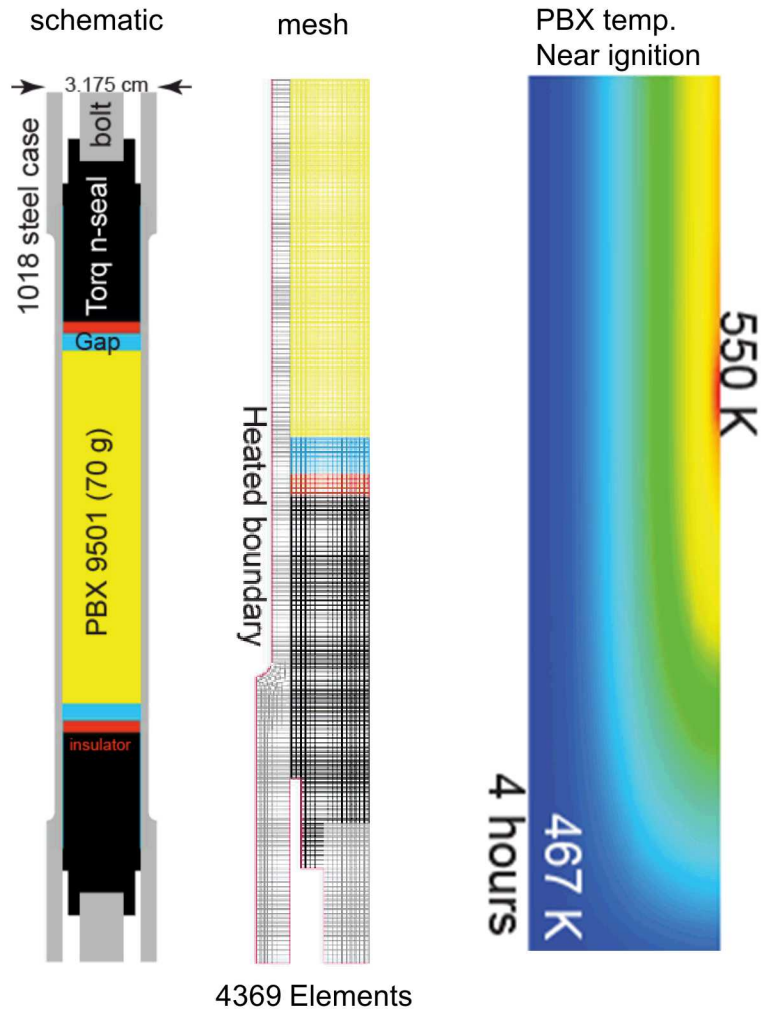
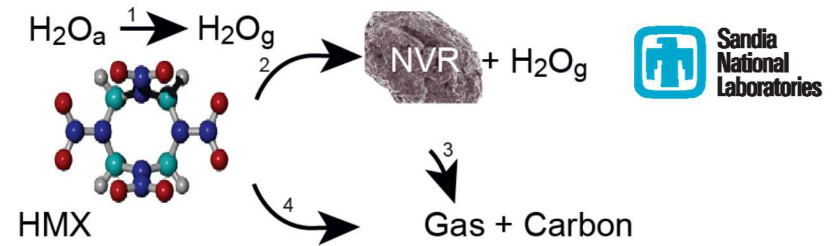


