

AD-A028789

USADAC TECHNICAL LIBRARY



5 0712 01019047 7

NWSY TR 76-2

THERMOCHEMISTRY AND THE
DEMILITARIZATION OF EXPLOSIVES

JULY 1976

NWS

NAVAL WEAPONS STATION, YORKTOWN, VIRGINIA 23691

by
Robert Petersen
Lewis R. Rothstein and John H. Smith

Naval Explosives Development Engineering Department



Approved for public release; distribution unlimited.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NWSY TR 76-2	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THERMOCHEMISTRY AND THE DEMILITARIZATION OF EXPLOSIVES		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert Petersen Lewis R. Rothstein John H. Smith		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Station Yorktown, Virginia 23691 (Code 50)		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NAVSEA Work Request 63601
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE July 1976
		13. NUMBER OF PAGES i-iv and 1-26
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Critical temperature Thermal reaction Autoclave melting Explosives Thermal stability Thermal analysis Thermal explosions		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See reverse side of this form.		

In exploring methods to maximize energy conservation for demilitarizing U.S. Navy ordnance, an *in situ* autoclave melting procedure was evaluated.

Verification of the technique was aborted because undesirable gassing occurred during the processing of an HBX-1 loaded Mk 25 Mod 1 Mine.

After reviewing the literature for both theoretical and experimental investigations of thermal explosions, it was found that:

- The literature is replete with warnings that "critical temperature" and "time-to-explosion" calculated for chemically pure explosive systems are most optimistic and a résumé of some of these warnings is warranted again here.
- Earlier hazard analysis evaluations of the autoclaving process by other investigators were overly optimistic because of simplifying assumptions.
- Prolonged heating and/or holding of melt-cast explosives, even at temperatures within established specified limits, may well lead to accelerating decompositions and fires if not to high order detonations.
- Further studies should be carried out to determine whether or not consecutive meltings and coolings of a given explosive can be carried out with impunity without some purification between each melting. This statement applies both to the common practice of using and reusing riser scrap as well as to a current Army procedure of "heat soaking" major caliber, Comp B loaded projectiles for long time periods to eliminate post-casting shrinkage cracks and gaps.

FOREWORD

1. This is a report documenting the demilitarizing of an HBX-1 loaded Mk 25 Mod 1 Mine by an *in situ* autoclave melting procedure and an analysis of why the technique was aborted and the thermo-chemistry involved.
2. The effort reported herein was authorized and funded under the Naval Sea Systems Command (SEA-9912) Work Request 63601 of 6 Nov 1975.

Released by

J.R. Rothstein (for)

W. McBRIDE, Director
Naval Explosives Development
Engineering Department
July 1976

Under authority of
LEO A. HIBSON, JR.
Commanding Officer

ACKNOWLEDGMENTS

The authors are grateful to Drs. R. N. Rogers at the Los Alamos Scientific Laboratory and T. B. Joyner at the Naval Weapons Center, China Lake for bringing our attention to several recent and some as yet unpublished manuscripts relevant to thermal explosions.

CONTENTS

	<u>Page</u>
FOREWORD	i
ACKNOWLEDGMENTS	ii
I. INTRODUCTION	1
II. EXPERIMENTAL OBJECTIVES OF THE AUTOCLAVE MELTING PROCESS	2
III. THERMOCHEMISTRY OF EXPLOSIVES	8
A. Thermal Explosion	9
B. Critical Temperatures	12
C. Time-to-Explosion	13
IV. APPLICATIONS AND LIMITATIONS OF THERMOCHEMICAL EXPLOSION THEORY	17
A. Evaluation of ABL Data	17
B. Evaluation of the Thermal Explosion Literature . . .	19
V. SUMMARY	24
VI. REFERENCES	25

TABLES:

I	Mk 25 Mod 1 Mine HBX-1 Analyses	7
II	Comparison Between Experimental and Calculated Critical Temperatures (T_m)	13
III	ABL Calculated Times-to-Explosion for Ordnance Items at Various Temperatures	18
IV	Adiabatic Self-heating of TNT	23

CONTENTS (cont'd)

	<u>Page</u>
FIGURES:	
1 Mk 25 Mine Being Installed in Autoclave.	4
2 Mk 25 Mine in Place in Autoclave	5
3 Autoclave Closed Ready for Heating	6
4 Approximation of Eq's. (11) and (12) to Nonlinear Curve of Ref 13	16
5 ABL Calculated Temp Versus Times-to-Explosion (TNT/Asphalt Mk 25 Mine)	21

THERMOCHEMISTRY AND THE DEMILITARIZATION OF EXPLOSIVES

I. INTRODUCTION

Prior to the national awareness of a limited energy supply, the main thrust of governmental operations concerned with the manufacture, use and disposal of explosive ammunition was to meet or better federal, state and local pollution and environmental standards.^{1 2} Rigid restraints were placed on deep-sea dumping and open air burning as acceptable means for disposal of obsolete or substandard ammunition. As a result, interest was revived in procedures for reclamation and recovery of explosive moieties for either reuse or commercial sale. The majority of these processes were based upon either steam or water washout of the explosive components which were then recovered by a variety of decantation and filtration techniques. Without recycling or reuse of the water effluents, these processes were both costly and energy consumptive.

The oil embargo of the early 1970's brought the need for energy conservation into sharp focus. The U.S. Navy's demilitarization programs were expanded to emphasize energy conservation as well as pollution control. In keeping with this energy conservation mandate, the Naval Explosives Development Engineering Department (NEDED), of the Naval Weapons Station (NAVWPNSTA), Yorktown demonstrated on a pilot scale that meltable, TNT-based explosives could be recovered safely by washout with recycled, pressurized hot water.³

As a further extension of the energy conservation concept, Battelle Columbus Laboratories, working under contract⁴ to the Western Division of the Naval Facilities Engineering Command, had calculated that even further energy conservation could be realized by completely melting TNT-based explosive *in situ* in the respective ammunition. Battelle's concept was to place the ordnance item in an autoclave heated by

¹National Environmental Policy Act (PL-91-90).

²Executive Orders 11507 & 11514.

³NAVWPNSTA Yorktown files (NEDED File #897 Jun 1971-Sep 1972).

⁴Kim, B.C., *et al.*, Battelle Columbus Laboratories, Final Report on Explosive Melt Out Study (N62474-74-C3913), Sep 1975.

10 to 15 pounds per square inch gage (psig) recycled steam until melting was completed. The molten explosive was then to be syphoned from the warhead, and either delivered directly to a solidifying flaker belt and, hopefully, be packageable for reuse and/or sale without further processing or else delivered to an incorporation kettle for reconstitution to specification grade standards.

For example, from preliminary experiments at the Naval Ammunition Depot (NAD), Hawthorne the energy requirements for autoclave demilitarizing TNT and HBX-1 loaded Mk 25 Mod 1 Mines were estimated to be an order of magnitude (10X) lower than the energy requirements for either a steam-out or washout process.^{4*}

Prior to the NAD Hawthorne experiments, Allegheny Ballistic Laboratory (ABL) had been contracted to run a hazard and risk analysis on the proposed process. Their calculations and estimates were that the probability of an explosion using the proposed autoclaving procedure for specified time periods were less than 5×10^{-9} .⁵ It was on the basis of these estimates that the Hawthorne experiments were conducted.

