Peak Overpressures For Internal Blast

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JUNE 1979

JUL 17 1979

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Naval Weapons Center
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FOREWORD

The destructive force of confined explosions, such as those occurring in grain elevators, coal mines, or ship compartments, was investigated. Peak overpressures generated by these explosions were calculated from basic considerations of conservation of mass, conservation of energy, and the second law of thermodynamics. Computations were made for a large number of confined explosions with conventional fuels, as well as with pure chemical explosives and their mixtures for a wide range of fuel-air ratios.

This investigation was undertaken as part of a continuing effort to strengthen our capabilities in support of blast studies. The work was performed during fiscal years 1974-1978 and funded by Director of Navy Laboratories Programs Task Assignment ZR000-01-01 and by the Naval Air Systems Command under the Strike Warfare Weaponry Technology Block Program, AIRTASK A03W 03P2/008B/7F323 000 000 (Appropriation 1781319).

E. M. Fisher, AIR-350, was the cognizant NAVAIR Technology Administrator. This report has been reviewed for technical accuracy by James A. Weeks.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NWC-TP-6089	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* PEAK OVERPRESSURES FOR INTERNAL BLAST		5. TYPE OF REPORT & PERIOD COVERED A final report 1974-1978
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) G. F. Kinney, R. G. S. Sewell, and K. J. Graham		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task Assign. ZR000-01-01 and AIRTASK A03W 03P2/008B/7F32 3000 000 (Approp. 1781319)
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555		12. REPORT DATE June 1979
		13. NUMBER OF PAGES 60
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)* Chemical Equilibrium Constant Volume Chemical Thermodynamics of Combustion Gases at High Temperatures Internal Blast Internal Blast Yields Overpressures, Internal Blast Products Composition		
20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*		

(handwritten annotations on form: "14", "6", "10", "15) 66 p.", "11", "9) Final rept. 1974-1978", "16) ZR 0000 1, F32 300", "17) ZR.0000 101, SF32 3000 00", "403 029")

(U) *Peak Overpressures for Internal Blast,*
by G. F. Kinney, R. G. S. Sewell and K. J.
Graham.   China Lake, Calif., Naval Weapons
Center, June 1979.   60 pp.   (NWC TP 6089, pub-
lication UNCLASSIFIED.)

(U) Rapid combustion of fuel in a confined
volume of air generates internal blast that can
be quite destructive. Peak overpressures have
been calculated for the internal blast result-
ing from the explosive combustion of both con-
ventional and explosive C-H-N-O fuels by using
a tabletop computer. The calculations utilize use
the principles of the conservation of mass, the
conservation of energy, and the second law of
thermodynamics. The calculational routine
allows for variations in the possible heat
transfer to cool confining walls, altitude of
the combustion, and the velocity of fuel in-
jection into the confining volume. The code
also computes items not normally available ex-
perimentally, such as the explosion flame tem-
perature and the composition, formula mass,
and heat capacity of the explosion products.
Results for representative internal blast situ-
ations are presented and discussed.

CONTENTS

INTRODUCTION

Internal blast is the concussion effect in a confined explosion. Confined air is suddenly warmed, generating a pressure rise that can be quite damaging. Examples of internal blast include blast from explosions in ship compartments, dust explosions in grain elevators or in coal mines, explosions of gasoline fumes in motorboat hulls or in refinery tanks, and natural gas explosions in kitchens or in entire buildings. Internal blast may also account for a situation such as the mysterious disappearance of an oil tanker at sea.

Suddenness of the pressure rise in these internal explosions results from a well-known effect of pressure, which increases the rate of chemical reaction—that of combustion. A small pressure rise from an initial temperature rise increases the rate of combustion, which in turn increases the rate of pressure rise, and so on, until some limiting condition is reached. For internal explosions, the limiting condition is the peak overpressure for internal blast.

With internal blast, and considering both conventional and explosive fuels composed of carbon, hydrogen, nitrogen, and oxygen, and including argon from the air, there are five types of atoms in the products. These products may involve as many as 12 different chemical species including unstable ones such as hydroxyl and monatomic hydrogen, monatomic oxygen, and monatomic nitrogen. To characterize these 12 species, 12 independent relations are required. Five of these are provided by the law of conservation of mass, one for each type of atom. The seven additional relations are obtained through the second law of thermodynamics where the minimum Gibbs free energy restriction is utilized in the form of chemical equilibrium constants. These form 12 simultaneous nonlinear algebraic equations that can be solved by a simple heuristic method that is described and illustrated, and for which a small tabletop computer is quite suitable.

To determine blast overpressure in an internal explosion, it is necessary to know the explosion temperature and composition of products at that temperature. To determine explosion temperature, the conservation of energy principle is utilized. The energies involved must include both thermal

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energies associated with chemical composition. When these
are known, the blast overpressure is computed through the
ideal gas law. Such computations are all described by ex-
ample.

Overpressures computed for internal explosions with TNT
agree well with experimental values. Such theoretical calcu-
lations also yield items not readily available experimentally;
e.g., explosion flame temperature and the composition, for-
mula mass, and heat capacity of explosion products. The pro-
gram also allows for the varying effects of (1) injecting a
fuel at high velocity, (2) altitude on blast overpressure,
and (3) heat transfer from a hot flame to cool confining
walls.

Overpressures in internal explosions depend on both the
amount and type of fuel causing the explosion. A fuel can be
characterized by its internal blast yield, which is the in-
verse ratio of the amount of a fuel of concern to the amount
of a reference fuel that provides the same overpressure. In-
ternal blast yields have been computed and are reported for
conventional fuels such as jet fuel, gases such as ethylene
and methane, and explosive fuels such as hexanitrobenzene and
pentaerythritoltetranitrate.

CHARACTERISTICS OF INTERNAL BLAST

PEAK OVERPRESSURES

Blast in an internal explosion is characterized largely
by its peak overpressure and duration. Peak overpressures
for an internal explosion ordinarily are only a few bars,
perhaps 10 or less, and are low compared with overpressures
for explosions in the unconfined atmosphere. Maximum peak
overpressures in internal explosions occur for the special
case of (1) no venting effects, and for (2) adiabatic condi-
tions with no cooling effects by heat transfer to confining
walls. Such maximum peak overpressures are a primary con-
cern in this report.

After the peak overpressure is attained, a quasi-expo-
nential pressure-decay phase is caused by cooling effects of
confining walls and by gas leakage by venting. This decay
effect is relatively slow compared with rates that ordinarily
occur in explosions in the unconfined atmosphere. The decay,
however, causes the pressure to approach an equilibrium value
that for vented explosions is also the ambient. For non-
vented explosions, this equilibrium pressure can be greater

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than ambient if additional gas volume is given by formation of species such as carbon monoxide, or can be less than ambient pressure with gas diminishing reactions such as formation of aluminum oxide.

The slow pressure-decay rates for internal explosions lead to relatively long overpressure duration times that are perhaps as long as a major fraction of a second. The time integral of the blast overpressure is the blast impulse per unit area. Blast impulse can be an important factor in blast damage capability, but for internal blast all this impulse may not be effective for structural damage. This situation arises because such decay time may exceed a critical time for the affected structure.[1]

EXPLOSIVE VERSUS CONVENTIONAL FUELS

Internal blast from explosions with conventional fuels is the direct result of a simple combustion process. Explosive fuels, however, differ somewhat in that an initial detonation sets up a transient explosive shock, one that is quickly dissipated and can often be neglected in the overall energy effects. For explosive fuels that also are oxygen-deficient (trinitrotoluene (TNT), for example), the initial detonation is followed by combustion in an afterburn; it is the combined detonation-combustion reaction that generates internal blast. For explosive fuels that are oxygen-rich (nitroglycerin, for example), there is no afterburn; internal blast is only : result of the warming effect of a detonation.

With conventional fuels the internal blast overpressure reaches a maximum at a fuel-air ratio that corresponds to optimum utilization of the oxygen present. Less fuel leaves unused oxygen, while more fuel does not give any increased energy release. Excess fuel serves only to increase the amount of products to be warmed, and the reduced temperature rise that results gives a decrease in developed overpressure. The characteristic maximum overpressure for conventional fuels contrasts with the behavior of explosive fuels that carry their own oxygen; developed overpressures for explosive fuels increase monotonically with the amount of fuel.

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[1] R. G. S. Sewell and G. F. Kinney. "Response of Structures to Blast: A New Criterion," *Ann. N. Y. Acad. Sci.*, Vol. 152 (1968), p. 532.

THEORETICAL BACKGROUND

Efforts to describe internal blast mathematically date back at least to 1945, when the Los Alamos Scientific Laboratory suggested an empirical equation,[2]

$$\Delta P = 3000(W/V) \tag{1}$$

in then acceptable units of overpressure ΔP in pounds per square inch, mass of explosive W in pounds, and confined volume of air V in cubic feet. In modern metric units of bars, kilograms, and cubic metres (steres) this can be written as

$$\Delta P = 13(W/V) \tag{2}$$

The metric pressure unit is the bar, defined in terms of SI units as 10^5 pascals (newtons per square metre), or as one-tenth of a megapascal. One bar corresponds to a pressure of 14.5 psi, approximately that of the ordinary atmosphere. The units of the term (W/V) of the equation, kilograms per cubic metre, are almost identical with ounces per cubic foot.

Overpressures computed through empirical Equation 2 for internal explosion with TNT in air are shown in Figure 1. Also shown are experimental values for ordinary sea level conditions.[3] Rough agreement is indicated.

Subsequently an equation for internal blast overpressure was derived using the ideal gas law, but ignoring many complicating effects.[4] This equation states that for adiabatic nonvented conditions the overpressure, pounds per square inch, is

$$\Delta P = 8.8(H/V) \tag{3}$$

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[2] Private communication between James Weeks and R. W. Carlson, *Confinement of an Explosion by a Steel Vessel*, Los Alamos Scientific Report LA-390 dated 1945.

[3] Hans R. W. Weibull. "Pressures Recorded in Partially Closed Chambers at Explosions of TNT Charges," *Ann. N. Y. Acad. Sci.*, Vol. 152 (1968), p. 357.

[4] National Defense Research Committee. *Effects of Impact and Explosion*. Vol. 1. Washington, D. C., NDRC, 1946. P. 91. (Summary Report of Technical Division 2, Vol. 1, publication UNCLASSIFIED.)
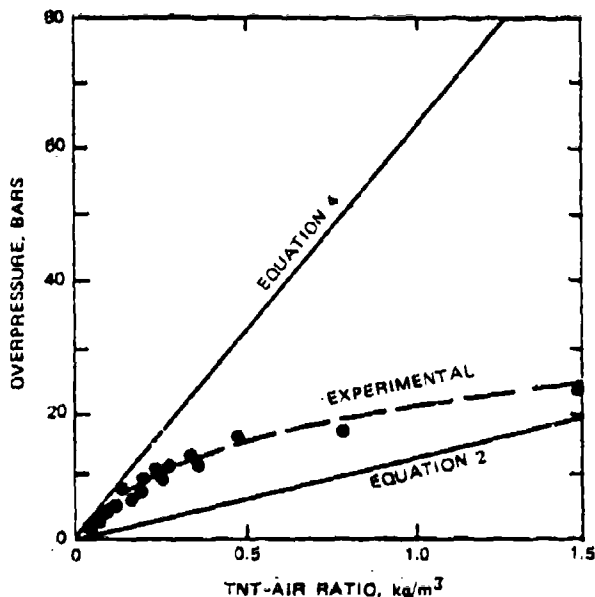
FIGURE 1. Internal Blast Overpressures
for TNT-Air Explosions.

where the term H/V is heat of combustion in kilocalories per
cubic foot of product gases. In metric units of the bar and
the joule per cubic metre, this equation becomes

$$\Delta P = 10^{-5}(k - 1)(H/V) \tag{4}$$

where k is the ratio of heat capacities for the confined gas,
taken as 1.4, as for air at room temperature. Derivation of
this equation ignores the effects of gases formed in the ex-
plosion, of temperature on heat capacity, and more import-
antly, the energy absorbing effects of chemical dissociations
in the explosion-combustion flame. Equation 4 may thus
greatly overstate internal blast overpressures, particularly
for explosions with appreciable fuel-air ratios (Figure 1).

An alternative approach to internal blast is afforded
by thermodynamics. Results of simplified analysis conform

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approximately to experimental values, presumably by compensation effects.[5] An improved and rigorous thermodynamic analysis of internal blast takes into account the complicating effects described above. Particularly important among these are chemical dissociations that set an effective ceiling on both explosion temperature and blast overpressure. Combustion products at mechanical, thermal and chemical equilibrium are considered in the analysis, omitting transient effects of initial explosive shock.

These thermodynamic calculations are based on an ideal solution of ideal gases. The principles of conservation of mass, conservation of energy, and of minimum Gibbs free energy are used. These considerations are taken up separately. Representative results from such calculations are shown in Figure 2. In this log-log plot, computed versus experimental overpressures generated for TNT-air internal explosions are compared. Good agreement is obtained over about three decades in fuel-air ratios, a result that leads to confidence in the computations.

In thermodynamic analysis for internal blast, a products composition is first found that corresponds to some more or less arbitrarily selected temperature. Products energy, which must include both thermal and chemical aspects, is then found for each component; the weighted sum of these gives a total energy for the products system. For adiabatic combustions this total energy equals that for the original fuel and air. Successive trial temperatures are then selected until the adiabatic condition of zero energy difference is found. Through this method energy accounting proceeds indirectly through formation energies for individual components rather than through direct considerations of the chemical reactions themselves.