*This set of data is considered validation data.*



# New PBX 9501 model

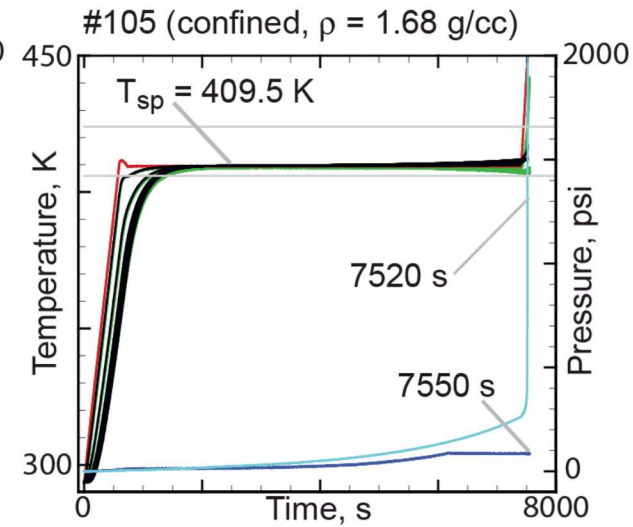
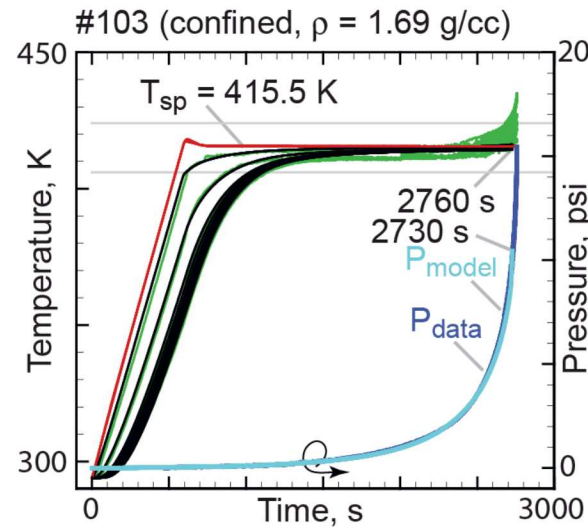
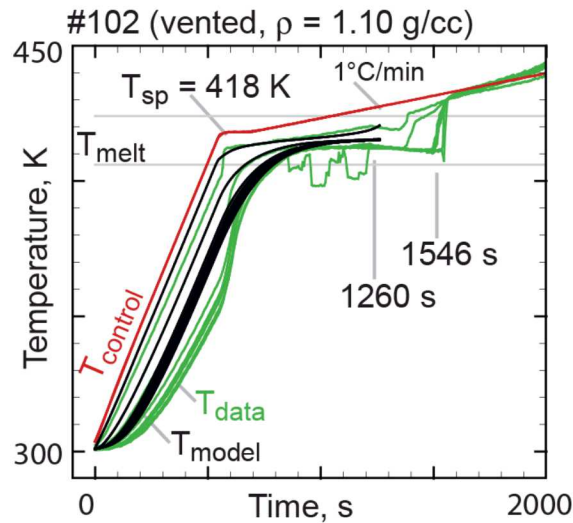
## China Lake pipe bomb experiment



**Measure ignition time: 3 h 53 m**

**Calculated ignition time: 4 h 2 m**

# Model predicts temperatures/pressures

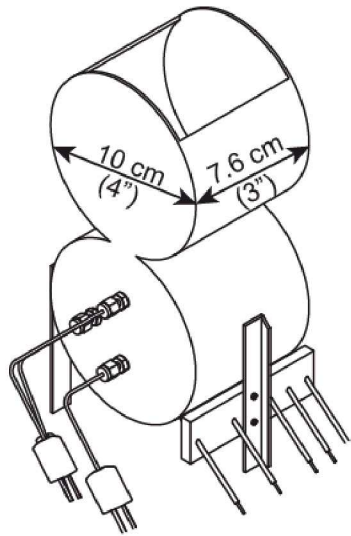


***Model does not calculate violence***

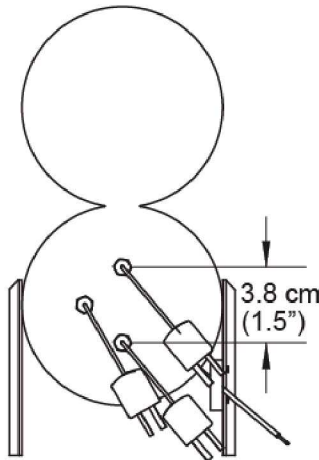


# Cookoff of Composition B (RDX & TNT)

## Oven test (a.k.a snowman)



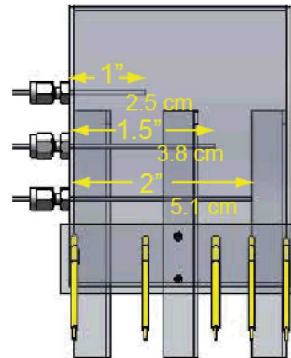
45 minutes



135 minutes



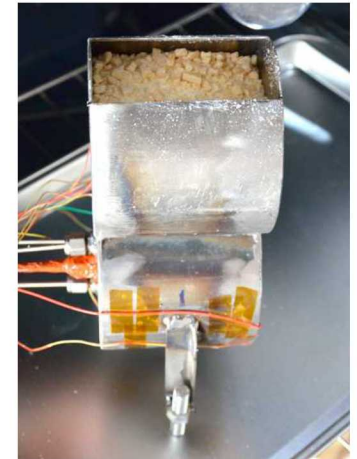
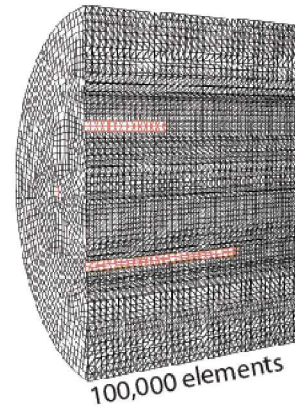
Lower cylinder  
fills with liquid