NEDED is chartered to either develop or approve all processes relevant to the loading or demilitarization of main charge explosives in Navy ammunition by Naval Sea Systems Command instruction and was directed to evaluate the autoclaving process in more detail. This report concerns itself with that evaluation, and, in addition, summarizes some significant data from the thermochemistry of explosives literature. The prime objective is to impress explosive process and design engineers, not normally conversant with the thermochemistry of explosives, with the limitations as well as the value of applied thermochemical explosion theory.

II. EXPERIMENTAL OBJECTIVES OF THE AUTOCLAVE MELTING PROCESS

NEDED's objectives essentially were to verify and refine the findings at NAD Hawthorne listed in the Battelle⁴ report. Namely that:

- Gross steam consumption for autoclave melting explosives in Mk 25 Mod 1 TNT and HBX-1 loaded Mines ranged from 0.24 to 0.30 pounds of steam per pound of explosive, respectively.
- Net steam consumption could be reduced to as low as 0.12 pounds of steam per pound of explosive by reducing heat losses from the melt-out chamber by better insulation.

⁴*Ibid.* (*p 14).

⁵Sawyer, S.O., & Williams, G.M. Allegheny Ballistics Laboratory Final Rept No. A0827-520-03-006, Hazards Analysis Report, Part II, Jan 1976 (prep for Battelle Columbus Laboratories).

- Melting times, using 10 to 15 psig steam and without agitation, were somewhere between 6 and 13 hours for the two mines respectively or, in any case, less than 16 hours. This latter objective was considered important because of the previously referenced ABL hazards estimates.⁵
- Molten hot melt could effectively be skimmed off from the bulk of the remaining explosive.
- Molten explosive could be syphoned directly from the war-head for immediate pelletization or for reconstitution if necessary.

The experimental setup at the NAVWPNSTA Yorktown was essentially equivalent to that at NAD Hawthorne as described in Battelle's report and as illustrated in Figures 1, 2 and 3.

A Mk 25 Mod 1 HBX-1 loaded Mine, containing approximately 1200 pounds of explosive was sealed into the autoclave and the following sequence of events noted and carried out:

- At 0000 hours, 15 psig steam was applied to the autoclave jacket.
- At 0200 hours, approximately 20 pounds of hot melt had exuded up into the vent tube and was removed with a dip stick.
- At 0830 hours, probing via the vent tube showed that explosive was melted through to the bottom of the mine but that a mass of explosive against the "lug" side of the mine still remained solid. Some bubbling or gassing was observed at this time.
- At 1130 hours, melting was not complete and, despite intermittent stirring, gassing had increased to a steady and excessive degree. Accordingly, the decision was made to abort the experiment. The steam to the autoclave was cut off at this time and the latter vented.
- At 1215 hours, approximately 250 pounds of molten explosive was syphoned into a reprocessing kettle. Steady bubbling continued in the molten explosive remaining in the mine. Therefore, cooling of this residual material was hastened by removing the "top-hat" and lid to the autoclave and by dumping approximately 600 additional pounds of the molten explosive into pellet trays.

⁵*Ibid.*



FIGURE 1. MK 25 MINE BEING INSTALLED IN AUTOCLAVE



FIGURE 2. MK 25 MINE IN PLACE IN AUTOCLAVE

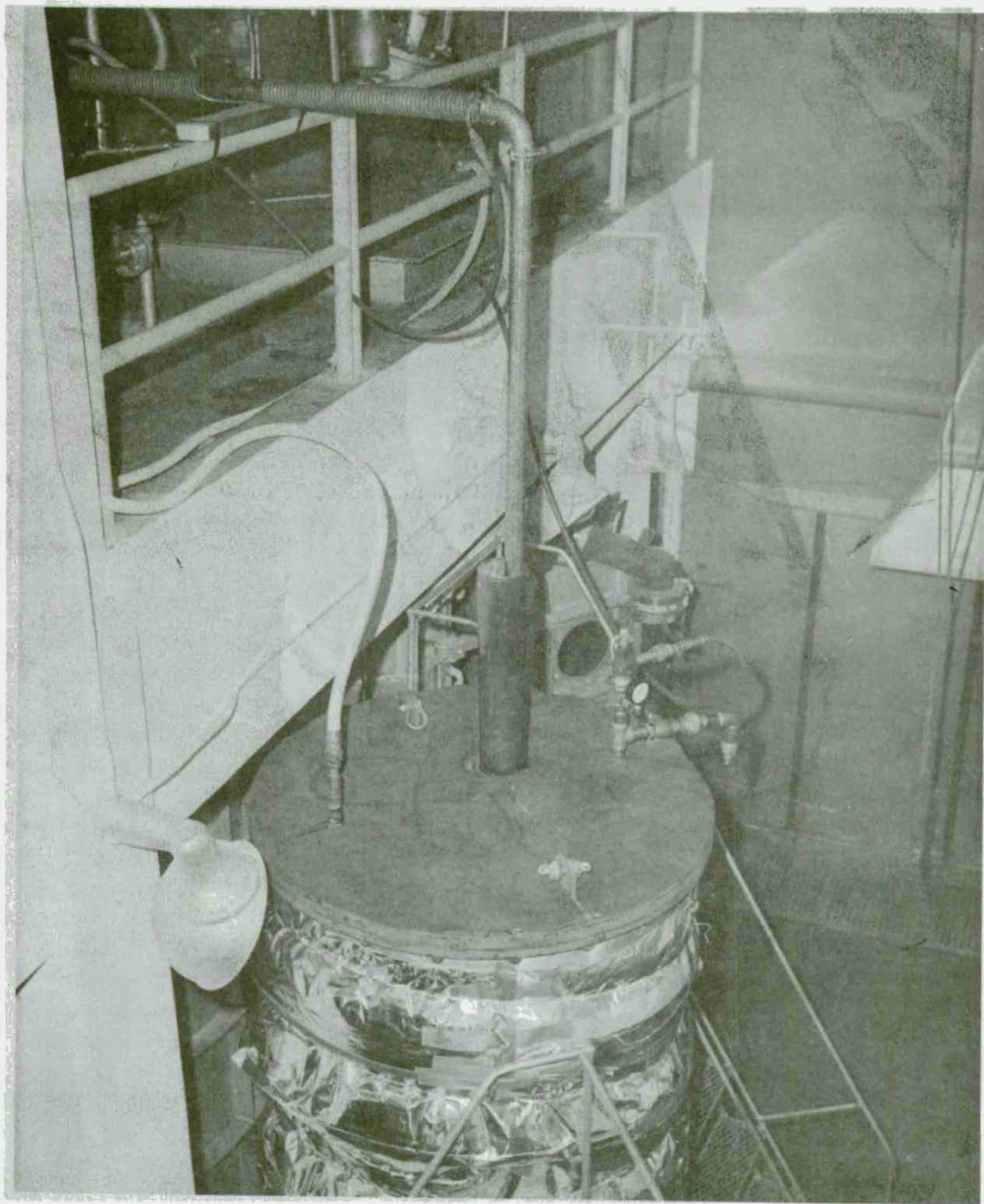


FIGURE 3. AUTOCLAVE CLOSED READY FOR HEATING

- No analysis was made of the escaping gas but it was the certain conviction of the cognizant engineer that the gas was a reaction product and not the release of entrapped air.
- Laboratory analyses of the syphoned HBX-1 (Sample No. 1), HBX-1 dumped into pellet trays (Sample No. 2), and a standard HBX-1 formulation (Sample No. 3) are shown in Table I.