Conventional fuels such as fuel oil contain primarily carbon and hydrogen, and explosive fuels such as TNT generally contain nitrogen and oxygen. These are all identified as C-H-N-O fuels. Air for the combustion reaction contains

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[5] Air Force Systems Command for Joint Technical Coordinating Group for Munitions Effectiveness. *Internal Blast Damage Mechanisms Computer Program*, by James F. Proctor, Naval Ordnance Laboratory, Silver Spring, Md. Dayton, Ohio, AFSC, Wright-Patterson Air Force Base, 10 April 1973. (Report 61-JTCG/ME-73-3, publication UNCLASSIFIED.)
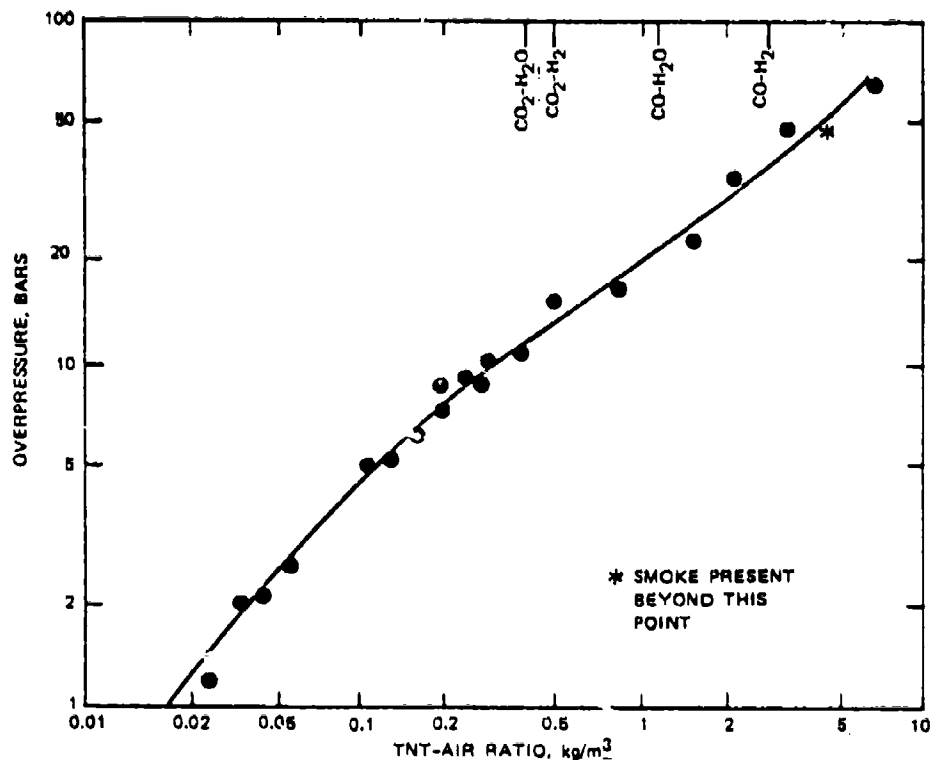
FIGURE 2. Computed (solid line) Versus Experimental (points) Overpressures for TNT-Air Internal Explosions.

nitrogen, oxygen, and argon, so that five different atomic species can be in the resulting products mixture.

It has been found that for explosion of C-H-N-O fuels in air there may be as many as 12 different chemical species in the hot gaseous products. These include the usual combustion products: carbon dioxide, CO_2; carbon monoxide, CO; water vapor, H_2O; hydrogen, H_2; nitrogen, N_2; oxygen, O_2; and argon, Ar. Nitric oxide NO, the unstable monatomics hydrogen H, oxygen O, and nitrogen N, and the unstable compound hydroxyl OH must also be included. These 12 species in the products constitute 12 unknowns so that 12 independent relations are required to find the amount of each component present. These 12 relations are given in the following discussions.

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CONSERVATION OF MASS RELATIONS

The conservation of mass principle is utilized in terms of individual elements. Thus all carbon in the products system is supplied by the fuel and can be expressed as the number of moles of carbon atoms, a_C. This equals the sum of the number of moles of carbon dioxide, CO_2, and carbon monoxide, CO, in the products; i.e., $a_C = CO_2 + CO$, where a chemical formula is used to indicate the number of moles of a designated species. This type of equation is identified as a material balance. Similarly the material balance for hydrogen atoms, a_H, equals twice the number of moles of water vapor, plus twice that for molecular hydrogen, plus that for monatomic hydrogen and hydroxyl OH. Such material balances for the five chemical elements are written as follows:

Carbon $\qquad a_C = CO_2 + CO$ $\hfill (5)$

Hydrogen $\qquad a_H = 2H_2O + 2H_2 + H + OH$ $\hfill (6)$

Oxygen $\qquad a_O = 2CO_2 + CO + H_2O + 2O_2 + O + OH + NO$ $\hfill (7)$

Nitrogen $\qquad a_N = 2N_2 + N + NO$ $\hfill (8)$

Argon $\qquad a_{AR} = Ar$ $\hfill (9)$

These material balances represent five of the required 12 relations; the remaining seven are obtained from free energy consideration.

NOMINAL PRODUCTS

Preliminary to computation of the composition of the products in an internal explosion is the assignment of nominal values for the number of moles of each to its components. There are several different sets of such nominal values, all based on material balance relations. In the method selected, oxygen is assigned first to conversion of carbon into carbon monoxide, then to conversion of carbon monoxide into carbon dioxide, then to conversion of hydrogen into water, and if any remains, to molecular oxygen. Such nominal compositions correspond well to actual combustions at lower temperatures; at high temperatures a more realistic nominal composition is obtained by considering the formation of water before the formation of carbon dioxide.

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STOICHIOMETRIC REFERENCE POINTS

Various stoichiometric reference points can be established in terms of the nominal products compositions. The CO_2-H_2O point corresponds to the fuel-air ratio for complete combustion to CO_2 and H_2O without excess oxygen. The CO_2-H_2 point represents a lesser oxygen supply (or a greater fuel supply) where the nominal products contain elemental hydrogen rather than water vapor. The CO-H_2O and the CO-H_2 points are similarly defined. Fuel-air ratios for these four stoichiometric points for internal explosions with TNT are indicated in Figure 2. Since there are no discontinuities in the pressure curve at these points, they do not represent situations for a sudden change in products composition. A representative computation of a stoichiometric reference point is presented in Appendix A.

A fuel supply less than that for the conventional CO_2-H_2O stoichiometric point corresponds to an oxygen-rich or fuel-lean combustion; a greater fuel supply corresponds to fuel-rich conditions. A fuel supply even greater than that for the CO-H_2 stoichiometric point may also correspond to the presence of solid carbon in nominal products. The CO-H_2 point is also the nominal smoke point; a greater fuel supply can be expected to generate a smoky flame.

GIBBS FREE ENERGY RELATIONS

The second law of thermodynamics states that a closed system in equilibrium at uniform pressure and temperature shows a minimum in its total Gibbs free energy. The same rules apply to the quasistatic situations with internal explosions. Gibbs free energy values for particular species are conveniently expressed in alternative form as equilibrium constants of formation; data are available in sources such as the JANAF thermochemical tables.[6] These tabulated data are readily converted into conventional thermodynamic equilibrium constants, and in turn into working equilibrium constants in terms of mole numbers, K_n (Appendix B).

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[6] National Bureau of Standards. *JANAF Thermochemical Tables*, D. R. Stull and H. Prophet, Project Directors. Washington, D. C., NBS, 1971.

The seven mole-number relations required here and obtained by Gibbs free energy considerations are shown below. In the chemical equation to the left, a chemical formula identifies a specific component in a mixture at chemical equilibrium. In the equilibrium constant equations to the right, a chemical formula represents the number of moles of that component present in the equilibrium mixture.

Dissociation of carbon dioxide:

$$CO_2 = CO + \tfrac{1}{2}O_2 \qquad K_n = CO \times O_2{}^{\frac{1}{2}}/CO_2 \qquad\qquad (10)$$
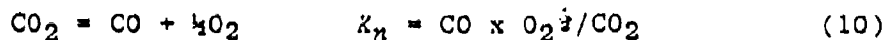
Dissociation of water vapor:

$$H_2O = H_2 + \tfrac{1}{2}O_2 \qquad K_n = H_2 \times O_2{}^{\frac{1}{2}}/CO_2 \qquad\qquad (11)$$

Formation of monatomic hydrogen:

$$\tfrac{1}{2}H_2 = H \qquad K_n = H/H_2{}^{\frac{1}{2}} \qquad\qquad (12)$$
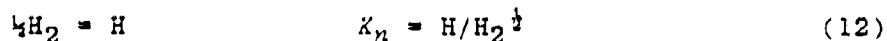
Formation of monatomic oxygen:

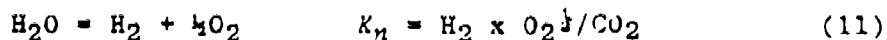$$\tfrac{1}{2}O_2 = O \qquad K_n = O/O_2{}^{\frac{1}{2}} \qquad\qquad (13)$$

Formation of hydroxyl:

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}O_2 = OH \qquad K_n = OH/\left(O_2{}^{\frac{1}{2}} \times H_2{}^{\frac{1}{2}}\right) \qquad\qquad (14)$$
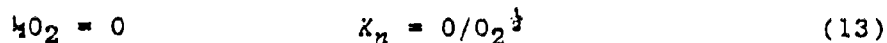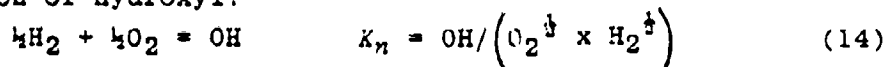
Formation of nitric oxide:

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 = NO \qquad K_n = NO/\left(N_2{}^{\frac{1}{2}} \times O_2{}^{\frac{1}{2}}\right) \qquad\qquad (15)$$
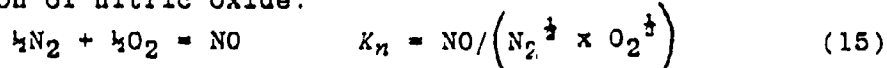
Formation of monatomic nitrogen:

$$\tfrac{1}{2}N_2 = N \qquad K_n = N/N_2{}^{\frac{1}{2}} \qquad\qquad (16)$$
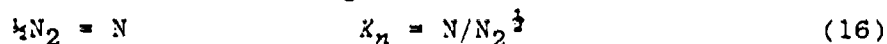
Numerical values for a mole number equilibrium constant K_n depend on the species involved, the temperature, and the volume of the system. In principle such extensive equilibrium data could be stored in the memory of a large computer and utilized as required. The needed tabulations can be considered condensed into relatively simple algebraic equations for the (logarithm of the) equilibrium constant of formation as a function of absolute temperature T. Thus

$$\log K_f = A + B/(T+C) \qquad\qquad (17)$$

where constants A and B are essentially those of the classic van't Hoff equation, and constant C, a curvature constant, provides for small discrepancies between experimental and van't Hoff values. Constants of Equation 17 are tabulated in Appendix C for the seven chemical equilibria in the internal blast generated by C-H-N-O fuels. The temperature range for these is from 4000 K, well above the temperatures of ordinary explosions, down to 1500 K, a quench temperature

below which rearrangement reactions for explosion products are so sluggish that chemical equilibrium may not be attained. The general suitability of these equations is readily verified.

DETERMINATION OF EQUILIBRIUM COMPOSITIONS

Twelve simultaneous equations for defining the equilibrium compositions described above (five linear material balances and seven nonlinear equilibrium expressions) are to be solved. Many methods for solution, some of them quite elegant, have been suggested. A relatively simple heuristic method of successive approximation, where each approximation seeks to improve on previous ones, is utilized here. The advantage of this method is that it can be adapted to manual solution and is also readily programmed for a small computer. A suitable algorithm is shown in Appendix D.

The iteration calculation begins with the nominal composition obtained through material balance considerations as described above. Then the program computes, through equilibrium constant expressions, the amount of other species (the minor components) that would be in chemical equilibrium with these nominal species (the major components) at the assigned temperature. The amounts of major components are corrected for minor components by using the material balance equations. The minor components are then recomputed, the major components recorrected, and so on, until all requirements for equilibrium have been met as shown by identical successive results in the computation.

As indicated in the algorithm of Appendix D, details for the iteration depend on whether the products mixture is oxygen-rich (the nominal products contain molecular oxygen) or oxygen-deficient (they contain molecular hydrogen or carbon monoxide or both). The calculations combine a material balance/equilibrium expression such as the one obtained by combining Equations 6 and 11. The number of moles of water vapor present is expressed as

$$H_2O = \frac{a'_H}{2}O_2^{\frac{1}{2}}/(K_n + O_2^{\frac{1}{2}}) \tag{18}$$

where

$$a'_H = a_H - H - OH$$

i.e., the number of hydrogen atoms available for the water vapor equilibrium. Such combined expressions have mathematical

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advantages because possible negative answers are avoided for amounts present.

When products composition has been determined, a blast overpressure can be computed from the known volume of the system and its assigned temperature by use of the ideal gas law. This overpressure, however, is not necessarily the blast maximum peak for that internal explosion. This maximum for nonvented explosions corresponds to adiabatic conditions where the energy of the products just equals that for the original fuel and air. Hence to ascertain this maximum, energy considerations become involved.

SOLID CARBON (SMOKE)

Internal explosions that are very fuel-rich may well show nominal products with elemental carbon. In such a circumstance the oxygen present is not sufficient to convert all carbon of the fuel to gaseous products. Particulate solid-phase carbon may form as a smoke. Systems such as these with a solid-phase component in chemical equilibrium with gases must be treated in a manner that differs mathematically from systems of gases only because the fugacity of a solid component is negligibly affected by pressure. Thus the fugacity does not appear as a variable in the mathematical expression for the equilibrium constant.

The pertinent relations for the smoke reaction are

Formation of solid carbon:

$$2CO = CO_2 + C \qquad K_n = CO_2/CO^2 \qquad (19)$$
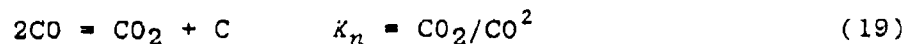
This mole number equilibrium constant K_n can be evaluated from the thermodynamic constants of formation for carbon dioxide and for carbon monoxide, perhaps as provided by the equations of Appendix C. A sample calculation is shown in Appendix B.

Calculations for the possible presence of solid carbon in equilibrium with gaseous products of explosion are first computed by the method of Appendix B, to find the number of moles of carbon dioxide and carbon monoxide that could be present. If the amount of carbon dioxide indicated by this computation exceeds that prescribed by smoke Equation 19 (i.e., if $CO_2 > K_n CO^2$), no solid carbon occurs in the products mixture. However, if the computed number of moles of

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carbon dioxide is less than that prescribed by smoke Equation 19 (i.e., if $CO_2 < K_n CO^2$), solid carbon may be present in the equilibrium mixture. In this circumstance a trial value for the number of moles of solid carbon, C, is selected. The material balance for elemental carbon (Equation 5) is modified to the form

$$a_C = CO_2 + CO + C \tag{20}$$

and the computation illustrated by the algorithm of Appendix D repeated. Calculations with successive trial values for solid carbon are continued until conditions of smoke Equation 19 are satisfied; i.e., until $CO_2 = K_n CO^2$. This second order iteration proceeds readily by computer where successive trial values can be selected automatically.

CONSERVATION OF ENERGY RELATIONS

The measure for energy effects in a system at a specified volume is the system's internal energy,[7] a thermodynamic item that differs from the energy item usually encountered—the enthalpy ("heat content"). Two rather different types of internal energy are involved; one thermal in nature, the other chemical. The thermal aspect is associated with temperature and heat capacity; the chemical aspect is associated with chemical composition. These two diverse aspects can, however, be combined into a single term if they relate to a common basis. The basis selected for computations is the elements in their ordinary form at a reference temperature of 25°C and pressure of the standard atmosphere (but pressure level is relatively immaterial for thermal items). On this basis, an element is assigned a chemical energy of zero, and its energy is given rather simply as the temperature integral of its heat capacity. A compound such as carbon dioxide (or an element not in its ordinary form such as monatomic oxygen) shows both this thermal aspect and an additional chemical aspect known as energy of formation. The total energy for such a material becomes the sum of these two separate aspects.

