AR-009-359

DSTO-TR-0226

Chemical Equilibrium Calculations for Detonation Products

Rodney A.J. Borg, Gary Kemister and David A. Jones

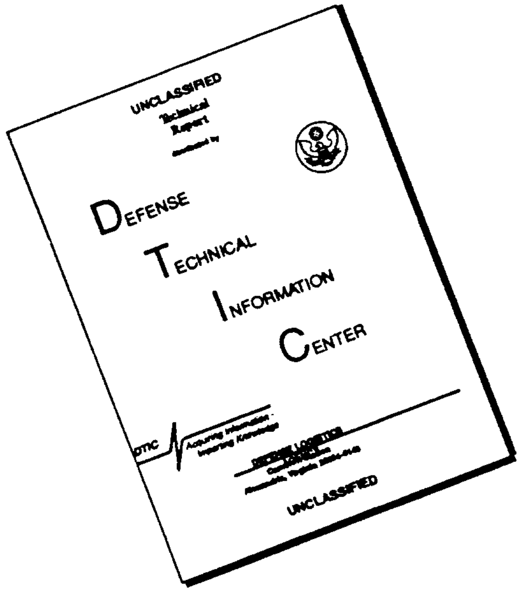
19960429 022

APPROVED FOR PUBLIC RELEASE

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

Chemical Equilibrium Calculations for Detonation Products

Rodney A.J. Borg, Gary Kemister and David A. Jones

Weapons Systems Division
Aeronautical and Maritime Research Laboratory

DSTO-TR-0226

ABSTRACT

We present a detailed description of the development, implementation, and application of a computer program to calculate the detonation parameters of condensed phase explosives. The code is based on Mader's BKW chemical equilibrium code, but contains important new features. A new algorithm to calculate the minimum in the free energy of the product composition has been included. This is a probabilistic algorithm, based on the method of Benke and Skinner, and its inclusion ensures that the true global minimum in the free energy will always be found. As well as the BKW equation of state to describe the detonation products, the new code also includes the JCZ3 equation of state. This is an intermolecular equation of state containing no adjustable parameters, and hence should be applicable to a wider range of explosives than could be considered using the BKW code. We have validated the code on a wide range of military explosives, using both the new probabilistic minimisation algorithm as well as the original method of steepest descent, for both the BKW and JCZ3 equations of state. We also present a detailed description of the application of the code to the non-ideal underwater explosive PBXN-111, and show that the performance of the explosive is best described using the JCZ3 equation of state.

RELEASE LIMITATION

Approved for public release

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

Published by

DSTO
Aeronautical and Maritime Research Laboratory
PO Box 4331
Melbourne Victoria 3001

Telephone: (03) 626 8111
Fax: (03) 626 8999

AR No. 009-359
October 1995

Chemical Equilibrium Calculations for Detonation Products

Executive Summary

This report describes the development and application of a chemical equilibrium computer code to calculate the detonation parameters of condensed phase explosives. The code is based on the Chapman-Jouguet theory of detonation, incorporates two different equations of state to describe the detonation products, and offers a choice of two different algorithms to minimize the free energy of the product composition.

We first describe the development of the code using the Becker-Kistiakowsky-Wilson (BKW) equation of state to describe the detonation products, and the method of steepest descent to minimize the free energy of the product composition. The code is then used to calculate detonation parameters for a number of standard ideal military explosives and shown to give results which are identical to those obtained from existing codes employing the same equation of state and minimization algorithm.

One weakness of the method of steepest descent is that it finds local minima, and to obtain accurate predictions of the detonation parameters it must be given an initial estimate of the detonation state which is relatively close to the final equilibrium state. For ideal military explosives this causes no problems, but one of the objectives in developing the current code was to apply it to highly non-ideal underwater explosives such as PBXN-111, in which case the procedure is far from straightforward. Hence there is a finite probability that the algorithm will find a local minimum, rather than the global minimum, and thereby give a misleading result for the detonation velocity and pressure.

To eliminate this possibility we also added a second algorithm to the code to minimize the free energy. This is a stochastic method which uses an adaptive probabilistic technique to locate minima, and is guaranteed to find the global minimum without the need to make an initial estimate of the final equilibrium state. We checked that the new algorithm gave identical results to the steepest descent technique for the ideal explosives already considered, and then used the code to calculate the detonation parameters for PBXN-111. Both algorithms gave essentially the same result, verifying that the true equilibrium composition was being found, but the calculated detonation pressure and velocity were significantly different from the experimental values.