TABLE I. MK 25 MOD 1 MINE HBX-1 ANALYSES

Sample No.	Composition (%)							Impact sensitivity ^a (cm)	VTS ^b (ml/g)
	H ₂ O	TNT	Hot melt	Al	Wax	RDX	CaCl ₂		
1	0.2	40.8	0.3	14.9	2.6	40.8	0.4	84.4	1.0
2	0.2	37.7	0.4	17.1	4.0	40.7	0.5	82.2	0.9
3	0.2	37.8	0.0	17.1	4.7	39.7	0.5	85.9	0.1

^a50% ht: Bruceton Method/NOL Machine/Type 12 tools/2.5 kg wt/ 25 trials/35 \pm 2 mg/ 5/0 sandpaper.

^bVacuum Thermal Stability: ml/g/48 hrs/100°C/STP.

A highly significant point to be noted from the vacuum stability results is the tenfold increase in gas evolved from remelted material versus the virgin standard. Further, methyl violet tests of these vacuum stability gas products from the reclaimed HBX-1 were positive for nitrogen oxides, whereas tests were negative for newly batched material tested under the same conditions. These factors will be readdressed later.

Consequent to this experiment, a thorough review of the thermochemistry of explosives literature was made. Section III summarizes the development of the thermochemical theory of explosions. Section IV reviews its applications and limitations.

III. THERMOCHEMISTRY OF EXPLOSIVES

Some 50 years ago, N. N. Semenov promulgated the theory of thermal explosion. Since that time, steady progress has been made in developing mathematical tools with which both explosive process and weapon design engineers are able to calculate "critical temperatures" (T_c) and "times-to-explosion" (t_e) for explosive compositions having specific geometric configurations and temperature environments.

Differences between calculated and experimentally determined values for T_c and t_e for "chemically pure" explosive systems have been steadily narrowed. This progress is due primarily to two factors: 1) more exact solutions to the heat conduction equation for thermal explosion have been developed, and 2) more accurate kinetic constants which are used in the heat balance equation have been generated for specific explosive systems.

Several excellent reviews relevant to this progress have been published and it is not the purpose here to add to that list. Rather our objective is to show that as agreement between theory and experiment is approached for chemically pure explosive systems, wider recognition should be given to major discrepancies between calculated and observed T_c and t_e values (particularly the latter) obtained from production grade, adulterated, or less pure, explosive systems.

While this note of caution will come as no surprise to long time investigators in this field, it is being reemphasized here for two reasons. The first is so that explosive engineers realize that in using the kinetic constants for pure explosives and in making simplified assumptions about the type of reaction mechanism occurring, they are calculating the "most optimistic" times-to-explosion. The second reason is to encourage an expanded and accelerated effort in the research and development community to further identify and treat competing reaction mechanisms that will lead to formulae from which "worst case" predictions can be made with higher confidence.

Therefore, the theory of chemical explosion is resurrected here only to the degree felt necessary for the uninitiated explosive engineer to gain some insight into its derivation and application. The summary of methods for calculating critical temperatures and times-to-explosion has been abstracted from several sources. Key among

them are those now referenced.^{6 7 8 9 10 11} Pioneering efforts by Frank-Kamenetskii, Chambré, Carslaw, Jaeger and Eyring, to name but a few, already have been liberally cross-referenced among the publications cited and are not listed as prime references. For those engineers less interested in thermal explosion theory than in how and why it may vary from experimental data, it is recommended they skip to Section IV.

A. Thermal Explosion

Materials that undergo self-heating by exothermic decomposition will do so at accelerated rates as the temperature rises. If conduction at the material boundary is not sufficient to dissipate the heat, thermal explosion will eventually occur. The highest boundary or surface temperature at which a "steady state" can exist is that wherein heat losses and heat production are in equilibrium. This temperature is defined as the critical temperature, i.e., the temperature which if exceeded, will result in a thermally induced explosion. Obviously, since heat flow is boundary controlled, critical temperature is strongly influenced by the geometry and size of the reacting entity.

This phenomenon of self-heating by many materials, including explosives, can be described by the heat conduction equation (neglecting convective heat flow) as:

$$\text{Self-heating} = \text{Heat Loss by Conduction} + \text{Production of Heat by Chemical Reaction}$$

Quantitatively, this expression is

$$\rho c \left(\frac{\partial T}{\partial t} \right) = \lambda \nabla^2 T + \rho Q Z e^{-E/RT} \quad (1)$$

⁶Longwell, P.A., NAVWEPS Rept 7646, Calculation of Critical Temperature and Time to Explosion for Propellants and Explosives, Mar 1961.

⁷AMCP 706-180, Principles of Explosive Behavior, Apr 1972.

⁸Zinn, J. & Mader, C.L., J. Appl. Phys. 31 (1960) 323.

⁹Rogers, R.N., Thermochimica Acta 11 (1975) 131-9.

¹⁰Hardee, H.C., Lee, D.O & Donaldson, A.B., Combustion and Flame 18 (1972) 403-10.

¹¹Enig, J.W., Proc. Roy. Soc. 305A (1968) 205.

where ρ = density g/cc
 c = specific heat cal/g $^{\circ}$ K
 T = temperature prior to explosion $^{\circ}$ K
 λ = thermal conductivity cal/cm $^{\circ}$ Ksec
 ∇ = Laplacian operator in Cartesian space coordinates x, y, z ,

$$\text{i.e.,} \quad = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

t = time sec
 Q = heat of reaction per unit mass cal/g
 Z = pre-exponential factor sec $^{-1}$
 E = activation energy cal/mol
 R = gas constant 1.987 cal/mol $^{\circ}$ K

Proximate and exact solutions to Eq. (1) have been derived with increasing ingenuity since its first proximate solution by Frank-Kamenetskii for the steady state condition (i.e., where $\frac{\partial T}{\partial t} = 0$) of a slab with both faces held at constant, adiabatic temperature.

In general, for symmetric geometries, conduction depends only on a single space coordinate so that ∇^2 reduces to $\frac{\partial^2}{\partial x^2} + \frac{m}{x} \left(\frac{\partial}{\partial x} \right)$ where $m = 0, 1$ or 2 for planar, cylindrical or spherical symmetry and x is the controlling space coordinate; e.g., for a sphere x = the radius, r , and $m = 2$ and, where $\partial c \frac{\partial T}{\partial t} = 0$, Eq. (1) reduces to

$$\lambda \left[\frac{\partial^2 T}{\partial x^2} + \frac{m}{x} \left(\frac{\partial T}{\partial x} \right) \right] + \rho Q Z e^{-E/RT} = 0 \quad (2)$$

or, more commonly, letting $\theta = \frac{RT}{E}$

$$\frac{d^2 \theta}{dx^2} + \frac{m}{x} \left(\frac{d\theta}{dx} \right) + \frac{\rho Q Z R}{\lambda E} e^{-1/\theta} = 0 \quad (3)$$

Until recently, exact solutions to the nonlinear Eq. (3) had not been developed. However, proximate solutions to Eq. (3) have been derived by:

- making the assumption that the temperature of the explosive, T , just prior to explosion is very close to a fixed reference temperature, T_0 , such as the boundary temperature, or in a specific case, the critical temperature,

$$\text{i.e., } \frac{E}{RT} \approx \frac{E}{RT_0} \left(1 - \frac{T-T_0}{T_0} \right) \text{ where } \frac{T-T_0}{T_0} \ll 1$$

- defining a new temperature variable

$$\theta = \frac{E}{RT_0^2} (T-T_0) \text{ and } d\theta = \frac{E}{RT_0^2} dt$$

- defining a dimensional positioned coordinate, ζ , as $\zeta = x/a$ where a is the significant dimension of the explosive, such as half of the thickness of a slab or the radius of a cylinder or a sphere.