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[7] P. J. Kiefer, G. F. Kinney, and M. C. Stuart. *Principles of Engineering Thermodynamics.* New York, Wiley and Sons, 1958.

CHEMICAL ENERGY

The chemical energy aspect for a constant volume system is given by the internal energy of formation, which by definition is the internal energy change for the formation reaction. This item is not directly available for most materials. It can, however, be obtained indirectly by standard thermochemical methods from data such as a heat of combustion as provided in standard sources for conventional fuels and for explosives.[8]

Several items with regard to these thermochemical computations are as follows:

1. Thermochemical data commonly relate to 1 mole of a material with definite chemical formula. If only a chemical analysis is available, it is convenient to express this in alternative form as an empirical chemical formula.

2. Many published thermochemical data follow the older algebraic convention where heat energy leaving a system, as from a combustion, is considered to be algebraically positive. By modern thermodynamic convention when the energy of the system is diminished by such an exothermic reaction, this diminution effect is algebraically negative. Hence to utilize published thermochemical data for thermodynamic calculations, particularly for data from older sources, a change in algebraic sign may be required.

3. Many published thermochemical data relate directly to combustion reactions. To use these data for the calculations, they first must be converted to formation values. The calculation is a conventional one illustrated in Appendix E. The calculation must take into account whether water formed in the combustion is considered to be a vapor, given a "lower" or "net" heating value (LHV), or a liquid, giving a "higher" or "gross" heating value (HHV).

4. The thermochemical kilocalorie is used as an energy unit in older thermochemical tables. The multiplying factor for conversion into joules is 4184 exactly.

5. Most tabulated thermochemical values are actually for an enthalpy and described as being for constant pressure

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[8] U. S. Army Materiel Command. *Properties of Explosives of Military Interest.* Washington, D.C., USAMC, 29 January 1971. (AMCP 706-177, publication UNCLASSIFIED.)

conditions. Conversion of these into internal energies proceeds readily because by definition the enthalpy is the sum of the internal energy and the pressure-volume product (Appendix E). Table E-1 of this appendix lists internal energies of formation for many of the fuels that are important here.

6. A formation energy represents a small difference between large numbers. Its numerical value is thus sensitive to small discrepancies in those numbers. These small discrepancies do not necessarily contribute substantial uncertainty into the internal blast calculations.

THERMAL ENERGY

The thermal component of an internal energy, the temperature integral of the heat capacity at constant volume, must relate to the selected reference temperature of 25°C. The pertinent interval for integration then becomes that from 25°C to the actual temperature for fuel, air, or explosion products, respectively.

Data on heat capacity for many fuels, particularly ones in a condensed phase, may not be readily available. Heat capacity may often be adequately approximated by the Kopp rule for additive atomic constants. These constants have been evaluated for metric units and are given in Appendix F. The values pertain to temperatures near room temperature, and within their inherent uncertainties apply to both constant volume and constant pressure conditions.

Ordinary air contains 78-mol-% nitrogen, 21-mol-% oxygen, and 1-mol-% argon. It is a diatomic ideal gas and at temperatures near 25°C its heat capacity at constant volume has the classic value of $C_v = 5/2 \, R$. In metric units the gas law constant R is 8.31434 J/(mol·K), so that the molar heat capacity for air at constant volume becomes

$$C_v = 5/2 \times 8.314 = 20.8 \text{ J/(mol·K)} \tag{21}$$

The number of moles of air, n, can be found by the ideal gas law with $n = PV/RT$. Since no chemical item is involved, the total internal energy for air at temperature T in kelvins and relative to the elements at 25°C is

$$E° = 20.8 \, (T - 298)n \tag{22}$$

The gaseous products from combustion-explosion reactions show heat capacities that are conveniently described by three

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coefficient equations.[9] These thermal items can be combined with pertinent chemical items, the internal energies of formation, to give a four-coefficient equation for the (total) internal energy for each component, relative to the elements at 25°C. Thus

$$E^\bullet = a + bT + cT^2 + d/T \tag{23}$$

where $E^\bullet$ is the standard internal energy per mole at temperature T and a, b, c, and d are arbitrarily selected coefficients. The four coefficients for this equation have been evaluated for the 12 components from data of the JANAF tables for the temperature range 500-4000 K.[6] These are tabulated in Appendix G. The total energy for a products mixture is then a summation of individual values per mole times the number of moles of each component present.

ADIABATIC COMBUSTIONS

The total energy of the products (sum of chemical plus thermal) just equals that for the original fuel plus air at the adiabatic flame temperature of a combustion-explosion reaction. A trial value for products temperature is assumed for computation of this flame temperature. Then by iteration, as described above, an associated equilibrium composition and internal energy of products for this assumed temperature are computed. Successive trial values for temperature are selected until the desired equality for the internal energies is found.

Given the adiabatic flame temperature, peak products pressure (for a nonvented internal explosion) can be computed by the ideal gas law $PV = (m/M)RT$ where m is the total mass of fuel plus air, and M the formula mass for the products. Blast overpressure is then obtained by subtracting the ambient atmospheric pressure.

INTERNAL EXPLOSIONS WITH TNT

The conventional explosive TNT (formula $C_7H_5N_3O_6$) also serves as a reference for explosives in general. In an

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[9] C. G. Maier and K. K. Kelley. "An Equation for the Representation of High-Temperature Heat Capacity Data," *J. Amer. Chem. Soc.*, Vol. 54 (1932), p. 3243.

internal explosion, TNT acts as an explosive fuel where its inherent oxygen content supplements that of the air and so may supply a substantial proportion of the oxygen for the combustion-explosion reaction. Calculations for internal explosions, as outlined above, readily permit this; the results of such calculations are reported below.

OVERPRESSURES

Overpressures generated in internal explosions with TNT were shown graphically in Figure 2 for overpressures in bars (10^5 pascals) over a three-decade range of TNT-air ratios in kilograms of TNT per cubic metre of air at 25°C and 1 bar. Also shown were the experimental results.[3] The agreement obtained is gratifying and leads to confidence in the thermodynamic computations.

Both calculated and experimental results for internal explosions with TNT show a point of inflection at an intermediate fuel-air ratio, although this was not recognized in the original report of these experiments. Beyond this point fuel-air ratios are such that the primary reaction is a detonation where increasing overpressures result largely from formation of additional gases. Below this inflection point the air provides sufficient oxygen so that combustion effects in the afterburn contribute to the overall temperature rise and resulting pressure increase.

Four stoichiometric points for combustions of TNT in air are shown in Figure 2. The overpressure curve proceeds smoothly through these points. The $CO-H_2$ point corresponds to the most fuel-rich and is also termed the smoke point because with a greater amount of fuel solid carbon may be one of the combustion products.

FLAME TEMPERATURES

Computations for internal blast overpressure also allow for other characteristics of the blast. Figure 3 shows adiabatic flame temperatures for the combined combustion-explosion reaction of TNT in air at 25°C and 1 bar for a wide range of TNT-air ratios. These temperatures are appreciably higher than those for constant pressure conditions.

In contrast with pressures for internal blast, which increase monotonically with fuel-air ratio, the blast temperature curve for TNT reaches a maximum at about 3055 K at

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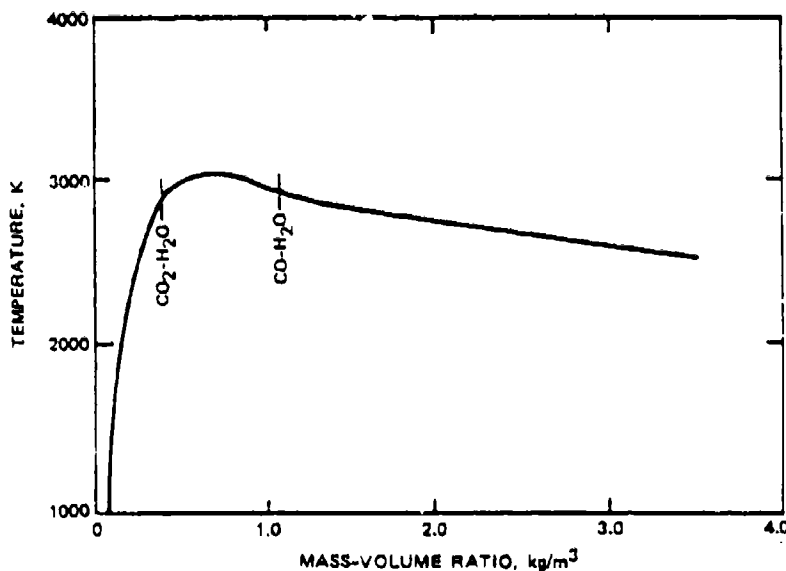
FIGURE 3. Temperatures in Internal Blast
With TNT-Air Explosions.

a TNT-air ratio of about 0.7 kg/m^3. This ratio lies between
the CO_2-H_2O and the CO-H_2O stoichiometric reference points
for TNT and is close to the fuel-air ratio at the point of
inflection in the overpressure curve. This maximum corres-
ponds to maximum utilization of oxygen in the afterburn.

PRODUCTS FORMULA MASS

Chemical dissociations at high temperatures give pro-
ducts such as monatomic oxygen and hydrogen and reduce the
overall formula mass for the products mixture (Figure 4).
Formula mass versus products temperature is plotted for a
representative TNT explosion in air—one with a fuel-air
ratio that corresponds approximately to maximum flame tem-
perature. The formula mass for these products decreases as
much as 10% at high temperatures. The corresponding increase
in the number of moles or gases present can make an appre-
ciable contribution to blast overpressures.

20
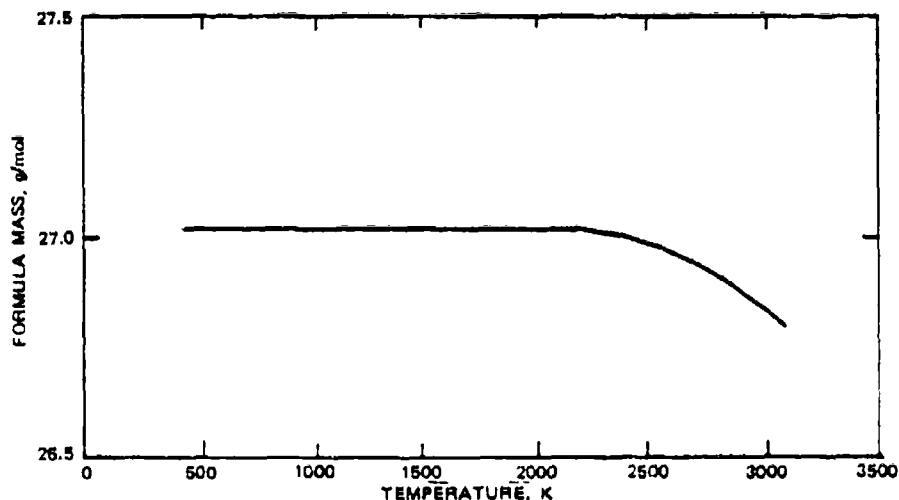
FIGURE 4. Formula Mass for Produ..s From
a TNT-Air Internal Explosion.

PRODUCTS COMPOSITION

The extent of chemical dissociation in the products of
an internal explosion with TNT is shown in Figure 5. Com-
position of products versus the TNT-air ratio (logarithmic
scales) is plotted. Maximum dissociation occurs in the gen-
eral region of the CO_2-H_2O and the CO_2-H_2 stoiciometric ref-
erence points and at approximately the fuel-air ratio for
peak adiabatic temperature. In general any particular pro-
duct of dissociation is present only in a small amount, but
together these dissociations have substantial influence on
products temperature because of their pronounced endothermic
nature.

PRODUCTS HEAT CAPACITY AND HEAT CAPACITY RATIO

Heat capacity data are important for many explosion cal-
culations. The heat capacity for a system at constant volume
is the temperature derivative of its internal energy, which
can be found directly from results of the energy calcula-
tions outlined above. The molar heat capacity C_v (in joules
per mole kelvin) has been computed for the products of the
explosion of 1 kg of TNT/m^3 of air at 25°C and 1 bar. These

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FIGURE 5. Composition of Products for Internal
Explosions With TNT-Air Mixtures.

data are presented as a function of products temperature in
Figure 6. This heat capacity is greatly influenced by chem-
ical dissociation effects and increases monotonically with
temperature. At higher temperatures it appreciably exceeds
both the conventional diatomic value of $5/2R = 20.8$ J/mol·K)
and the triatomic value of $7/2R = 29.1$ J/(mol·K).

Calculations such as those for compressible fluid flow
may utilize heat capacity data in the form of a ratio of
constant pressure to constant volume. For ordinary gases a

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FIGURE 6. Molar Heat Capacity C_v
for Products From an Internal TNT-
Air Explosion.

simple relationship may not apply here because of the effects
of chemical dissociation on formula mass. A corr sponding
ratio $k = (C_v + R)/C_v$ ersus temperature is plotted, however,
in Figure 7 for the products for three different TNT-air
ratios. The ratio decreases monotonically with temperature
in each instance, but a changing products composition appears
o prevent any simple correlation between heat capacity ratio
and fuel-air ratio.

OTHER EXPLOSIVE FUELS

Explosive fuels generally show internal explosion over-
pressures similar to those for TNT—overpressures that in-
crease monotonically with fuel-air ratio. The more highly
oxygenated fuels require less oxygen from the air for com-
plete reaction and consequently show lesser afterburn effects.
Figure 8 shows overpressures for reference internal explo-
sions with TNT, an oxygen-deficient explosive (oxygen balance
of -74% to CO_2 and -25% to CO)[8] with pronounced afterburn
effects that depend on the TNT-air ratio. Shown for compari-
son are the overpressures for internal explosions with

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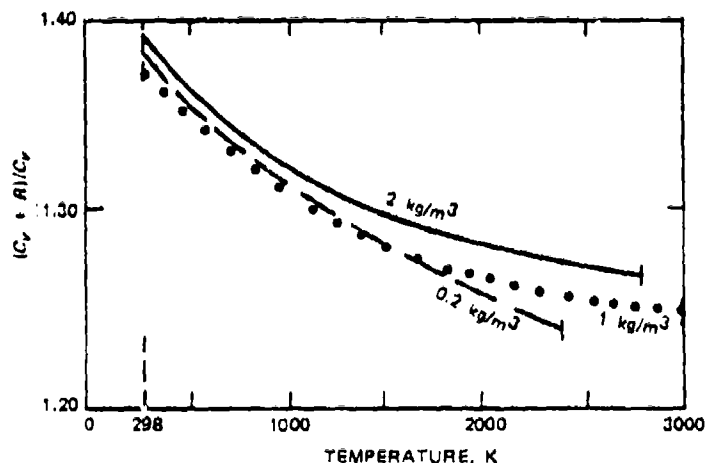
FIGURE 7. Heat Capacity Ratio $k =$ $(C_y + R)/C_y$ for Explosion Products.

pentaerythritol tetranitrate (PETN), an explosive approximately balanced in oxygen (oxygen content between the CO_2-H_2O and the CO-H_2O stoichiometric reference points and with oxygen balances of -10% to CO_2 and +15% to CO). Because a small afterburn effect is possible, only a small inflection point is indicated in the overpressure curve. Also shown is the overpressure curve for the oxygen-rich explosive mannitol hexanitrate (MHN) with more oxygen even than that for the CO_2-H_2O stoichiometric reference point, and with an oxygen balance of +7% to CO_2 and +28% to CO. No afterburn is possible, and there is no point of inflection in the overpressure curve.