270 minutes



Mesh



Post test oven



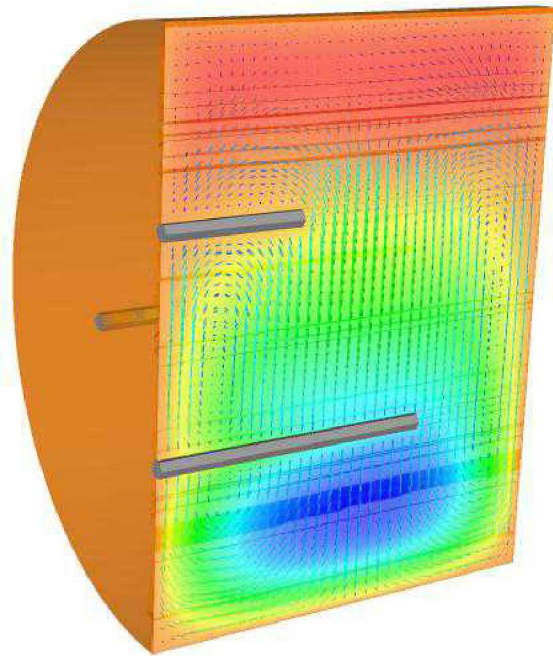


# 3D Modeling of Snowman Test #3

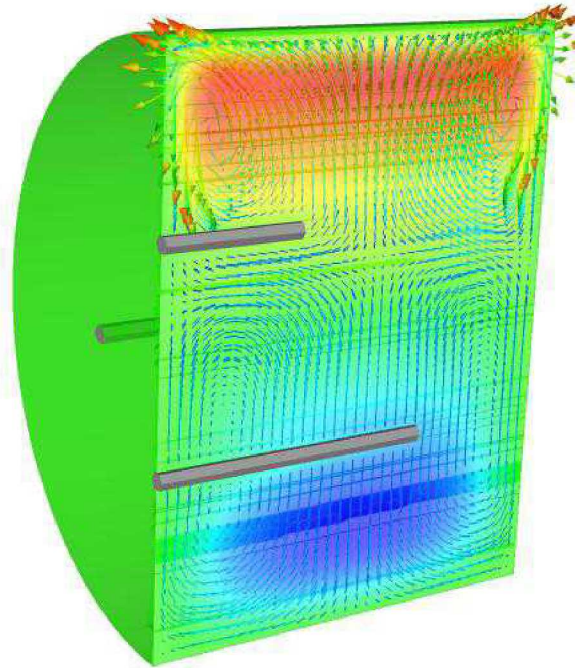
Onset of self heating

Self heating

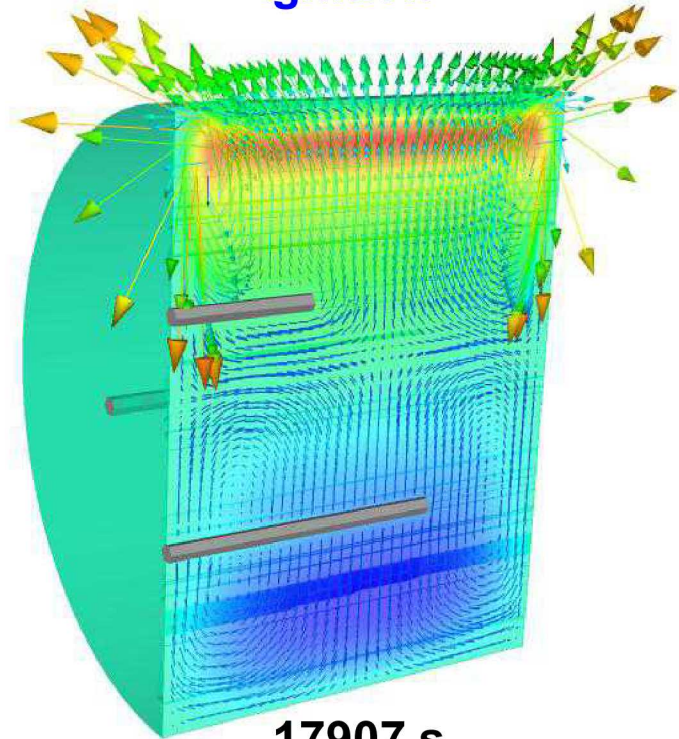
Ignition



16704 s



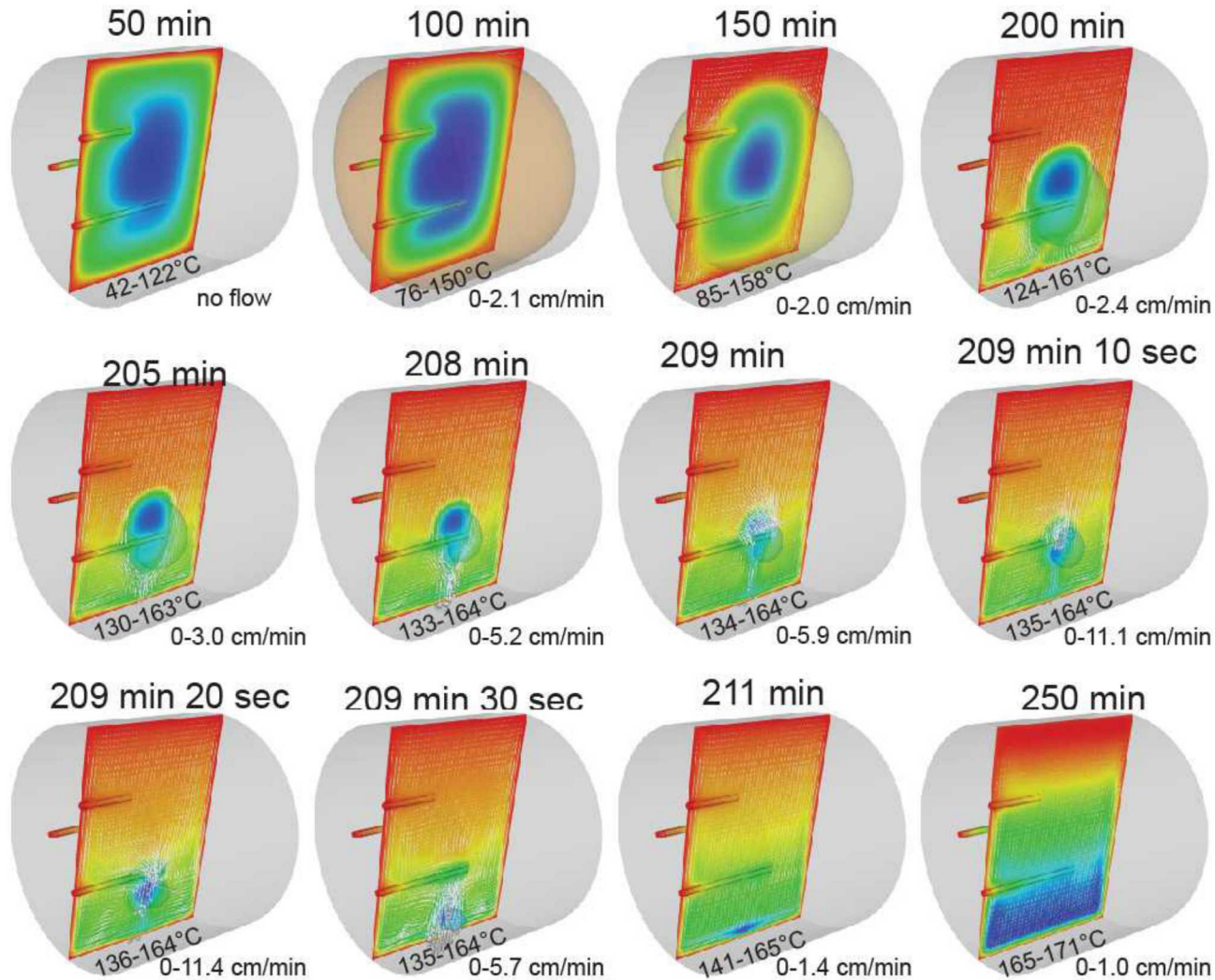
17704 s



17907 s

*Slice through center of 3D simulation*

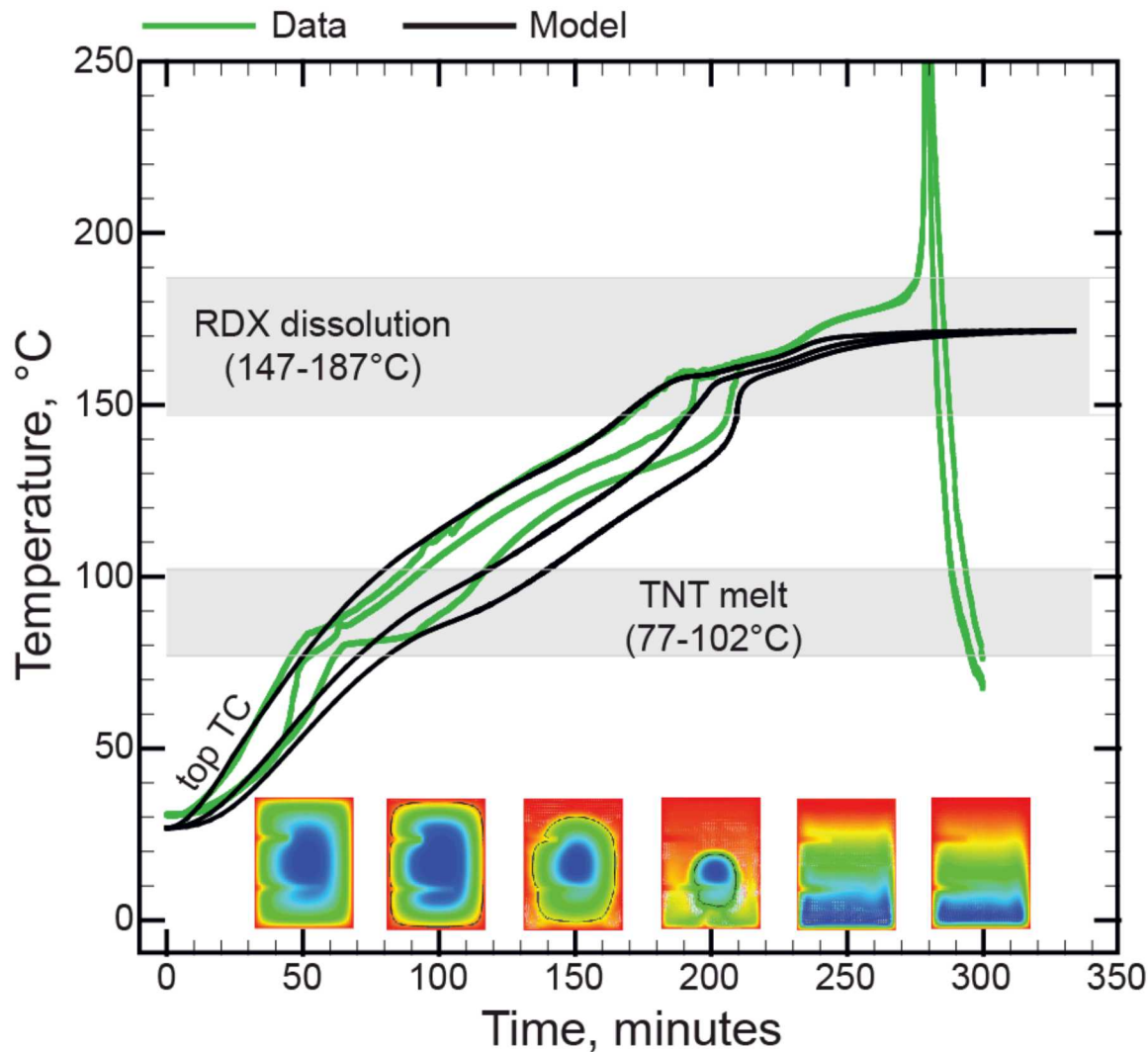
# Oven test results



- Melts from outside to the inside.
- Solid plug gets smaller and starts to fall toward the bottom of the can.
- Liquid heats up and eventually self-heats and ignites at the top of the can.



# Oven test results



- Temperature pinch occurs in middle of RDX dissolution range.
- Model predicts slightly longer ignition times.
- Discrepancy in ignition time could be related to the method of melting the Comp-B flakes.
- In the experiment, the flakes were melted in the combined system.



# Summary and Conclusions

- Models used for safety assessments to predict ignition time, ignition location, and pressurization.
- Models can correlate material state at ignition to device failure.
- For high density pressed PBX, the decomposition gases are retained within the explosive.
- Confinement, press density and venting can affect time to ignition.
- Modeling cookoff of melt-castable explosives is more complicated because of the flow.

# Future Work, Acknowledgements

- Possible follow on studies:
  - Mod/Sim of Detonation within input stream of mixed material (RDX+Coal)
    - If material does explode/detonate, does it propagate to other material?
    - How much dilution is required to stop propagation
    - Effects of chunk size in feed stream
    - Some of this could be done using hydrodynamics code (CTH or other)
  - Develop thermal ignition model for IMX-101
    - Is RDX already the “worst case”?
  - Are there experiments that would be valuable to the project?
    - Cookoff tests of mixtures?
- Acknowledgements:
  - Mike Kaneshige, Rich Behrens, Sean Maharrey – Experiments
  - Mike Hobbs – Models
  - Leanna Minier, Sophia Lefantzi – Management Support