Appropriate substitutions of these values in Eq. (3) result in

$$\frac{d^2 \theta}{d\zeta^2} + \frac{m}{\zeta} \left(\frac{d\theta}{d\zeta} \right) = \left(\frac{a^2 \rho Q Z E}{\lambda R T_0^2} e^{-E/RT_0} \right) \zeta \theta \quad (4)$$

This proximate equation has been solved for various geometries and boundary conditions. Of particular importance is the parameter in the above equation generally identified as δ , the so-called "shape factor," where

$$\delta = \frac{a^2 \rho Q Z E}{\lambda R T_0^2} e^{-E/RT_0} \quad (5)$$

(At the critical temperature, $T_0 = T_c$.)

The maximum or "critical" value for the parameter δ , i.e., δ_{cr} , was calculated by early investigators to be a constant dependent upon size and shape; i.e., $\delta_{cr} = 0.88, 2.00$ and 3.32 for the infinite slab, cylinder and sphere, respectively. Zinn and Mader solved Eq. (4) numerically for these geometries with nonadiabatic, nonsteady state systems. Later, Enig, Longwell, Conrad, Hardee, *et al.*, calculated δ values for other boundary conditions for the significant dimension of the explosive body and showed that the δ_{cr} values just listed are limiting values. Ultimately, Shouman, Donaldson and Tsao¹² offered an exact solution for the heat transfer equation. However, since many of the sizes and shapes of high explosives systems of interest to the design engineer have δ values that approach those values listed, their utility is of general application and therefore, Eq. (5), as we shall next see, is valid for use with simple systems.

B. Critical Temperatures

For the cases just described, where $\delta_{cr} = 0.88, 2.00$ or 3.32 , Eq. (5) [which in fact is the integrated solution to Eq. (4) for slabs, cylinders or spheres at steady state - constant surface temperature conditions] can be transposed logarithmically to

$$T_c = \frac{E}{R \ln \left(\frac{\rho a^2 Q Z E}{\lambda R T_c^2 \delta} \right)} \quad (6)$$

and the critical temperature T_c can be iteratively calculated if the physical (ρ, a, δ) and chemical (Q, Z, E, λ) parameters are known.

Rogers has neatly demonstrated⁹ the general validity of Eq. (6) by calculating T_c from differential scanning calorimetric determinations of chemical parameters and comparing these results with an independently measured T_c . The excellent agreement between experimental and calculated T_c values is reproduced in Table II.

¹²Shouman, A.R., Donaldson, A.B. & Tsao, H.Y., Exact Solution to the One Dimensional Stationary Energy Equation for a Self-Heating Slab, Combustion and Flame 23 (1974) 17-28.

⁹*Op cit.*

TABLE II. COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED CRITICAL TEMPERATURES (T_m)

	T_m ($^{\circ}\text{C}$)		Values used					
	Exp	Calc	a (cm)	ρ (g/cc)	Q (cal/g)	Z (sec^{-1})	E. (kcal/mol)	$\lambda \times 10^4$ (cal/cm $^{\circ}\text{Csec}$)
HMX	253-255	253	0.033	1.81	500	5×10^{19}	52.7	7.0
RDX	215-217	217	0.035	1.72	500	2.02×10^{18}	47.1	2.5
TNT	287-289	291	0.038	1.57	300	2.51×10^{11}	34.4	5.0
PETN	200-203	196	0.034	1.74	300	6.3×10^{19}	47.0	6.0
TATB	331-332	334	0.033	1.84	600	3.18×10^{19}	59.9	10.0
DATB	320-323	323	0.035	1.74	300	1.17×10^{15}	46.3	6.0
BTF	248-251	275	0.033	1.81	600	4.11×10^{12}	37.2	5.0
NQ	200-204	204	0.039	1.63	500	2.84×10^7	20.9	5.0
PATO	280-282	288	0.037	1.70	500	1.51×10^{10}	32.2	3.0
HNS	320-321	316	0.037	1.65	500	1.53×10^9	30.3	5.0

The important point to be learned from Roger's work is that good kinetic constant data is attainable at or near the critical temperature in many cases and, consequently, T_c values can be calculated with some confidence. But, as will be discussed later in Section IV, unfortunately, this is not necessarily true of time-to-explosion calculations.

C. Time-to-Explosion

Again referring to Eq. (1), in those special cases where there is no transfer of heat from the mass (adiabatic conditions), the term $\lambda \nabla^2 T$ approaches zero and Eq. (1) reduces to

$$c \left(\frac{\partial T}{\partial t} \right) = QZ \ell^{-E/RT} \quad (7)$$

Also, again making the same simplifying assumptions used for deriving Eq. (4), namely $\frac{E}{RT} \approx \frac{E}{RT_0} \left(1 - \frac{T-T_0}{T_0} \right)$ and $\theta = \frac{E}{RT_0^2} (T-T_0)$, Eq. (7) can be expressed as

$$\int_0^{t_e} dt = t_e = \frac{cRT_0^2}{QZE} \ell^{E/RT_0} \int_0^{\theta_e} \ell^{-\theta} d\theta \quad (8)$$

Since it can be shown that $\theta_e \approx 1$, the time to ignition or explosion, t_e , is then approximated to be

$$t_e \approx \frac{cRT_0^2}{QZE} \ell^{E/RT_0} \quad (9)$$

where T_0 is the initial temperature of the adiabatically controlled system.

Eq. (7) is often conveniently used in the form $\ln \frac{dT}{dt} = \ln \frac{QZ}{c} - E/RT$

which is analogous to the empirical equation $\ln t_e = A + B/T$ that

fits adiabatic temperature-time profiles for many explosives. However,

many other systems do not fit this simple linear relationship.

Prior to the work of Shouman, *et al.*,¹² Zinn and Rogers¹³ had shown that from plots of the nonlinear relationship

$$\log_{10} t_e/\tau = \text{function} \left(\frac{E^*}{T_C} - \frac{E^*}{T_S} \right) \quad (10)$$

times-to-explosion values, t_e , could be read from the curve for specific sample surface temperatures, T_S , where E^* is the activation energy of the rate controlling reaction and $\tau = \frac{a^2 \rho C}{\lambda}$. Anderson¹⁴ approximated the function represented by Eq. (10) with two empirical straight line equations limited to different ranges of the function, i.e.,

$$\log_{10} t_e/\tau = 0.1400 - 0.0875 E^* \left(\frac{1}{T_C} - \frac{1}{T_S} \right) \quad (11)$$

for t_e/τ in the range 0.17 to 1.2 and

$$\log_{10} t_e/\tau = 1.134 - 0.1824 E^* \left(\frac{1}{T_C} - \frac{1}{T_S} \right) \quad (12)$$

for t_e/τ in the range 0.001 to 0.17.

Figure 4 reproduces Anderson's fit of his empirical equations to the Zinn/Rogers' nonlinear curve.