Overpressures developed in internal explosions with many explosive fuels, both oxygen-rich and oxygen-deficient, have been computed for a wide range of fuel-air ratios with air initially at 1 bar and 25°C (Tables 1 and 2). For these explosive fuels the overpressure always increases with the fuel-air ratio, but actual overpressures depend on the type of fuel. A characterization of this aspect of internal blast follows.

INTERNAL BLAST YIELDS

In the low overpressure range, the overpressures developed by a given fuel-air ratio of PETN are less than those for TNT. The internal blast yield for PETN is therefore

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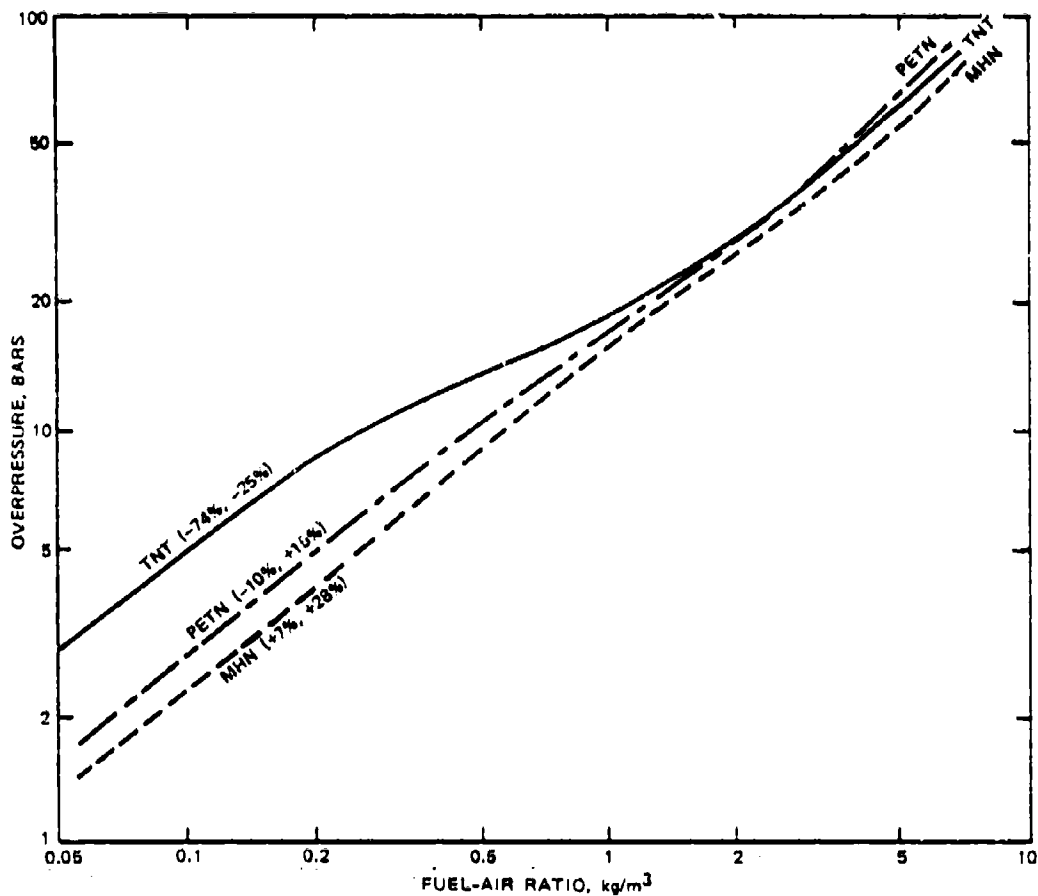
FIGURE 8. Overpressures for Internal Explosions With
Three Explosives Having Different Oxygen Content.

defined to be less than that for TNT (Figure 8). Such in-
ternal blast yields are conveniently expressed relative to
TNT, an explosive with a definite chemical formula and re-
producible characteristics. The internal blast yield for
PETN in the low overpressure range is only 52% of that for
TNT on a mass basis; i.e., 52 grams of TNT give the same in-
ternal blast overpressure as 100 grams of PETN (in the low
overpressure range). On a volume basis where relative den-
sity must be taken into account, the yield for PETN is 56%
of that for TNT; i.e., 56 cm^3 of TNT give the same internal
blast as 100 cm^3 of PETN (in the low overpressure range,
which corresponds to explosions in a relatively large volume
of air).

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TABLE 1. Internal Blast Overpressures (Bars) for Chemical Explosives.

Formula	Name	Fuel-air ratio, kg/m³								
		0.05	0.10	0.30	0.50	0.80	1.0	1.4	2.0	5.0
CH3NO2	NM, Nitromethane	2.040	3.780	9.089	12.898	17.402	20.143	26.383	32.980	70.147
C3H9N9	TAZ, Triaminoguanidine azide	2.495	4.568	11.144	15.149	⁻ᵃ	⁻ᵃ	⁻ᵃ	⁻ᵃ	⁻ᵃ
C3H5N3O9	NG, Nitroglycerin (glyceryl trinitrate)	1.304	2.420	6.180	9.371	13.428	15.839	20.369	26.915	69.205
C3H6N6O6	RDX, Cyclonite, cyclotrimethylenetrinitramine	1.785	3.267	8.219	12.014	16.549	19.335	24.740	32.792	72.644
C4H8N8O8	HMX, Cyclotetramethylenetetranitramine	1.745	3.194	8.049	11.818	16.307	19.046	24.346	32.166	71.126
C5H8N4O12	PETN, Pentaerythritoltetranitrate	1.543	2.834	7.134	10.698	14.743	17.212	21.937	28.857	63.316
C6N6O12	HNB, Hexanitrobenzene	1.436	2.668	6.751	10.103	14.039	16.342	20.736	27.171	59.273
C6HN5O10	Pentanitrobenzene	1.650	3.019	7.654	10.984	14.870	17.215	21.760	28.483	62.206
C6H2N4O8	Tetranitrobenzene	1.954	3.548	8.648	12.007	15.939	18.339	23.213	30.374	66.353
C6H3N3O6	TNB, 1,3,5-Trinitrobenzene	2.361	4.256	9.804	12.991	16.926	19.374	24.489	30.900	63.895
C6H4N2O4	DNB, 1,2-Dinitrobenzene	3.009	5.369	10.989	13.685	16.319	17.802	20.562	26.372ᵃ	46.694ᵃ
(C6H7N3O11)x	NC, Cellulose trinitrate, 14.1% nitrogen	1.701	3.106	7.690	11.131	15.060	17.418	21.958	28.622	61.634
C6H8N6O18	Mannitol hexanitrate	1.232	2.297	4.170	8.949	12.901	15.245	19.966	26.936	56.910
C7H5N3O6	TNT, 1,3,6-Trinitrotoluene	2.639	4.739	10.418	13.469	17.026	19.069	22.862	28.307	57.828ᵃ
C7H5N5O8	Tetryl, 2,4,6-trinitrophenyl-methylnitramine	2.223	4.019	8.523	12.887	16.992	19.570	24.586	31.943	68.051
C7H6N2O4	DNT, 2,4-Dinitrotoluene	3.287	5.834	9.398	13.101	14.583	15.368	17.862ᵃ	21.774ᵃ	41.704ᵃ
C12H4N8O8	TACOT, Tetranitro-1,2,5,6-tetraazadibenzocyclooctatetraene	2.691	4.836	10.569	13.738	17.653	19.978	24.256	32.292	78.818
C12H6N8O12	DIPAM, 3,3-Diamino-2,2',4,4',6,6'-hexanitro-biphenyl	2.226	4.022	9.468	12.678	16.508	18.865	23.348	29.754	60.493

ᵃ Smoke present.

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TABLE 2. Internal Blast Overpressures (Bars) for Explosive Mixtures.

Name	Composition	Fuel-air ratio, kg/m³								
		0.05	0.10	0.30	0.60	0.80	1.0	1.4	2.0	5.0
Comp. B-3	60% RDX, 40% TNT	2.132	3.878	9.359	12.939	17.249	19.943	25.172	32.864	70.668ᵃ
Cyclotol 56/38	56% RDX, 38% TNT, 6% wax	2.449	4.422	10.244	13.708	17.887	20.414	26.208	32.146	66.123
Cyclotol 75/25	75% RDX, 25% TNT	1.989	3.620	8.909	12.693	16.968	19.687	24.982	32.783	71.426
LX-01	52% NM, 33% TNM, 15% 1-nitroxopane	1.846	3.368	8.372	12.133	16.621	19.379	24.726	32.616	71.901
Octol 75/25	75% HMX, 25% TNT	1.996	3.616	8.998	12.680	16.950	19.665	24.948	32.728	71.291
PBX-9007	90% RDX, 9.1% polystyrene, 0.5% di-2-ethylhexyl-phthalate, 0.4% rosin	2.768	4.111	9.832	13.486	17.924	20.670	25.939	33.604	11.227
Pentolite 50/50	50% PETN, 50% TNT	2.193	3.975	8.554	12.900	17.112	19.771	24.972	32.667	70.929
PLX-2	50% Nitromethane, 50% acetone	3.483	6.164	11.352	12.235	12.881	13.124	13.329	16.847	34.384
PLX-3	75% Nitromethane, 25% acetone	2.624	4.710	10.693	13.021	14.846	15.900	17.871	20.866	33.773

ᵃ Smoke present.

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Internal blast yields can readily be assigned by a graphical method that utilizes plots of blast overpressure versus logarithm of the fuel-air ratio. The plots for the two materials are superimposed so that overpressures in the range of interest closely coincide. The relative internal blast yield for this range of overpressures is then given as the inverse ratio of the two corresponding fuel-air ratios.

Blast yields relative to TNT for a large number of explosive fuels are given in Table 3. Two values are included for each of these explosive fuels, one for the low overpressure range (on the order of 5 bars) and one for high overpressures (20 to 30 bars). These two values may be quite different.

In the low overpressure range, the yield includes contributions from the afterburn effect, which can be quite significant for oxygen-deficient explosives. At low overpressures an oxygen-deficient explosive fuel with substantial afterburn effects (dinitrotoluene, for example), can generate a more damaging internal explosion than an oxygen-rich explosive such as mannitol hexanitrate.

The higher overpressures generated in internal explosions with explosive fuels result primarily from detonations, and so are little influenced by the afterburn. An explosive fuel with high oxygen content does not utilize all its oxygen, and the excess oxygen is simply a diluent that reduces the yield in the higher overpressure range. Maximum internal blast yields in the high overpressure range are obtained from explosive fuels that are approximately balanced in oxygen.

The pronounced effect of the oxygen content of an explosive on its internal blast yield is illustrated in Figure 9. The overpressure in both the low and high ranges are shown for the seven members of the benzene series of nitrated materials. Neither benzene (C_6H_6) nor mononitrobenzene ($C_6H_5NO_2$) detonates, and hence they do not achieve the high overpressure range. They do, however, show appreciable overpressures in the low overpressure range as generated by combustion reactions. In this range these particular overpressures are substantially higher than those for the highly nitrated materials with their greater proportion of noncombustible constituents.

In the high overpressure range, materials with either low oxygen or high oxygen content lead to lower overpressures than the overpressures obtained from the same amount of an oxygen-balanced material. To illustrate for the seven-member

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TABLE 3. Internal Blast Yields.

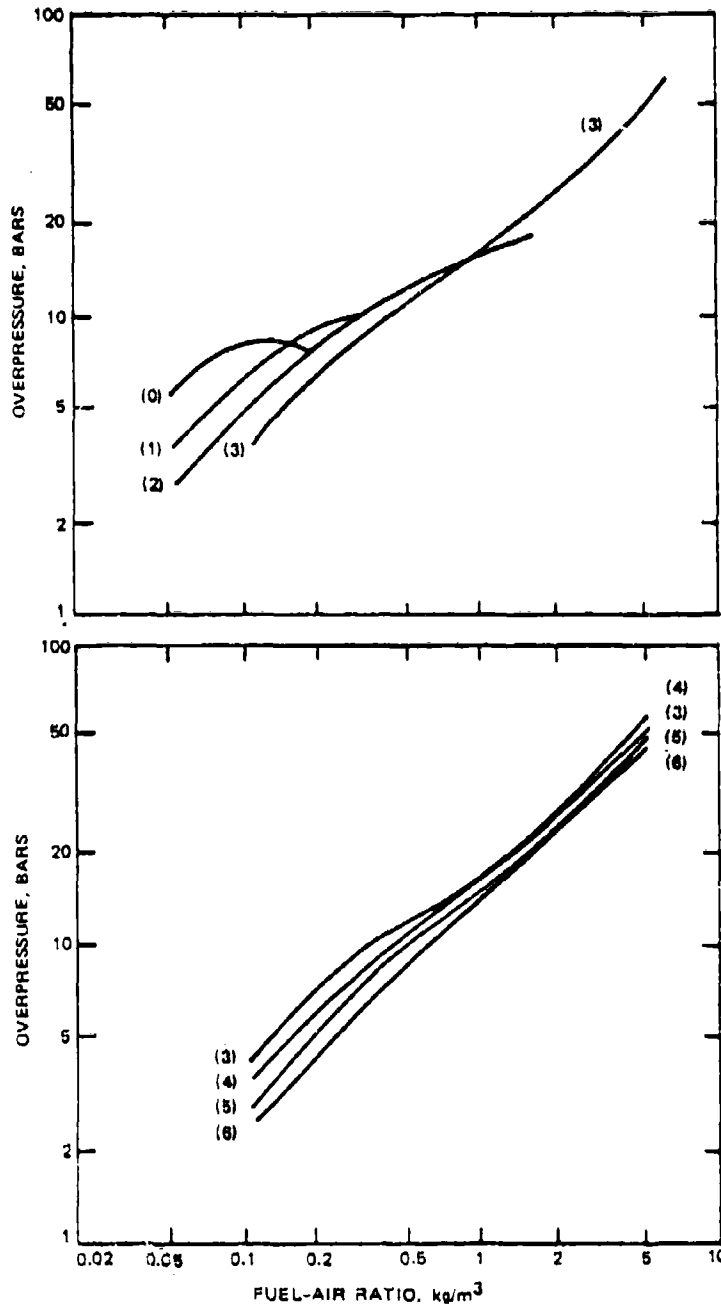| Formula	Name	Yield, %TNT			
		At low overpressures		At high overpressures	
		By mass	By volume	By mass	By volume
A. Pure Explosives					
CH_3NO_2	NM, Nitromethane	71	49	120	83
CH_9N_9	TAZ, Triaminoguanidine azide	91	79	...	...
$C_3H_6N_3O_9$	NG, Nitroglycerin	40	39	97	94
$C_3H_6N_6O_6$	RDX, Cyclonite, cyclotrimethylene-trinitramine	63	65	111	115
$C_4H_8N_8O_8$	HMX, Cyclotetramethylenetetra-nitramine	61	70	115	132
$C_5H_8N_4O_{12}$	PETN, Pentaerythritoltetranitrate	52	56	103	110
$C_6N_6O_{12}$	HNB, Hexanitrobenzene	48	57	94	112
$C_6HN_5O_{10}$	Pentanitrobenzene	56	64	107	123
$C_6H_2N_4O_8$	Tetranitrobenzene	68	74	118	129
$C_6H_3N_3O_6$	TNB, 1, 3, 5-Trinitrobenzene	83	85	115	118
$C_6H_4N_2O_4$	DNB, 1, 2-Dinitrobenzene	109	103	81	78
$(C_6H_7N_3O_{11})_x$	NC, Cellulose trinitrate, 14.1% nitrogen	57	58	100	102
$C_6H_8N_6O_{18}$	Mannitol hexanitrate	41	43	89	93
$C_7H_5N_3O_6$	TNT, 2, 4, 6-Trinitrotoluene	100	100	100	100
$C_7H_5N_5O_8$	Tetryl, 2, 4, 6-Trinitrophenylmethyl-nitramine	78	82	115	121
$C_7H_6N_2O_4$	DNT, 2, 4-Dinitrotoluene	127	102	67	54
$C_{12}H_4N_8O_8$	TACOT, Tetranitro-1, 2, 5, 6-tetra-zadibenzocyclooctatetraene	91	102	122	137
$C_{12}H_6N_8O_{12}$	DIPAM, 3, 3-Diamino-2, 2', 4, 4', 6, 6'-hexanitrobiphenyl	78	85	103	112
B. Explosive Mixtures					
...	Comp. B-3	75	75	117	116
...	Cyclotol 56/38	87	89	111	113
...	Cyclotol 75/25	71	74	125	130
...	LX-01	66	49	114	132
...	Octol 75/25	69	76	120	132
...	PBX-9007	78	80	125	128