¹²*Op cit.*

¹³Zinn, J. & Rogers, R.N., J. Phys. Chem. 66 (1962) 2646.

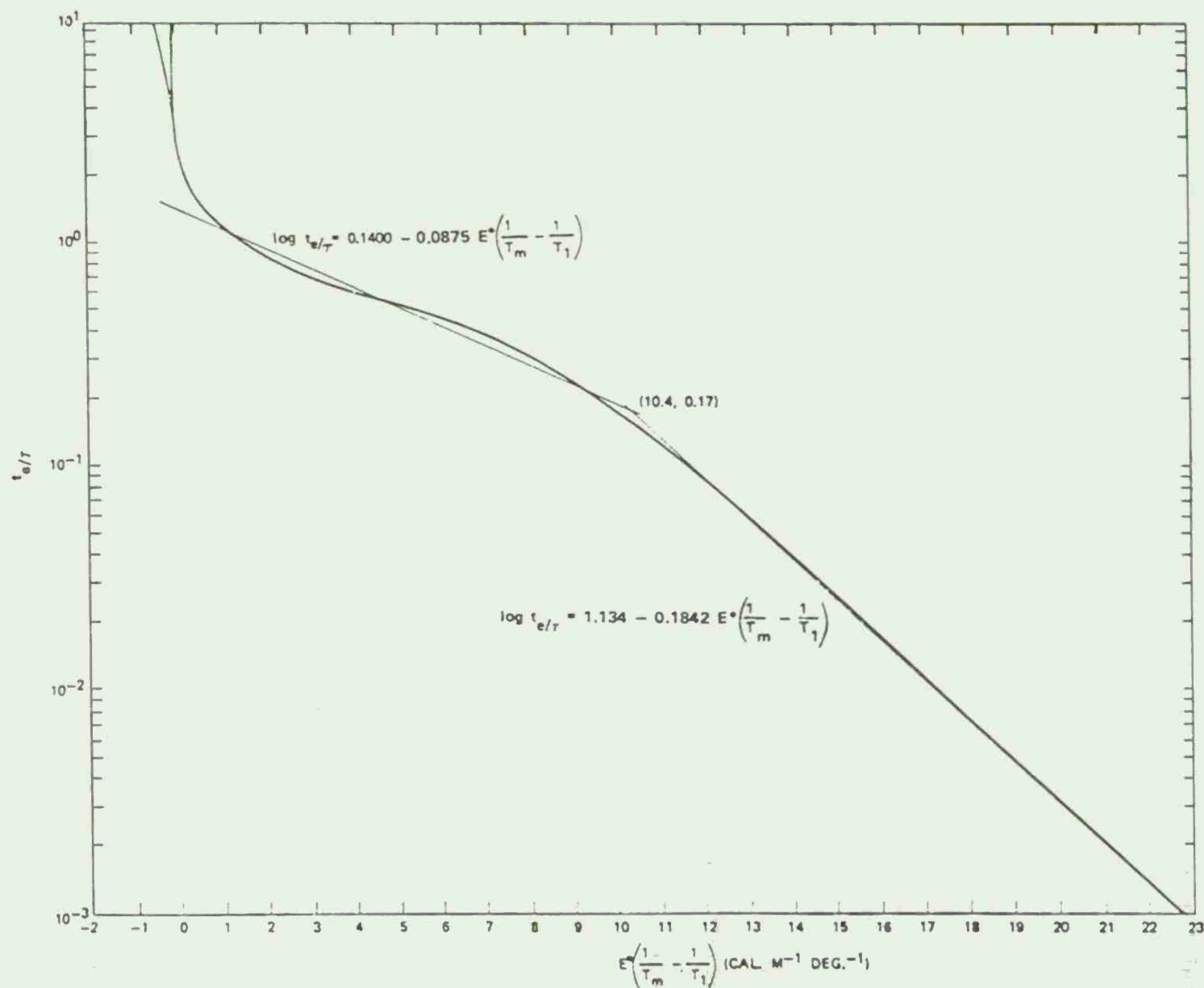


FIGURE 4. APPROXIMATION OF EQ'S. (11) AND (12) TO NONLINEAR CURVE OF REF 13

Table III is constructed from data presented in three tables by Sawyer and Williams⁵ who calculated critical temperatures and times-to-explosion for the ordnance items listed using Eq's. (6), (11) and (12), and physical and kinetic parameters cited by Anderson¹⁴ and Joyner.¹⁵ Appropriate δ_{cr} values are used for those charges that were not simple, solid slabs, cylinders or spheres. Thus, as an example, for hollow cylindrical charges, a corresponding δ_{cr} was used in the calculations.

The 5×10^{-9} probabilities were derived statistically by Sawyer and Williams from tables¹⁶ and the equation

$$Z = \frac{1-SM}{SM(CV)} - 1.84 \quad (13)$$

where Z = standard normal deviate

CV = coefficient of variation in thermal response data

SM = time-to-explosion/exposure time.

Anderson's equations had been verified experimentally in several cases and, on the face of it, would seem to imply that the same kinetic parameters apply in Eq. (6) as in Eq's. (11) and (12) and that, therefore, one might expect a similar degree of confidence in calculated times-to-explosion values t_e , as in those for critical temperature, T_c . That this is often far from the case comprises the remainder of this report.

IV. APPLICATIONS AND LIMITATIONS OF THERMOCHEMICAL EXPLOSION THEORY

A. Evaluation of ABL Data

Table III suffers from a serious flaw due to simplifying assumptions in its construction. The originators state that "...quantitative engineering analysis was made to determine...exposure times/temperatures corresponding to an acceptable risk level." This statement does not heed the warnings in some of their prime data sources.

⁵*Op cit.*

¹⁴Anderson, C.M., NWC TP 5245, Cookoff Prediction of Explosives by Thermal Analysis Techniques, Jul 1972.

¹⁵Joyner, T.B., NWC TP 4709, Thermal Decomposition of Explosives (U), Parts 1,2,4&9, dtd Mar 1969, Apr 1969, Jun 1970 & Oct 1973 (resp)
CONFIDENTIAL.

¹⁶J. Am. Statistical Assn., Jun 1970, p 637.

TABLE III. ABL CALCULATED TIMES-TO-EXPLOSION FOR ORDNANCE ITEMS AT VARIOUS TEMPERATURES

Item	Critical temp (°F)	Contents (molten)	Times-to-explosion ^a (hrs)									
			212°F		228°F		241°F		250°F		259°F	
			A	B	A	B	A	B	A	B	A	B
<u>Mines</u> Mk 25	221	HBX-1/Asphalt	>126.0 ^b	>81.0	114.0	74.0	74.6	49.0	55.8	37.0	42.0	28.0
Mk 25	180	TNT/Asphalt	127.0	82.0	84.8	55.0	62.6	41.0	50.7	33.0	41.3	27.0
Mk 39	221	HBX-1/Asphalt	>126.0	>81.0	114.0	73.0	74.6	48.0	55.8	36.0	42.0	27.0
Mk 50	239	HBX-3/Asphalt	>29.0	>18.0	>29.0	>18.0	>29.0	>18.0	23.5	15.0	17.9	11.5
<u>Torp WH</u> Mk 17	221	HBX-1/Asphalt	>111.0	>72.0	99.8	65.0	65.6	43.0	49.0	31.0	36.9	24.0
Mk 37	244	HBX-3/Asphalt	>19.2	>12.5	>19.2	>12.5	>19.2	>12.5	18.6	12.0	14.0	9.0
<u>Dep Chg</u> Mk 8	205	TNT/Asphalt	157.0	100.0	104.0	67.0	77.0	50.0	62.4	41.0	50.8	33.0
<u>Bombs</u> Mk 82	239	H-6/Asphalt	>26.3	>17.0	>26.3	>17.0	>26.3	>17.0	21.3	10.5	16.1	5.7
Mk 82	203	TNT/Asphalt	27.1	17.5	18.1	11.8	13.3	8.7	10.8	7.0	8.8	5.7

A = 0.5 probability at 50% confidence.

B = 5×10^{-9} probability at 95% confidence.

^aTime zero is when item is first subjected to the given temperature.

^bAnderson's technique of calculating times-to-explosion requires the use of certain parameters which are extracted from experimental data. For several items, times-to-explosion could not be determined at certain temperatures because required parameters were outside the given range. For such cases, times-to-explosion were calculated using end-of-the-range parameters. The symbol > appears before each number so calculated, indicating that the time-to-explosion is actually greater for the given temperature than indicated by that number given.

The questionable assumptions were:

- That kinetic parameters derived from "chemically pure" systems would be the same for the aged bomb compositions.
- That the kinetic parameters derived for the critical temperature calculations are the same rate controlling factors as those for times-to-explosion.
- That no side, autocatalytic or other competing reactions are occurring in any of the systems treated.

In short, our objective here is to reemphasize that a better understanding of the chemical ambiguities involved in explosive systems is essential to meaningful data reduction by mathematicians, statisticians and heat transfer specialists, as well as by explosive design and process engineers. Section IV.B summarizes relevant caveats that apparently were not taken into account.

B. Evaluation of the Thermal Explosion Literature

1. Autocatalysis

Longwell⁶ warns of the autocatalytic decomposition of nitrocellulose (used in D-2 waxes and all HBX-type explosive compositions) and points out that calculated values of T_c and t_e "...should be used with margins of safety dictated by engineering judgments that are strongly influenced by the magnitude of the cost of being wrong."

2. Solid-state decomposition

Rogers⁹ emphasizes the key points: 1) that critical temperatures are determined by the maximum rate attainable in the condensed phase reaction for the explosive in question, and 2) that kinetic constants from these rapid reactions can be measured "quite accurately" but that times-to-explosion may be largely determined by difficult-to-measure, premolten, solid-state reactions which "...can vary tremendously with changes in purity and crystal perfection."

3. Catalysis

Joyner¹⁵ speaks of the catalytic role of iron oxides (rust) causing as much as tenfold acceleration rates in TNT-based systems and extrapolation of his TNT/asphalt (clean) data shows that at 120°C there is already a 1 percent decomposition in only 3 hours.

⁶Op cit.

⁹Op cit.

¹⁵Op cit.

He also warns of the many potential side reactions of past and current weapons systems containing some or all of the following ingredients in various states of purity: TNT, RDX, hot melt, wax, CaCl_2 , H_2O , Al, rust, NH_4NO_3 , KNO_3 , paint, etc.

Joyner's¹⁷ basic warning is that in order to substantiate theory, most experimental data is generated from highly purified materials where reaction products are usually free to escape. Until fairly recently, no serious efforts have been made to simulate "real world" reaction conditions. The kinetic constants generated by Joyner, and used by Anderson and ABL, were those derived from highly purified components with escaping reaction products.

Urbanski¹⁸ also describes accelerated reaction rates for TNT-metal systems.

4. Temperature control

The AMCP handbook⁷ warns of the importance of both accurate temperatures and close temperature controls for any heating operations such as melting, drying, etc. Even assuming that none of the problems cited in B.1, 2 and 3 exist in aged ordnance, the statistical calculations for 5×10^{-9} probabilities of explosion made by ABL give the explosive process engineer a false sense of security. Figure 5, generated from their calculated values in Table III for the TNT-asphalt Mk 25 Mine, illustrates this point. It can be seen that relatively small temperature changes, i.e., only about 10°C , can lead to a 50% probability of explosion rather than a 5×10^{-9} probability for the same systems heated for the same time period.

That such temperature fluctuations are far from an unlikely occurrence in production operations is discussed next.

5. Explosion in the TNT melt shop at Muiden, Holland

Groothuizen¹⁹ and his coworkers have reported on their investigation of the KNSF melt shop explosion in June 1966. While the TNT reclamation process going on prior to the explosion does not completely parallel the autoclave melt-out process, there are, nonetheless, uncomfortable similarities.

¹⁷Joyner, T.B., private communication, Dec 1975.

¹⁸Urbanski, T., Chemistry & Technology of Explosives, Vol I, Pergamon Press Ltd., 1967.

⁷*Op cit.*

¹⁹Groothuizen, T.M., Lindeijer, E.W. & Pasman, H.J., Explosivestoffe 5 (1970) 97.