FIGURE 9. Overpressures for the
Nitrated Benzene Series.

nitrated benzene series, tetranitrobenzene (an explosive approximately balanced for the $CO-H_2O$ stoichiometric reference point) is most effective from a yield viewpoint at high overpressure (Figure 10).

INTERNAL EXPLOSIONS WITH CONVENTIONAL COMBUSTIBLES

Overpressures generated in the internal blast for three conventional fuels—benzene, JP-4 (a hydrocarbon fuel with an empirical formula C_9H_{17}), and ethylene oxide—are plotted as a function of fuel-air ratio (Figure 11). The corresponding curve for the explosive fuel TNT is included for comparison. All the curves for three conventional combustibles show a maximum overpressure on the order of 9 to 11 bars that characteristically lies between the CO_2-H_2O and the $CO-H_2O$ stoichiometric reference points. The two hydrocarbon fuels, benzene and JP-4, show typical behavior even though their hydrogen-carbon ratios are quite different. Ethylene oxide (C_2H_2O), an oxygen-containing fuel, also shows a maximum in its overpressure curve, but one that is broader and that occurs at an appreciably greater fuel-air ratio. This is a consequence of the diluting effect of oxygen in the molecule. For some purposes the greater mass of ethylene oxide required to achieve a maximum blast overpressure can be a disadvantage, while the broad range for high overpressures can be an advantage.

The internal blast behavior of selected conventional fuels is summarized in Tables 4 and 5 for initial conditions with air at 1 bar and 25°C. The maximum overpressure that each fuel can generate in confined air is shown along with the required fuel-air ratio. The tables also show maximum flame temperatures and the associated fuel-air ratio. In general the fuel-air ratio for maximum temperature is approximately that for maximum blast overpressure. This is to be expected because at lesser ratios some of the available oxygen is not utilized, while at greater ratios any excess fuel contributes only to the mass of products to be warmed and gives reduced temperature and pressure rises.

The flame temperatures given in Tables 4 and 5 for combustions at constant volume are appreciably greater than those for constant pressure conditions: (1) the heat capacity at constant volume is less than that at constant pressure so that a given energy release produces a greater temperature rise, and (2) the chemical dissociations in the flame are partially suppressed by the higher pressure conditions of constant volume.

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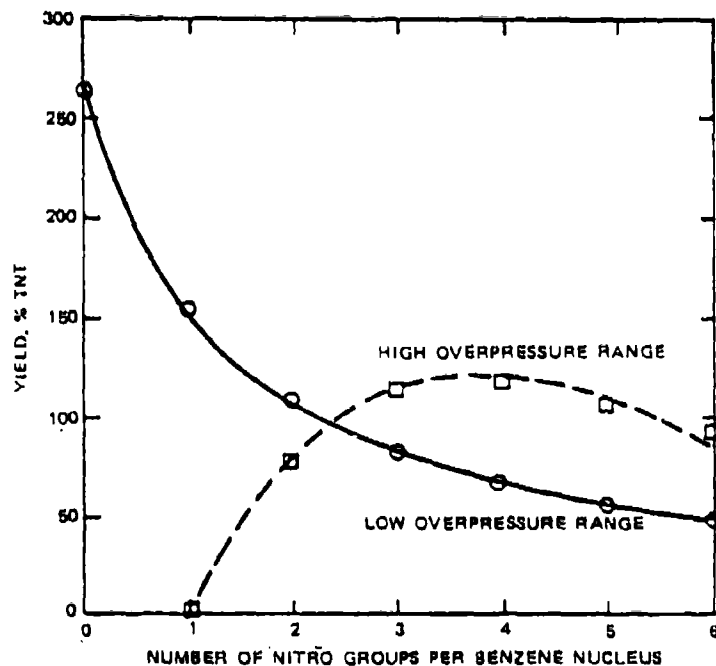
FIGURE 10. Internal Blast Yields
for the Nitrated Benzene Series.

GASEOUS FUELS

A confined mixture of a gaseous fuel such as methane in
air can explode only when its fuel-air ratio is within cer-
tain limits.[10]   For a mixture of methane in air, the lower
flammability limit is 5 mol% (5 vol%) and the vapor flam-
mability limit is 15%.   Only within these limits can a mix-
ture of methane in air produce an internal explosion.   Adia-
batic values for the internal blast overpressures computed
for these limiting ratios are 5.5 and 7.0 bars, respectively.
Maximum overpressure for a methane-air explosion is 8.0 bars,
which occurs at 10.0 vol% methane, a composition intermedi-
ate between the flammability limits, and also between those

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[10] Bernard Lewis and G. von Elbe.   *Combustion, Flames,
and Explosions of Gases.*   New York, Academic Press, 1951.
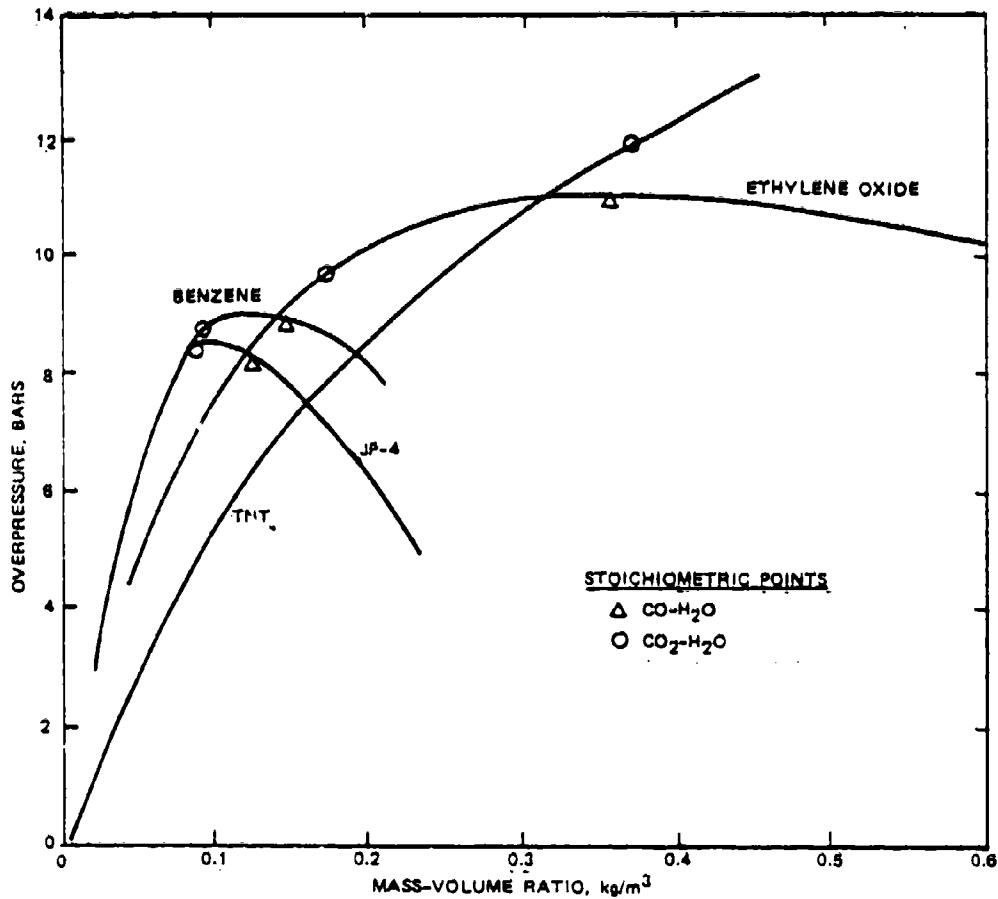
FIGURE 11. Blast Overpressures Versus Fuel-Air
Ratio for Three Nonexplosive Fuels.

for the CO_2-H_2O (9.5%) and the CO-H_2O (12.3%) stoichiometric
points. Calculations for the internal blast from various
gaseous fuels are based on initial conditions of 25°C and 1
bar total pressure for the mixture (Table 5).

Table 5 also provides the corresponding internal blast
yields expressed in terms of methane for gaseous fuels. The
yield is the volume of a gas (moles) or the mass, relative
to methane, required to produce the same overpressure upon
its explosion in air. Such yields vary with the nature of
the gas, with values particularly sensitive to oxygen con-
tent of the gas molecule. Yields in terms of volume are

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TABLE 4. Internal Blast From Conventional Combustibles.

Formula	Name	Maximum overpressure		Maximum temperature		Yield, % benzene	
		Bars	kg/m^3	K	kg/m^3	By mass	By volume
A. Liquids							
C_2H_4O	EO, Ethylene oxide	10.832	0.35	2768	0.175	66	67
$C_6H_5NO_3$	Nitrobenzene	10.476	.25	2834	.20	60	82
C_6H_6	Benzene	9.122	.12	2855	.12	100	100
C_6H_{12}	Cyclohexane	9.036	.10	2646	.08	112	103
C_6H_{14}	n-Hexane	9.050	.10	2651	.08	114	86
C_9H_{17}	JP-4, Jet fuel	8.669	.10	2531	.10	123	112
$C_{10}H_{16}$	THDC, exo-Tetrahydrodicyclopentadiene	9.054	.10	2668	.10	107	125
$C_{11}H_{10}$	α-Methylnaphthalene	8.894	.10	2727	.10	104	125
$C_{12}H_{20}$	RJ-4-1, Tetrahydromethylcyclopentadiene dimer	9.124	.10	2676	.10	101	105
$C_{13}H_{22}$	PHF, cis-trans-Perhydrofluorene	8.119	.10	2671	.10	105	112
$C_{14}H_{18.4}$	RJ-5	8.088	0.10	2717	0.10	104	120
B. Solids							
$(C_6H_{10}O_5)_x$	Starch	7.917	0.10	2606	0.10	76	...
$C_{6.16}H_{5.26}N_{0.10}O_{0.65}$	Coal dust, bituminous	8.336	.10	2623	.10	88	...
$C_{6.88}H_{0.60}N_{0.01}O_{0.11}$	Coal dust, anthracite	9.656	0.20	2450	0.20	37	...

TABLE 5. Internal Blast From Gaseous Fuels.

Formula	Name	At lower explosive limit			At maximum explosive limit			At upper explosive limit			Yield, % methane	
		Vol., %	Over-pressure, bars	Flame temp., °C	Vol., %	Over-pressure, bars	Flame temp., °C	Vol., %	Over-pressure, bars	Flame temp., °C	By mass	By volume
H_2	Hydrogen	4.0	1.54	487	74.2	12.47	3138	74.2	12.47	3138	227	29
H_3N	Ammonia	15.5	8.28	1770	27.0	8.75	2261	27.0	8.75	2261	39	41
H_4N_2	Hydrazine	4.7	3.88	1104	10.0	7.26	1935	50.0	...	...	38	76
CO	Carbon monoxide	12.5	4.44	1413	40.0	7.69	2547	74.2	4.60	1269	19	33
CHN	Hydrogen cyanide	2.0	1.97	612	20.0	9.62	2706	40.0	...	...	49	83
CH_4	Methane	5.0	5.11	1533	10.0	8.03	2336	15.0	7.35	1908	100	100
CH_4O	Methanol	6.7	5.66	1628	15.0	8.72	2264	15.8	8.69	2216	41	82
C_2N_2	Cyanogen	6.0	7.59	2237	10.0	11.59	3245	32.6	...	...	40	130
C_2H_2	Acetylene	2.6	4.17	1281	10.0	9.62	2768	80.0	10.81	2817	95	164
C_2H_4	Ethylene	2.8	4.73	1425	10.0	8.86	2341	15.0	7.93	1766	98	170
$C_2H_5NO_2$	Ethyl nitrite	3.0	5.06	1435	25.0	14.48	2188	25.0	14.48	2188	36	133
C_2H_6	Ethane	3.0	5.42	1599	7.5	8.44	2247	10.0	7.73	1853	99	188
C_2H_6O	Ethanol	3.3	5.31	1540	7.9	8.81	2303	7.9	8.81	2303	66	158
C_3H_6O	Acetone	2.6	4.17	1243	7.5	8.55	2376	12.8	7.64	1765	60	217
C_3H_8	Propane	2.1	5.46	1606	4.0	8.46	2347	9.3	6.94	1433	96	190
C_4H_6	1, 3 Butadiene	2.0	5.88	1750	5.0	9.10	2443	8.0	8.32	1666	93	314
C_4H_{10}	n-Butane	1.9	6.06	1768	4.0	8.76	2312	8.4	6.30	1180	94	340
$C_4H_{10}O$	Diethyl ether	1.9	4.79	1406	5.0	8.04	2383	10.0	7.56	1509	68	314
C_5H_{12}	n-Pentane	1.4	5.70	1667	3.0	8.83	2377	6.0	7.18	1453	88	395
C_6H_6	Benzene	1.4	5.52	1654	4.0	8.81	2326	7.1	7.87	1639	81	395
C_6H_{14}	n-Hexane	1.2	5.76	1680	2.0	8.24	2315	7.4	5.34	1153	89	480
C_8H_{18}	n-Octane	1.0	5.98	1736	1.9	8.86	2397	1.9	8.86	2397	87	620

appreciably greater for the more dense gases than for the lighter gases.