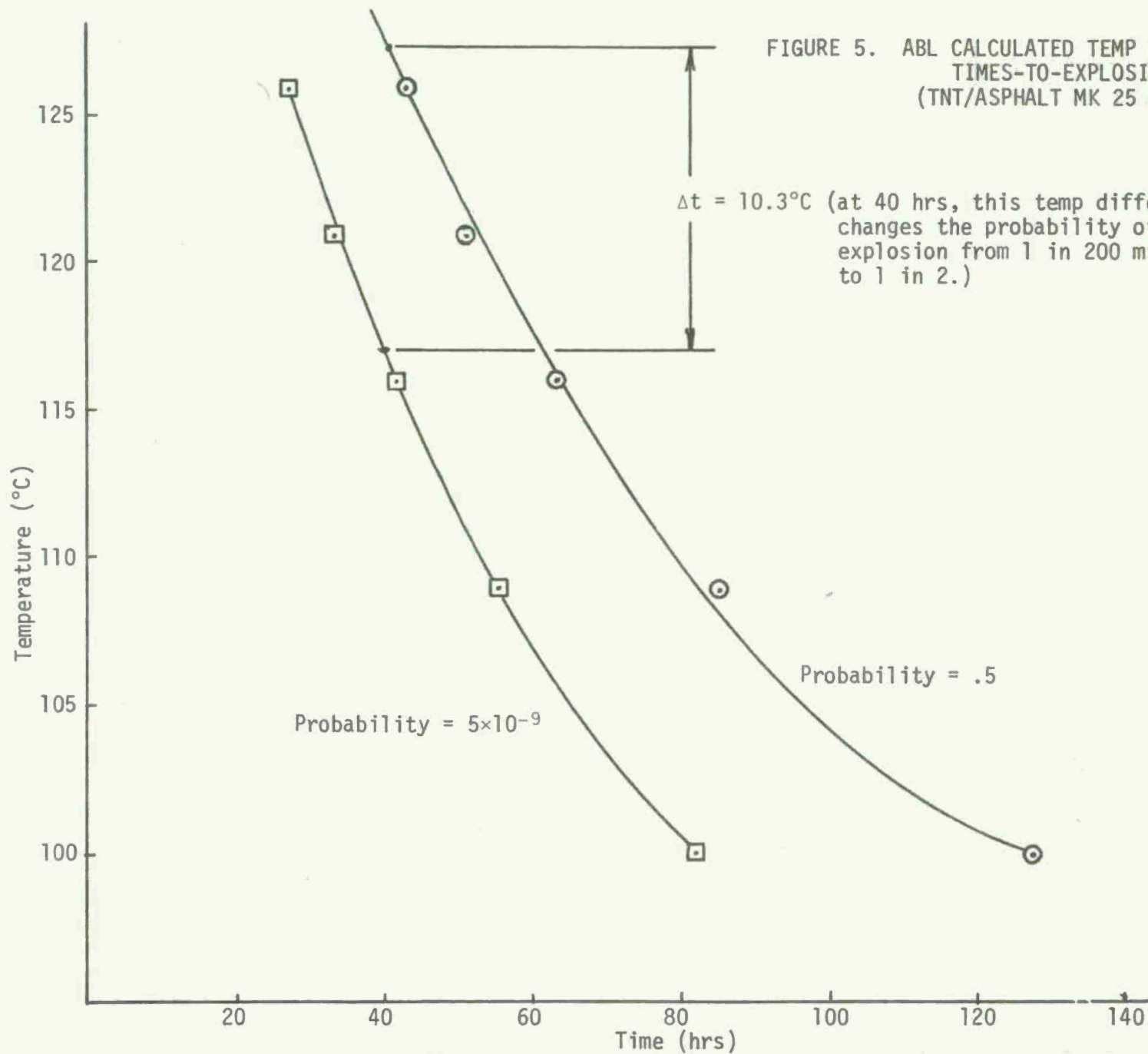


FIGURE 5. ABL CALCULATED TEMP VERSUS TIMES-TO-EXPLOSION (TNT/ASPHALT MK 25 MINE)

In the KNSF melt shop, the melt tank was an agitated, steam-jacketed vessel with bottom and side drain cocks and an inside diameter of 3 feet. The melt tank was used to reclaim TNT from various sources for reloading into other weapons and contained about 1000 pounds of TNT at the time the explosion occurred.

Unfortunately, the operating conditions prior to the explosion were not completely known. For examples: the explosion occurred at 4:00 p.m. on 2 June with the melt tank being put in operation on 31 May but it is not clear whether it was continuously being heated from 31 May to 2 June or only on one shift per day; temperatures may have gone as high as 150°C, or even higher, for reasons not clearly listed; various contaminants such as cardboard, KCl, NH_4NO_3 , KNO_3 , etc., may or may not have been present in the scrap being melted; the agitator was not in operation at explosion time.

Nonetheless, what is important were the results of the post-explosion investigation. Four samples were formulated from TNT and supposed contaminants and held adiabatically while the heat evolution of reaction was measured against time. Samples were:

- (1) Pure TNT
- (2) TNT + 2% NH_4NO_3 + 1% cardboard + trace KCl
- (3) TNT + 0.2% KNO_3
- (4) TNT + 0.5% propellant + 0.5% soap powder + 0.5% cardboard + 0.5% Fe + 2% NH_4NO_3 + trace KCl

For the first three cases, "...heat generated increased significantly with temperature (2.3 to 3 times per 10°C)....At the same temperature (180°C) the respective heat generations for samples (2) and (3) were 20 and 35 times higher than the pure TNT (1)." In sample (4), which in many ways most resembles typical aged Navy ordnance that will be demilitarized in the future, only one measuring point was obtained. "The reason was that 5 hours after the test started, the mixture suddenly ignited. Prior to that, the temperature had risen only a few degrees. The temperature just before ignition was 134° to 135°C."

Other findings by Groothuizen, *et al.*, are instructive. In their investigations of cardboard contaminants, they concluded that "...it is indeed possible that by absorption of TNT on a solid having a large specific surface, the rate of decomposition is greatly increased. This appeared from tests with active carbon as a contaminant in which the TNT ignited 15 minutes after the mixture had reached the oven temperature of 135°C."

They hypothesized that the abrupt ignition of TNT when cardboard is present is due to the formation of a solid mass of TNT together with an insoluble decomposition product. In this mass, convection is impossible and the slow dissipation of heat by conduction only can lead to local self-heating and hot spots. This explanation is supported by the fact that abrupt ignition also took place when glass wool was substituted for cardboard.

Also, in an earlier study, this same laboratory²⁰ had made another highly significant finding - the effect of ageing.

In brief, measurements were made of the adiabatic self-heating of TNT versus time for both pure TNT and for TNT that had been aged by successive melting, cooling and remelting, etc. Data obtained fitted the familiar Arrhenius type equation:

$$q = Ca e^{-Ea/RT} \quad (14)$$

where q = heat generated watts/kg
 R = gas constant cal/mol $^{\circ}$ K
 Ea = apparent energy of activation cal/mol
 Ca = pre-exponential factor watts/kg
 T = temperature $^{\circ}$ K

The data obtained is highly instructive and is reproduced in Table IV.

TABLE IV. ADIABATIC SELF-HEATING OF TNT

Sample	Temp range ($^{\circ}$ C)	Depth of conversion as $^{\circ}$ C self-heating	$\log_{10} Ca$ (w/kg)	Ea (Kcal/mol)
Pure TNT	145-196	0-51	20.60	43.0
Remelted TNT	150-160	51-61	15.46	31.3
Re-remelted TNT	126-144	61-79	13.51	27.2

²⁰Pasman, H.J., Groothuizen, T.M. & Vermeulen, C.M., Explosivestoffe 7 (1969).

The striking increase in depth of conversion, 61-79 at 126° to 144°C for re-melted TNT versus 0-51 at 145° to 195°C for pure TNT, coupled with the marked decrease in the exponential apparent energy of activation, E_a , raises serious questions about the advisability of melt-recast processes without some intermediate purification of the explosive system. This is in keeping with the tenfold decrease in vacuum stability and the methyl violet reaction previously described in the NAVWPNSTA Yorktown work in Section II.

In addition, Groothuizen, *et al.*, observed gassing prior to ignition or explosion in their controlled experiments. This factor also parallels the NAVWPNSTA Yorktown experiment. When the original autoclave experiment was run at NAD Hawthorne, gassing was also noted but was attributed to trapped air.

As a final note of warning, it is a current Army practice to subject major caliber projectiles to long (several days) heat soaking at elevated temperatures to heal cracks and case separations of their explosive charges.

Potential decomposition problems are obviously present and it is recommended that further studies along the lines of Groothuizen and his co-workers be carried out to assure that acceptable safety margins exist.

V. SUMMARY

- During the autoclave melt-out of aged Mk 25 Mines, decomposition reactions began to take place at times well below those predicted from thermochemical theory for pure components in the system.
- Ample warnings exist in the thermochemistry of explosion literature testifying to the fact that many side and solid-state reaction kinetics may be the rate determining steps for times-to-explosion in less than pure systems of the above types.
- A purely statistical estimate of probabilities of explosion even for pure systems can be beguiling without mention of the tremendous impact of small changes in temperature on overall explosion times.
- The differences between theoretically calculated and experimentally determined values for critical temperatures and times-to-explosion have been steadily narrowed for pure systems by a succession of outstanding investigations. However, a better understanding and more kinetic data are

required of impure reaction systems before any quantitative thermal explosion predictions can be made about them. This is particularly true when prolonged and/or repeated heating of any kind is involved.

VI. REFERENCES

- 1 National Environmental Policy Act (PL-91-90).
- 2 Executive Orders 11507 & 11514.
- 3 NAVWPNSTA Yorktown files (NEDED File #897 Jun 1971-Sep 1972).
- 4 Kim, B.C., *et al.*, Battelle Columbus Laboratories, Final Report on Explosive Melt Out Study (N62474-74-C-3913), Sep 1975.
- 5 Sawyer, S.O., & Williams, G.M., Allegheny Ballistics Laboratory Final Rept No. A0827-520-03-006, Hazards Analysis Report, Part II, Jan 1976 (prep for Battelle Columbus Laboratories).
- 6 Longwell, P.A., NAVWEPS Rept 7646, Calculation of Critical Temperature and Time to Explosion for Propeilants and Explosives, Mar 1961.
- 7 AMCP 706-180, Principles of Explosive Behavior, Apr 1972.
- 8 Zinn, J. & Mader, C.L., J. Appl. Phys. 31 (1960) 323.
- 9 Rogers, R.N., *Thermochimica Acta* 11 (1975) 131-9.
- 10 Hardee, H.C., Lee, D.O. & Donaldson, A.B., *Combustion and Flame* 18 (1972) 403-10.
- 11 Enig, J.W., *Proc. Roy. Soc.* 305A (1968) 205.
- 12 Shouman, A.R., Donaldson, A.B. & Tsao, H.Y., Exact Solution to the One Dimensional Stationary Energy Equation for a Self-Heating Slab, *Combustion and Flame* 23 (1974) 17-28.
- 13 Zinn, J. & Rogers, R.N., *J. Phys. Chem.* 66 (1962) 2646.
- 14 Anderson, C.M., NWC TP 5245, Cookoff Prediction of Explosives by Thermal Analysis Techniques, Jul 1972.
- 15 Joyner, T.B., NWC TP 4709, Thermal Decomposition of Explosives (U), Parts 1,2,4&9, dtd Mar 1969, Apr 1969, Jun 1970 & Oct 1973 (resp) CONFIDENTIAL.

- 16 J. Am. Statistical Assn., Jun 1970, p 637.
- 17 Joyner, T.B., private communication, Dec 1975.
- 18 Urbanski, T., Chemistry & Technology of Explosives, Vol I, Pergamon Press Ltd., 1967.
- 19 Groothuizen, T.M., Lindeijer, E.W. & Pasman, H.J., Explosivestoffe 5 (1970) 97.
- 20 Pasman, H.J., Groothuizen, T.M. & Vermeulen, C.M., Explosivestoffe 7 (1969).

INITIAL DISTRIBUTION

Copies

Commander, Naval Sea Systems Command	
Washington, DC 20362	
(SEA-0332)	1
(SEA-04H3)	1
(SEA-9843)	1
(SEA-99111)	1
(SEA-9912)	1
(SEA-992E)	1
 Commander, Naval Air Systems Command	
Washington, DC 20361	
(AIR-53232A)	1
 Chief of Naval Material	
Navy Department	
Washington, DC 20360	
(MAT-0323)	1
 Director, Naval Research Laboratory	
Washington, DC 20375	
Attn: Dr. J. M. Schnur (Code 5513)	1
 Director of Navy Laboratories	
Room 300, Crystal Plaza Bldg. 5	
Washington, DC 20390	1
 Chief of Naval Research	
800 North Quincy Street	
Arlington, VA 22217	
Attn: Technical Library	1
 Commander, Naval Sea Systems Command	
Naval Ammunition Production Engineering Center	
Naval Weapons Support Center	
Crane, IN 47522	
(SEA-9926)	1
 Commander, Naval Weapons Support Center	
Crane, IN 47522	
Attn: D. Groh	1
Technical Library	1
 Commanding Officer, Naval Weapons Station	
Concord, CA 94520	
Attn: WQEC	1

INITIAL DISTRIBUTION (cont'd)

	<u>Copies</u>
Commanding Officer, Naval Ammunition Depot Hawthorne, NV 89415 Attn: Technical Library	1
Commander, Naval Surface Weapons Center Dahlgren Laboratory Dahlgren, VA 22448 Attn: Dr. B. Smith (Code DG) Technical Library	1 1
Commander, Naval Surface Weapons Center White Oak Laboratory Silver Spring, MD 20910 Attn: Dr. Donna Price M. J. Stosz	1 1
Commander, Naval Weapons Center China Lake, CA 93555 Attn: Dr. R. Reed, Jr. Taylor B. Joyner Carl M. Anderson	1 1 1
Commanding Officer, Naval Ordnance Station Indian Head, MD 20640 Attn: Technical Library	1
Commanding Officer, Navy Ships Parts Control Center Mechanicsburg, PA 17055 (Code 732C)	1
Commander, Pacific Missile Test Center Point Mugu, CA 93042 Attn: R. W. Slyker	1
Commanding Officer, Naval Weapons Station Yorktown, VA 23691 (Code 016)	1
Administrator, Defense Documentation Center for Scientific and Technical Information (DDC) Bldg. No. 5, Cameron Station Alexandria, VA 22314	12
U.S. Bureau of Mines 4800 Forbes Avenue Pittsburgh, PA 15213 Attn: Technical Library	1

INITIAL DISTRIBUTION (cont'd)

Copies

Commanding Officer, Picatinny Arsenal	
Dover NJ 07801	
Attn: Dr. Harold J. Matsuguma	1
Donald E. Seeger	1
Leon Saffian	1
Paul Reibel	1
Commanding General, Aberdeen Proving Ground	
Aberdeen, MD 21005	
Attn: Technical Library	1
Commanding Officer	
Western Division, Naval Engineering Facilities Command	
P.O. Box 727	
San Bruno, CA 94066	
Attn: William Moore	1
Commanding Officer, Army Engineering Research and	
Development Laboratory	
Fort Belvoir, VA 22060	
Attn: Technical Library	1
Director, Holston Defense Corporation	
Kingsport, TN 37660	
Attn: J. T. Rogers	1
Commanding General, Army Ammunition Plant	
Joliet, IL 60434	
Attn: Technical Library	1
Commander, Wright Air Development Center	
Wright-Patterson Air Force Base	
Dayton, OH 45433	
Attn: Technical Library	1
Commander, Air Force Armament Laboratory	
Eglin Air Force Base, FL 32542	
Attn: Technical Library	1
Director, Los Alamos Scientific Laboratory	
P.O. Box 1663	
Los Alamos, NM 87544	
Attn: Raymond N. Rogers	1
A. Popolato	1

INITIAL DISTRIBUTION (cont'd)

	<u>Copies</u>
Director, Lawrence Livermore Laboratory	
University of California	
P.O. Box 808	
Livermore, CA 94551	
Attn: M. Finger	1
Technical Library	1
 Mason & Hanger, Silas Mason Co., Inc.	
Iowa Army Ammunition Plant	
Middletown, IA 52638	
Attn: F. J. Brodsky	1
 Hercules Inc., Alleghany Ballistics Laboratory	
P.O. Box 210	
Cumberland, MD 21502	1
 Battelle Columbus Laboratories	
505 King Avenue	
Columbus, OH 43201	
Attn: B. C. Kim	1
 Ablard Enterprises, Inc.	
10851 Amherst Avenue	
Silver Spring, MD 20902	
Attn: James E. Ablard	1
 Chairman, Department of Defense Explosives Safety Board	
Washington, DC 20315	1