FLAME EMISSIVITY

Overpressures reported in Tables 4 and 5 were computed for adiabatic conditions; i.e., they do not provide for heat transfer from hot explosive products to cool confining walls either by radiant energy or by conduction-convection processes. Heat transfer effects are very time-dependent and so are more important for the relatively slow explosions with conventional fuels than for the rapid ones with explosive fuels. With an explosive fuel the detonation is very rapid indeed and also serves to accelerate combustion effects in the afterburn because of an increased temperature. The relatively minor effect of heat transfer with explosive fuels is indicated in Figure 2, where the peak overpressures computed for TNT on an adiabatic basis agree quite well with those observed experimentally.

The importance of heat transfer in the relatively slow internal explosions with conventional combustibles exploding in coal mines or in grain elevators can be deduced from experimental data,[11] which data are compared in Figure 12 with results of the adiabatic calculations made as described above. Figure 12(a) is for coal dust in air; Figure 12(b) for starch in air; and Figure 12(c) for methane in air for two conditions, quiescent mixtures and initially turbulent mixtures. Figure 12(c) illustrates the effect of rate of combustion on peak overpressure developed in internal explosions. Turbulent mixtures with their more rapid rate of combustion have less time for heat transfer, and there is a corresponding lesser reduction in peak overpressure from the adiabatic values. The cooling effect of confining walls can nevertheless cause a 10 to 20% reduction in peak blast overpressure from explosions with conventional combustibles.

These effects of heat transfer can be expressed quantitatively in terms of the amount of energy transferred during

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[11] U.S. Bureau of Mines. *Explosion Development in Closed Vessels*, by John Nagy, E. C. Seiler, J. W. Conn, and H. C. Varakis. Washington, D.C., U.S. Bur. Mines, 1971. (Bureau of Mines Report of Investigations 7507, publication UNCLASSIFIED.)
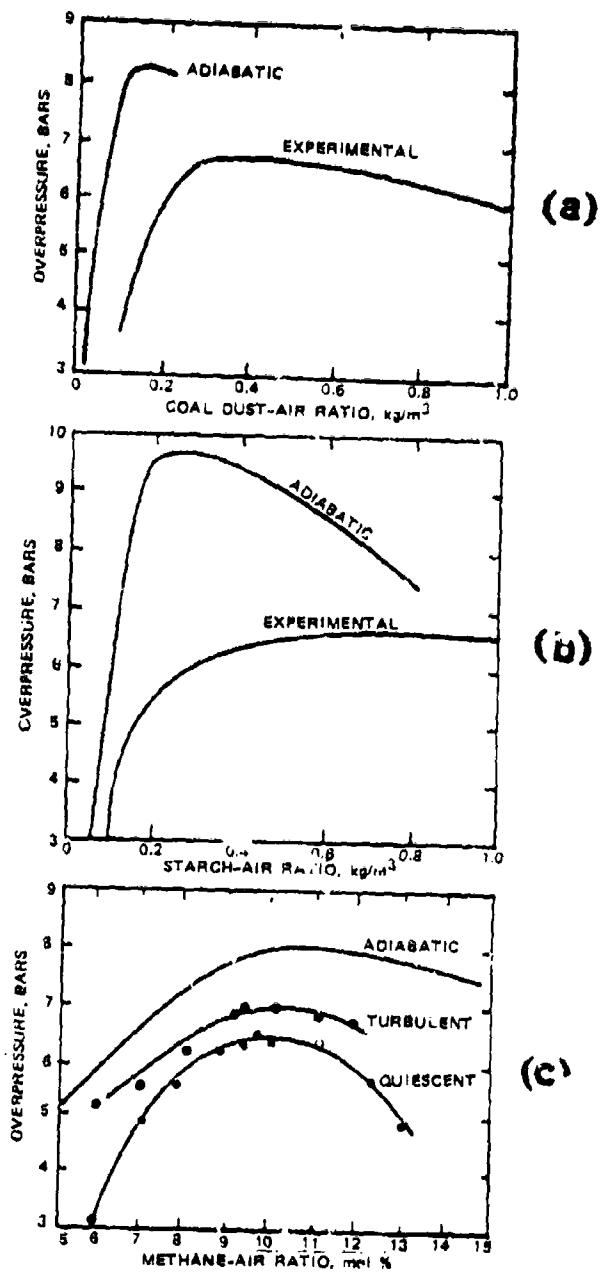
FIGURE 12. Peak Overpressures
Reduced by Transfer

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the explosion process. This computation finds, by iterative methods, the products temperature and its associated internal energy that correspond to the observed overpressure. These are then compared with adiabatic values as computed by methods described above.

The important mechanism for heat transfer at high temperature is thermal radiation, and its associated coefficient is the overall flame emissivity. This overall emissivity is a tenuous item that depends on factors such as flame temperature, spectral distribution of the energies present, path length for the radiant energy, and on possible conduction-convection effects. An overall emissivity can still be assigned in any particular circumstance when the rate of heat flow, plus the emitting and absorbing areas and their temperatures, is known. Such is the case for several of the experimental explosions reported.[11] Appendix H illustrates a representative computation.

The results of a series of emissivity calculations are given in Table 6. Appreciable scatter is observed and reflects experimental difficulty in providing reproducible conditions. Tentative conclusions, however, can be deduced. Turbulent flames show appreciably higher overall emissivities than do quiescent flames, with average emissivity values of 0.55 and 0.22, respectively. This enhanced emissivity of the turbulent flame can be correlated with the observation that turbulent flames are more luminous and substantially thicker than quiescent ones and are therefore more effective thermal emitters. The table also indicates that confining vessel volume has a lesser effect than does the degree of turbulence.

INJECTION VELOCITY EFFECT

The kinetic energy of injection must be added to the system when fuel for an internal explosion is injected into a confining volume. Figure 13 shows the effect of injection energy on cyclohexane explosions. A gain in overpressure of 0.7 bar is realized for a fuel-air ratio of 0.1 kg/m^3 (optimum for sea level) as the velocity of fuel injection is increased from 0 to the rather substantial 3000 m/s, a velocity that corresponds to a Mach number of 8.7 in ordinary air. Thus it appears that the injection effect is not important except for large injection velocities. The system is over-fueled at a greater fuel-air ratio (0.15 kg/m^3), but an increase in the injection velocity from 0 to 3000 m/s gives a larger overall increase in overpressure of 1.8 bars.

TABLE 6. Methane Flame Emissivities.

Vessel vol., m³	Methane in air, %	Observed overpressure, bars	Flame temp., K	Adiabatic overpressure, bars	Adiabatic flame temp., K	Overall emissivity
A. Initially Quiescent Conditions						
Cylindrical, 0.0012	9.4	5.52	1807	7.89	2586	0.74
	9.8	5.53	1906	7.99	3176	.51
Cylindrical, 0.0090	9.4	6.54	2212	7.89	2586	.16
	9.7	6.49	2191	7.97	2601	.19
	6.0	3.42	1300	5.90	2038	.65
	7.1	4.97	1759	6.68	2285	.21
	7.9	5.59	1941	7.19	2408	.18
	8.9	6.13	2097	7.70	2543	.23
	9.4	6.23	2122	7.89	2586	.23
	9.4	6.45	2186	7.89	2586	.17
	9.4	6.23	2124	7.89	2586	.38
	9.4	6.38	2166	7.89	2586	.27
Cubical, 0.0283	9.5	6.66	2244	7.91	2591	.13
	9.7	6.51	2197	7.97	2601	.19
	9.9	6.17	2090	8.01	2607	.23
	9.9	7.59	2496	8.01	2607	.03
	10.1	6.45	2161	8.05	2610	.22
	11.1	6.34	2083	8.07	2672	.20
	12.3	5.69	1848	7.91	2466	.25
	13.1	4.98	1615	7.77	2383	.32
	14.1	3.64	1218	7.55	2276	.62
Rectangular, 3.20	9.1	6.30	2147	7.78	2562	.23
	9.3	6.38	2168	7.85	2578	.26
	9.4	6.13	2095	7.89	2586	.29
Rectangular, 25.6	9.5	6.63	2238	7.91	2591	.17
	9.6	6.60	2199	7.91	2591	0.18
B. Initially Turbulent Conditions						
	6.0	5.16	1820	5.90	2038	0.43
	7.0	5.61	1950	6.62	2247	.57
	8.1	6.13	2100	7.30	2440	.65
	9.2	6.83	2299	7.81	2571	.53
	9.4	6.94	2326	7.89	2586	.48
Cubical, 0.0283	9.4	7.25	2415	7.89	2586	.26
	9.4	8.67	2786	7.89	2586	−0.23 (?)
	9.5	6.53	2209	7.89	2591	1.02 (?)
	10.4	6.91	2295	8.05	2610	.53
	11.1	6.80	2213	8.07	2672	.50
	11.9	6.67	2137	7.98	2503	0.53
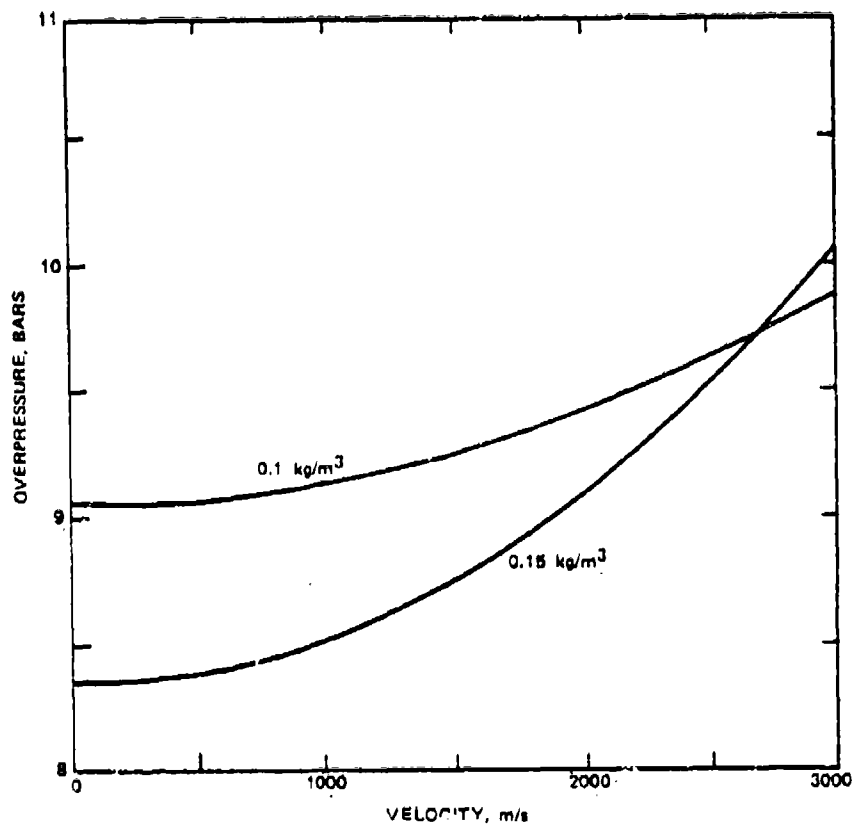
FIGURE 13. Increased Velocity of Fuel
Injection Causes Moderate Increase in
Blast Overpressure.

ALTITUDE EFFECT

An increase in altitude reduces the amount of oxygen in
the system when a fuel burns in a confined volume of air at
ambient pressure.[12] For a constant amount of fuel, this

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[12] *Handbook of Tables for Applied Engineering Science,*
2nd ed. "U.S. Standard Atmosphere, 1962," Cleveland, Ohio,
CRC Press, 1976. P. 651.

causes a shift toward richer mixtures and a reduction in the
maximum overpressure that can be developed. This decrease
in maximum overpressure is shown in Figure 14 for TNT and a
conventional hydrocarbon fuel, with both at a fuel-air ratio
of 92 g/m^3, a ratio that is near the optimum for the hydro-
carbon fuel.

The effect of the reduction in overpressure with alti-
tude can be somewhat compensated for by varying the amount
of fuel injected to keep the fuel-air ratio near the optimum
(Figure 14). This, however, represents a lesser total amount
of fuel and air present so that again the overpressure de-
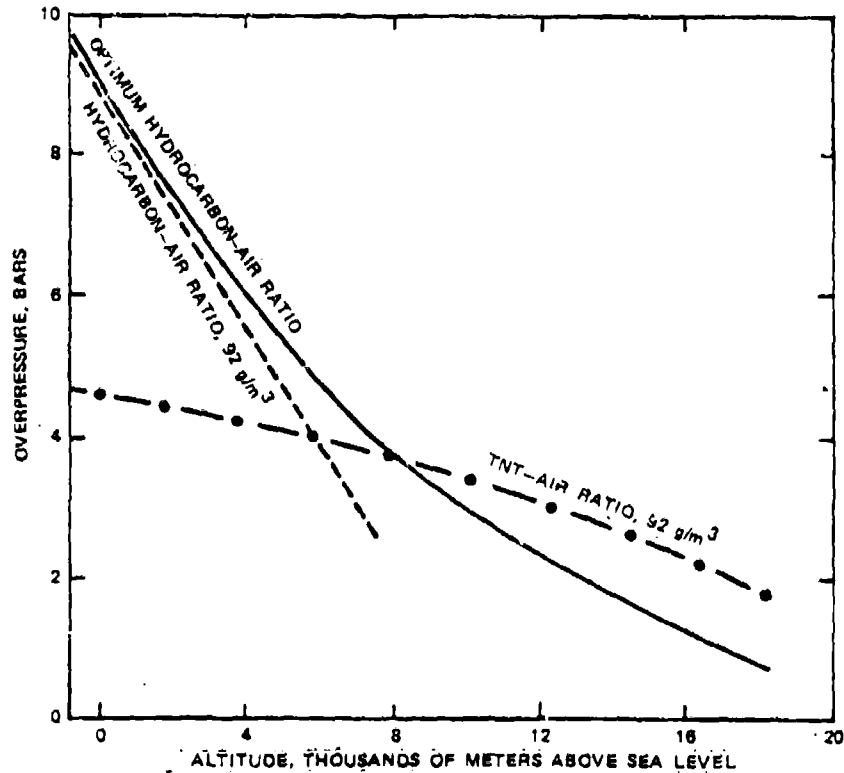creases sharply with altitude.

FIGURE 14. Internal Blast Overpressure
Decrease at Increased Altitude.

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SUMMARY

Confined explosions such as those in grain elevators, coal mines, or ship compartments can be very damaging. The peak overpressures that such explosions can generate have been computed from first principles of conservation of mass, conservation of energy, and minimum Gibbs free energy. The amounts of the various chemical species that are present, including those resulting from chemical dissociation in the products mixture at explosion temperature, are found by using iterative methods. This iteration is readily performed on a small tabletop computer. The peak overpressure is then found by the ideal gas law from products composition and temperature. Other items such as formula mass and heat capacity for the products can also be determined. Computer overpressures agree closely with experimental observations on confined explosions of TNT in air for a three-decade range of fuel-air ratios.

Peak overpressures have been computed for a large number of confined explosions with explosive fuels, both pure chemical explosives and mixtures of these, and for a wide range of fuel-air ratios. They pertain directly to nonvented adiabatic explosions that occur so rapidly that there is little time for gas leakage or for heat transfer effects. These overpressures increase monotonically from very low values at low fuel-air ratios up to more than 70 bars at high fuel-air ratios (Tables 1 and 2).

The relative effectiveness of an explosive fuel in generating blast overpressure can be described in terms of an internal blast yield. This is the inverse ratio of the amount of an explosive relative to some standard, here taken as TNT, that is required for producing the same overpressure. These yields depend on both the type of explosive and the fuel-air ratio. Thus oxygen-deficient explosives in the low fuel-air range show pronounced afterburn effects that contribute to the pressure rise. But in the high fuel-air range, relatively less oxygen is available and afterburn is less important. Also, for oxygen-rich explosives afterburn effects are not pertinent. Considerations such as these make it possible to correlate the chemical structure of an explosive with the internal blasts it can generate. These considerations also indicate that two different internal blast yield values should be assigned to a given explosive—one yield value for the low overpressure range and one for the high. These yield pairs are given in Table 3 for representative chemical explosives and explosive mixtures.

Internal explosions with ordinary combustibles such as fuel oil, coal dust, or starch can also be important. For these explosions the maximum adiabatic overpressures attained are usually on the order of 8 bars, at a definite fuel-air ratio that characteristically lies between the CO_2-H_2O and the CO-H_2O stoichiometric reference points. At fuel-air ratios below the maximum overpressure there is unutilized oxygen from the air, and above it the extra fuel acts only as material to be warmed, depressing the temperature rise and associated pressure rise. Maximum adiabatic overpressures, along with associated flame temperatures and fuel-air ratios, are given for a number of liquid and solid combustibles in Table 4 and for combustible gases in Table 5. Values at the lower and upper explosive limits are also included in Table 5. Blast yields relative to benzene (for liquids and solids) or relative to methane (for gases) are also tabulated.

All peak overpressures reported above are for adiabatic explosions; i.e., ones without heat transfer from explosion flame to confining walls. They pertain directly to explosive fuels where the detonation and afterburn, if any, are very rapid indeed. In internal explosions with conventional combustibles however, the combustion reaction may be sufficiently slow so that noticeable heat transfer can occur. Thus for methane explosions in air, observed overpressures are only about 80% of those computed for adiabatic conditions. From such data it is calculated that the overall thermal emissivity for quiescent methane flames is about 0.22, and about 0.55 for the more luminous flames from a turbulent methane-air mixture.

The calculated overpressure effects of fuel injection at high velocity are quite modest. In addition, calculations for the effect of altitude on internal blast show a negative trend, i.e., lower air pressures at higher altitudes reduce the amount of oxygen available for the explosion reaction, resulting in a substantial decrease in overpressure.

REFERENCES

1. R. G. S. Sewell and G. F. Kinney. "Response of Structures to Blast: A New Criterion," *Ann. N. Y. Acad. Sci.*, Vol. 152 (1968), p. 532.

2. Private communication between James Weeks and R. W. Carlson, *Confinement of an Explosion by a Steel Vessel*, Los Alamos Scientific Report LA-390 dated 1945.

3. Hans R. W. Weibull. "Pressures Recorded in Partially Closed Chambers at Explosions of TNT Charges," *Ann. N. Y. Acad. Sci.*, Vol. 152 (1968), p. 357.

4. National Defense Research Committee. *Effects of Impact and Explosion*. Vol. 1. Washington, D. C., NDRC, 1946. P. 91. (Summary Report of Technical Division 2, Vol. 1, publication UNCLASSIFIED.)

5. Air Force Systems Command for Joint Technical Coordinating Group for Munitions Effectiveness. *Internal Blast Damage Mechanisms Computer Program*, by James F. Proctor, Naval Ordnance Laboratory, Silver Spring, Md. Dayton, Ohio, AFSC, Wright-Patterson Air Force Base, 10 April 1973. (Report 61-JTCG/ME-73-3, publication UNCLASSIFIED.)

6. National Bureau of Standards. *JANAF Thermochemical Tables*, D. R. Stull and H. Prophet, Project Directors. Washington, D. C., NBS, 1971.

7. P. J. Kiefer, G. F. Kinney and M. C. Stuart. *Principles of Engineering Thermodynamics*. New York, Wiley and Sons, 1958.

8. U. S. Army Materiel Command. *Properties of Explosives of Military Interest*. Washington, D. C., USAMC, 29 January 1971. (AMCP 706-177, publication UNCLASSIFIED.)

9. C. G. Maier and K. K. Kelley. "An Equation for the Representation of High-Temperature Heat Capacity Data," *J. Amer. Chem. Soc.*, Vol. 54 (1932), p. 3243.

10. Bernard Lewis and G. von Elbe. *Combustion, Flames, and Gases*. New York, Academic Press, 1951.

11. U. S. Bureau of Mines. *Explosion Development in Closed Vessels*, by John Nagy, E. C. Seiler, J. W. Conn, and H. C. Varakis. Washington, D. C., U. S. Bur. Mines, 1971. (Bureau of Mines Report of Investigations 7507, publication UNCLASSIFIED.)

12. *Handbook of Tables for Applied Engineering Science*, 2nd ed. "U.S. Standard Atmosphere, 1962," Cleveland, Ohio, CRC Press, 1976. P. 651.

Appendix A

STOICHIOMETRIC POINT CALCULATIONS

1. Find nominal products from the reaction of TNT with air to the $CO-H_2O$ stoichiometric reference point in air at 25°C and 1 bar.

2. What is the corresponding products composition in mole percent, and the corresponding fuel-air ratio in kilograms per cubic metre (stere)? The formula for TNT is $C_7H_5N_3O_6$, and its formula mass is 227.13 g/mol. Air is 21% oxygen, 78% nitrogen, and 1% argon.

Answers. Selecting 1 mole of TNT as a basis and expressing the pertinent combustion reaction in the form of a chemical equation,

$$C_7H_5N_3O_6 + 1.75\ O_2 \rightarrow 7\ CO + 2.50\ H_2O + 1.50\ N_2$$
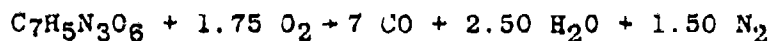
The number of moles of air corresponding to 1.75 moles of oxygen is 1.75/0.21 = 8.33. Nitrogen supplied by this air is thus 8.33 x 0.78 = 6.50 moles, to which is added 1.50 moles from the TNT reaction to give a total of 8.00 moles nitrogen in the products. Argon is 8.33 x 0.01 = 0.08 mole. Expressed in tabular form,

Component	Moles	Mole %
CO	7.00	39.8
H_2O	2.50	14.2
N_2	8.00	45.5
Ar	0.08	0.5
Total	17.58	100.0

The volume of the 8.33 moles of air in this reaction, at 25°C and 1 bar, is given by the ideal gas law as 8.33 x 0.083 14 x 298.15 = 206.6 litres, or 0.2066 m^3. The mass of 1 mole of TNT is 0.227 13 kilogram so that the fuel-air ratio becomes 0.227 13/0.2066 = 1.100 kg/m^3. Corresponding calculations for the CO_2-H_2O point show a fuel-air ratio of 0.367 kg/m^3, and for the CO_2-H_2 and $CO-H_2$ points, ratios of 0.481 and 3.848 kg/m^3, respectively.

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Appendix B

FREE ENERGY COMPUTATIONS

1. What is the thermodynamic equilibrium constant K_p for the dissociation of 1 mole of carbon dioxide at 2500 K as given by data from the JANAF tables?[6]

Answer. Expressing the dissociation as a chemical equation,

$$CO_2 = CO + 1/2\ O_2$$
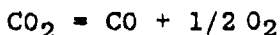
its thermodynamic equilibrium constant K_p is

$$K_p = \frac{(CO) \times (O_2)^{\frac{1}{2}}}{(CO_2)}$$

where parentheses denote the fugacity of an indicated material (the thermodynamic item fugacity corresponds to a "partial pressure").

The tables provide directly the (logarithm to base ten of the) equilibrium constant of formation for each component of the equilibrium. Such values are to be combined just as are the fugacities in the equilibrium constant expression. For carbon dioxide at 2500 K, the formation logarithm is 8.280 and the constant itself is 1.905×10^8. Corresponding values for carbon monoxide are 6.840 and 6.918×10^6. For molecular oxygen, an element in its ordinary form, the values are zero and unity, respectively. Combining,

$$K_p = \frac{6.918 \times 10^6 \times (1)^{\frac{1}{2}}}{1.905 \times 10^8} = 3.63 \times 10^{-2}$$

The numerical value $K_p = 3.63 \times 10^{-2}$ applies at the specified temperature of 2500 K with fugacities relative to the arbitrary standard of 1.013 25 bars (the standard atmosphere).

2. What is the corresponding mole number equilibrium constant K_n at 2500 K for the dissociation of carbon dioxide in a system with a volume of 1 m^3?

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Answer. The calculation proceeds by noting that a fugacity in an ideal gas mixture is given as the product of a mole fraction and system pressure. Thus the fugacity for carbon dioxide (CO_2) = CO_2 x P/n, where CO_2 is the mole number for the carbon dioxide present, P the pressure in the system, and n the total number of moles of gases. For ideal gases $PV = nRT$, and the ratio P/n is also given as RT/V where R is the gas law constant, T the absolute temperature, and V the volume of the system. Substituting into the expression for the thermodynamic equilibrium constant and rearranging,

$$K_p = \left(\frac{CO \times C_2^{\frac{1}{2}}}{CO_2} \right) (RT/V)^{\frac{1}{2}} = 3.63 \times 10^{-2}$$

where again a chemical formula indicates the number of moles of the specified species in the equilibrium mixture. The central term, with mole numbers only, also defines a mole number equilibrium constant K_n, or

$$K_n = \frac{CO \times O_2^{\frac{1}{2}}}{CO_2} = K_p(V/RT)^{\frac{1}{2}} = 3.63 \times 10^2 \ (V/RT)^{\frac{1}{2}}$$

In this expression the item (V/RT) has units of a fugacity at the standard atmosphere. Then selecting litres for volume, the appropriate value for R is 0.082 06 litre (l·atm)/(mol·K), so that at 2500 K

$$K_n = 3.63 \times 10^{-2} \times (1000/0.082\,06 \times 2500)^{\frac{1}{2}}$$
$$8.017 \times 10^{-2}$$

Such mole number constants greatly facilitate equilibrium calculations for systems with specified volume and temperature.

3. Compute the mole number equilibrium constant for the smoke reaction in a system with a volume of 1 m^3 at 2500 K.

Answer. The smoke reaction equilibrium can be represented as

$$2\,CO = CO_2 + C_{(s)}$$
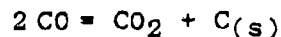
Noting that the fugacity of solid carbon is unity, the thermodynamic equilibrium constant becomes

$$K_p = (CO_2)/(CO)^2$$

Thermodynamic equilibrium constants of formation for carbon dioxide and carbon monoxide at 2500 K are indicated above as 1.905×10^8 and 6.918×10^6. The thermodynamic constant for the smoke reaction becomes

$$K_p = (CO_2)/(CO)^2 = 1.905 \times 10^8/(6.918 \times 10^6)^2 = 3.980 \times 10^{-6}$$

This thermodynamic constant K_p is converted to the mole number constant K_n by the method illustrated in paragraph 2 above, or

$$K_n = CO_2/CO^2 = K_p(RT/V) = K_p \times 0.082\,06 \times 2500/1000$$

$$K_n = 8.166 \times 10^{-7}$$

Appendix C

EQUILIBRIUM CONSTANTS OF FORMATION

Logarithm to base ten of the thermodynamic equilibrium constant of formation K_f for selected combustion species is presented as a function of absolute temperature T in kelvins. Values are based on ideal gases and the standard state of 1 standard atmosphere (1.013 25 bars) and apply over the temperature range 1500-4000 K.

$$\log_{10} K_f = A + B/(T + C)$$

TABLE C-1. Coefficients for Calculating Equilibrium Constants of Formation.

Chemical Formula	A	B	C
CO_2	-0.099	21 096	18
CO	4.069	7 437	184
H_2O	-3.100	13 415	20
O	3.545	-13 553	16
H	3.242	-12 277	35
OH	0.662	-1 723	-112
N	3.582	-25 435	14
NO	0.645	-4 652	-15
H_2, O_2 N_2, Ar $C_{(s)}$	0	0	0

Appendix D

THE ALGORITHM

START → ENTER ATOMS, TEMPERATURE, ETC.

↓

NOMINAL COMPOSITION BY MATERIAL BALANCES

↓

| CO_2, O_2, H_2O | ←oxygen rich— | N_2, Ar | —oxygen deficient→ | CO_2, CO, H_2 or CO_2, H_2, H_2O |

↓

N_2 MATERIAL BALANCE

↓

H_2) COMBINED MOLE NUMBER CONSTANT
H_2O) AND MATERIAL BALANCE IN HYDROGEN

↓

O, H, OH, N, NO

BY MOLE NUMBER CONSTANTS

oxygen rich ↙   ↘ oxygen deficient

CO MOLE NUMBER CONSTANT FOR CO_2		CO_2 MATERIAL BALANCE IN OXYGEN
CO_2 MATERIAL BALANCE IN CARBON		CO MATERIAL BALANCE IN CARBON
O_2 MATERIAL BALANCE IN OXYGEN		O_2 MOLE NUMBER CONSTANT FOR CO_2

↘   ↙

CHECK FOR CONVERGENCE —YES→ TO PERCENT CALCULATIONS

↓ NO

RECYCLE ← NEW TRIAL VALUE FOR O_2
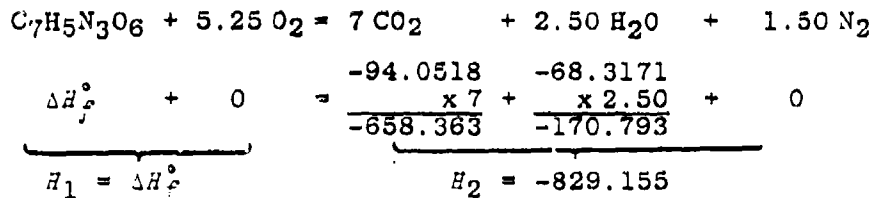MEAN OF COMPUTED AND OLD TRIAL VALUES

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Appendix E

INTERNAL ENERGY OF FORMATION

1. The heat of combustion of TNT is listed as 3620 cal/g. What is the corresponding value for the standard enthalpy of combustion ΔH_c° in kilojoules per mole? The item ΔH_c° includes the Greek letter Δ that represents a difference; subscript c indicates that the difference is for a combustion reaction between the fuel and oxygen. The letter H indicates the thermodyna. c property, the enthalpy (heat content). The superscript $\bullet$ indicates a standard value with each component a pure material at standard temperature and pressure — 25°C and 1 standard atmosphere.

Answer. The formula for TNT is $C_7H_5N_3O_6$, and the corresponding formula mass is 227.13 g/mol. Then on a mole basis the above heat of combustion is 3620 x 227.13/1000 = 822.2 kcal/mol. In the modern thermodynamic convention, where negative enthalpy difference indicates a loss of energy, ΔH_c° = -822.2 kcal/mol = -3440.1 kJ/mol.

2. Presume that the combustion of TNT value pertains to a higher heat of combustion with water taken as a liquid, as customary for unspecified conditions, and find a corresponding standard enthalpy of formation ΔH_f° for TNT.

Answer. It is convenient to use the format of a chemical equation for the combustion reaction. Each component is then assigned its standard formation value; the sum for the products, H_2, minus that for the reactants, H_1, becomes the enthalpy difference for the reaction. The standard formation value for carbon dioxide is -94.0518 kcal/mol, that for liquid water is -68.3171, and the values for oxygen and nitrogen, of course, are zero. Writing the equation for the idealized combustion,

$$C_7H_5N_3O_6 + 5.25\,O_2 = 7\,CO_2 \quad + \quad 2.50\,H_2O \quad + \quad 1.50\,N_2$$

$$
\begin{array}{ccccccc}
 & & & -94.0518 & & -68.3171 & \\
\Delta H_f^\circ & + & 0 & = \quad \underline{\times\,7} & + & \underline{\times\,2.50} & + \quad 0 \\
 & & & -658.363 & & -170.793 &
\end{array}
$$

$$\underbrace{}_{H_1\ =\ \Delta H_f^\circ} \qquad \underbrace{}_{H_2\ =\ -829.155}$$

$$\Delta H_c^\bullet = (H_2 - H_1) \approx (-829.155 - \Delta H_f^\bullet) = -822.2 \text{ kcal/mol}$$

where

$$\Delta H_f^\bullet = -829.155 - (-822.2) = -6.955 \text{ kcal/mol} = -29\,100 \text{ J/mol}$$

3. What is the corresponding standard internal energy of formation, $\Delta E_f^\bullet$?

Answer. By definition, internal energy E is the enthalpy H minus the pressure-volume product PV. For n moles of gases, this product is nRT. Thus for the formation reaction, the internal energy of formation $\Delta E_f^\bullet = \Delta H_f^\bullet - RT\Delta n$. For TNT formation,

$$7\,C(s) + 2.50\,H_2 + 1.50\,N_2 + 3\,O_2 = C_7H_5N_3O_6 \text{ (s)}$$
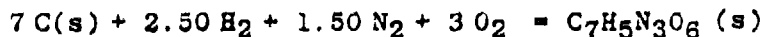
$$n_1 = 2.50 + 1.50 + 3 = 7, \text{ and } n_2 = 0, \text{ and } \Delta n = -7$$

Thus $\Delta E_f^\bullet = -29\,100 + 8.314\,34 \times 298.15 \times 7 = -11\,750 \text{ J/mol}$. This value, along with others, is included in Table E-1 of this appendix. Differences indicated there are not unusual ones and, as noted above, do not introduce appreciable uncertainty into energy computations.

TABLE E·1. Tabulated ΔE_f^o Values for 25°C.

Name	Formula				Formula mass, g/mol	ΔE_f^o, J/mol
	C	H	N	O		
Acetone	3.00	6.00	0	1.00	58.1	−208 474
Acetone/nitromethane, 50/50	2.02	4.53	0.48	1.48	59.2	−146 751
Acetylene	2.00	2.00	0	0	26.0	226 731
Ammonia	0	3.00	1.00	0	17.0	−40 420
Benzene	6.00	6.00	0	0	78.1	52 956
Benzene	6.00	6.00	0	0	78.1	87 885
1, 3-Butadiene	4.00	6.00	0	0	54.1	96 179
Butane	4.00	10.00	0	0	58.1	−116 232
Carbon dioxide	1.00	0	0	2.00	44.0	−393 510
Carbon monoxide	1.00	0	0	1.00	28.0	−111 805
Carbon (s)	1.00	0	0	0	12.0	0
Cellulose trinitrate	6.00	7.00	3.00	11.00	297.2	−627 600
Comp. B-3	2.04	2.50	2.15	2.68	100.0	20 048
Cyanogen	2.00	0	2.00	0	52.0	309 072
Cyclohexane	6.00	12.00	0	0	84.2	−141 362
Cyclotol, 75/25	1.78	2.58	2.36	2.69	100.1	22 051
Diethyl ether	4.00	10.00	0	1.00	74.1	−229 401
1, 2-Dinitrobenzene	6.00	4.00	2.00	4.00	168.1	13 050
1, 3-Dinitrobenzene	6.00	4.00	2.00	4.00	168.1	−13 745
1, 4-Dinitrobenzene	6.00	4.00	2.00	4.00	168.1	−20 828
DIPAM	12.00	6.00	8.00	12.00	454.3	−51 872
DNT	7.00	6.00	2.00	4.00	182.1	−39 524
Ethane	2.00	6.00	0	0	30.1	−79 710
Ethanol	2.00	6.00	0	1.00	46.1	−229 111
Ethylene	2.00	4.00	0	0	28.1	54 946
Ethylene oxide	2.00	4.00	0	1.00	44.1	−91 792
Ethyl nitrite	2.00	5.00	1.00	2.00	75.1	−96 328
Glyceryl trinitrate (nitroglycerin)	3.00	5.00	3.00	9.00	227.1	−332 681
n-Hexane	6.00	14.00	0	0	86.2	−162 319
n-Hexane	6.00	14.00	0	0	86.2	−181 478
Hexanitrobenzene	6.00	0	6.00	12.00	348.1	54 000
Hexanitrobenzene	6.00	0	6.00	12.00	348.1	138 000
HMX	4.00	8.00	8.00	8.00	296.2	77 404
H-6	2.35	3.24	2.02	2.52	100.0	7 143
Hydrazine	0	4.00	2.00	0	32.1	100 311
Hydrogen	0	2.00	0	0	2.0	0
Hydrogen cyanide	1.00	1.00	1.00	0	27.0	130 541
Hydroxyl	0	1.00	0	1.00	17.0	42 090
Indan	9.00	10.00	0	0	118.2	−9 501
JP-4	9.00	17.00	0	0	128.3	−402 771
JP-5	8.00	17.00	0	0	113.3	−400 000
LX-01	1.52	3.73	1.69	3.39	100.0	−104 140
Mannitol hexanitrate	6.00	8.00	6.00	18.00	452.2	−608 956
Methane	1.00	4.00	0	0	16.1	−72 394
Methanol	1.00	4.00	0	1.00	32.1	−197 448
α-Methylnaphthalene	11.00	10.00	0	0	142.2	77 840
Monatomic hydrogen	0	1.00	0	0	1.0	216 700
Monatomic nitrogen	0	0	1.00	0	14.0	356 780
Monatomic oxygen	0	0	0	1.00	16.0	246 280
Naphthalene	10.00	8.00	0	0	128.2	73 425

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TABLE E-1. (Contd.)

Name	Formula				Formula mass, g/mol	ΔE_f°, J/mol
	C	H	N	O		
Nitric oxide	0	0	1.00	1.00	30.0	90 370
Nitrobenzene	6.00	6.00	1.00	2.00	123.1	18 231
Nitromethane	1.00	3.00	1.00	2.00	61.1	−107 835
Nitromethane/acetone, 75/25	1.52	3.78	0.74	1.74	100.0	−129 929
n-Octane	8.00	18.00	0	0	114.3	−158 618
Octol	1.78	2.58	2.36	2.69	100.0	20 210
Oxygen	0	0	0	2.00	32.0	0
PBX-9007	1.97	3.22	2.43	2.44	100.0	31 859
Pennsylvania coal dust	6.16	5.26	0.10	0.55	100.0	−103 498
Pentane	5.00	12.00	0	0	72.2	−134 048
Pentanitrobenzene	6.00	1.00	5.00	10.00	303.1	60 000
Pentolite, 50/50	6.16	6.25	3.41	8.51	334.4	−97 903
cis-trans-Perhydrofluorene	13.00	22.00	0	0	178.4	−104 924
PETN	5.00	8.00	4.00	12.00	316.2	−489 774
Propane	3.00	8.00	0	0	44.1	−96 410
RDX	3.00	6.00	6.00	6.00	222.2	111 471
Rhode Island coal dust	6.89	0.50	0.01	0.11	100.0	−90 749
RJ-4-I	12.00	20.00	0	0	164.3	−113 585
RJ-5	14.00	18.40	0	0	186.1	41 235
Starch	6.00	10.00	0	5.00	162.2	−946 371
TACOT	12.00	4.00	8.00	8.00	368.2	560 341
TAZ	1.00	9.00	9.00	0	147.2	464 350
Tetranitrobenzene	6.00	2.00	4.00	8.00	258.1	30 000
Tetryl	7.00	5.00	5.00	8.00	227.1	38 910
exo-THDC	10.00	16.00	0	0	136.3	−104 924
TNT	7.00	5.00	3.00	6.00	227.2	−11 750
TNT	7.00	5.00	3.00	6.00	227.2	−13 677
TNT	7.00	5.00	3.00	6.00	227.2	−12 170
1, 2, 4-Trinitrobenzene	6.00	3.00	3.00	6.00	213.1	35 291
1, 3, 5-Trinitrobenzene	6.00	3.00	3.00	6.00	213.1	−6 550
Trinitrotriazidobenzene	6.00	0	12.00	6.00	336.2	1 160 000
Water (l)	0	2.00	0	1.00	18.0	−282 090
Water (v)	0	2.00	0	1.00	18.0	−240 590

Appendix F

THE KOPP RULE FOR ADDITIVE ATOMIC HEAT CAPACITIES
(CONDENSED PHASES NEAR ROOM TEMPERATURE)

TABLE F-1.   Additive Atomic Constants.

Atom	$J/(mol \cdot K)$	Atom	$J/(mol \cdot K)$
C	7.5	O	16.7
H	9.6	F	20.9
B	11.3	P, S	22.6
Si	15.9	All others	25.9

The heat capacity for TNT, formula $C_7H_5N_3O_6$, is estimated to be about

$$(7 \times 7.5) + (5 \times 9.6) + (3 \times 25.9) + (6 \times 16.7) =$$
$$278 \ J/(mol \cdot K)$$

Appendix G

INTERNAL ENERGIES FOR COMBUSTION PRODUCTS

Standard internal energy E° in joules per mole relative to the elements at 25°C as a function of absolute temperature T in kelvins. Temperature range 500-4000 K, ideal gases.

$$E^\circ = a + b(T/1000) + c(T/1000)^2 + d(1000/T)$$

TABLE G-1. Coefficients for Calculating Internal Energies.

Formula	Coefficients			
	a	b	c	d
CO_2	-423 070	50 948	589	5280
CO	-126 080	27 200	327	2440
H_2O	-264 870	36 258	1938	5455
H_2	-8 800	20 898	1327	1112
O_2	-11 085	25 788	994	1176
N_2	-14 275	26 783	370	2508
O	245 030	12 152	76	-252
H	213 050	12 472	0	0
OH	28 533	23 013	929	1725
N	468 340	12 000	0	0
NO	76 195	27 835	260	2247
Ar	-3 718	12 472	0	0
$C_{(s)}$	-7 500	25 000	0	0

Appendix H

EMISSIVITY COMPUTATIONS

In one experiment a 10.1% mixture of methane in air in a container at 27°C and 986 millibars and initially quiescent conditions was ignited by a central electric spark. The blast overpressure generated was 6.45 bars, in contrast with the adiabatic value computed as 8.05 bars.

1. Compute actual products temperature and internal energy for this explosion and compare with those for adiabatic conditions.

Answer. By iterative calcuations for composition as described above, and for series of trial temperatures, the temperature corresponding to observed overpressure was 2161 K. The corresponding internal energy, relative to the elements, at 25°C is -295 kJ/m^3. The heat flow is the difference, or 801 kJ/m^3 for this explosion.

2. In centrally initiated internal explosions the flame front is found to be spherical and to advance at a uniform rate.[11] For the above explosion the rate of advance was measured as 0.333 m/s. Compute overall flame emissivity (the ratio of actual thermal emission to that of a blackbody at the same temperature).

Answer. The Stefan-Boltzmann relation, in engineering format, is

$$\dot{Q} = \sigma f_A f_B (T_1^4 - T_2^4) \tag{H-1}$$

where $\dot{Q}$ is the rate of radiant heat transfer and σ is the Stefan-Boltzmann constant, 5.67×10^{-8} W/m·K^4. Item f_A is an area factor that for a completely enclosed flame is its emitting surface area. For a centrally initiated spherical flame front at radial distance r from point of initiation, the emitting area is

$$f_A = 4\pi r^2$$

Item f_B of Equation H-1 is a blackness factor; for a flame completely enclosed by cool walls this is gi n as the

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emissivity ε of the flame. In Equation H-1 temperature T_1 is that of the flame and T_2 that of the walls, but T_2 becomes negligible for large temperature differences. Since the rate of flame advance dr/dt is a constant $\dot{r}$, Equation H-1 is then integrated as

$$Q = \int_0^r 5.67\varepsilon(4\pi r^2)\left(\frac{T}{100}\right)^4 \frac{dr}{\dot{r}}$$

Solving for the emissivity ε,

$$\varepsilon = \left(\frac{Q}{V}\right)\left(\frac{\dot{r}}{5.67(T/100)^4}\right)$$

where V is the equivalent spherical volume, and Q/V the heat flow in joules per cubic metre.

For the above described internal explosion with a heat flow at 801 kJ/m^3,

$$\varepsilon = 801\,000 \times \frac{0.333}{5.67(21.61)^4} = 0.22$$

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