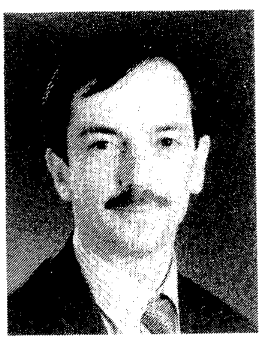
To improve agreement with experiment we then implemented the JCZ3 equation of state in the code. JCZ3 is based on an intermolecular potential and contains no adjustable parameters, and hence was considered to be more appropriate for highly non-ideal explosives than the BKW equation of state. Implementation of JCZ3 was validated on a variety of standard explosives, and then applied to calculate the detonation parameters of PBXN-111. This resulted in much better agreement with experiment, and also in very good agreement with calculations using related equations of state based on intermolecular potentials.

Authors

Rodney A.J. Borg

Weapons Systems Division

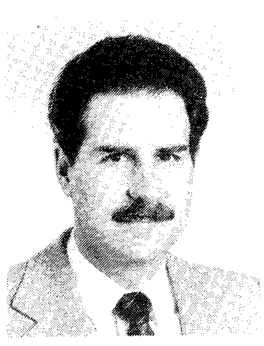
Rodney Borg graduated from the University of Melbourne with a B.Sc (Hons) in Chemistry in 1987. He joined the then MRL in 1988 and undertook a Ph.D. from Flinders University in Physical Chemistry in 1993. Since then he has worked on various experimental and theoretical projects with high explosives. He is currently involved with computational studies of bullet impact events.



Gary Kemister

Weapons Systems Division

Gary Kemister graduated from Sydney University in 1980 with a B.Sc (Hons I) and in 1985 with a Ph.D. in theoretical chemistry. After working at Oxford University, University of North Carolina at Chapel Hill, Sydney University and La Trobe University on various aspects of electronic structure of materials he joined the Defence Department in 1991 working for the Analytical Studies Unit in Force Development and Analysis Division in Canberra. In 1993 he moved to Explosive Ordnance Division (now part of Weapons Systems Division) at Maribyrnong and is currently working on numerical simulations of the physics and chemistry of explosions.



David A. Jones

Weapons Systems Division

David Jones graduated from Monash University in 1972 with a BSc (Hons), and in 1976 with a PhD in Theoretical Physics After working at Strathclyde University, London University and the University of New South Wales he joined AMRL in 1983 to work on the numerical and analytical modelling of shaped charge warheads. From February 1987 to May 1988 he was a Visiting Scientist at the Laboratory for Computational Physics and Fluid Dynamics at the Naval Research Laboratories in Washington DC. While there he worked on advanced computational fluid dynamics algorithms and their application to the numerical modelling of detonation and explosive effects.

Contents

1. Introduction

Calculations based on the Chapman-Jouguet (CJ) theory of steady state detonation have proven very successful in the past in reproducing the experimentally determined detonation velocities and pressures of ideal explosive compositions [1,2]. The CJ theory assumes that the flow is one-dimensional, the reaction zone is infinitely thin, and that completion of reaction coincides with the sonic point in the flow (which is then defined as the CJ point). Calculation of the detonation pressure and velocity at the CJ point then requires the use of a chemical equilibrium code to determine the product composition with the minimum free energy (which we refer to as minimizing the free energy), and appropriate equations of state to describe the detonation products at the very high temperatures and pressures involved in the detonation process. There are a number of computer programs capable of performing these calculations and for many years AMRL has been using a version of Mader's BKW code for this purpose [3]. When applied to ideal CHNO explosives the agreement between calculated and experimental detonation velocity and pressure has been excellent [4].

Recently in Australia there has been considerable interest in the composite explosive PBXN-111 (previously known as PBXW-115) for use in underwater munitions [5-9]. This is a highly non-ideal composition however, and the use of a chemical equilibrium code to calculate a detonation velocity and pressure for such explosives is far from straightforward. Mader has made some progress in this area by using the BKW chemical equilibrium code and limiting the extent of reaction of some of the constituents. This mimics the effect of the late-time reactions which occur in non-ideal explosives, and Mader has been able to get excellent agreement with experimental data for detonation velocity and pressure using this method [1]. This procedure determines the equation of state of the detonation products, which can then be used in a hydrocode calculation to simulate aquarium test data and predict the position of measured shock wave and confinement/water interface positions. Good agreement with some of the experimental data has been obtained using this approach [10], but the method has the disadvantage of requiring a new determination of the equation of state when the experimental conditions are changed.

Jones and Kennedy [11] have adopted a different approach to the modeling of highly non-ideal composite explosives by using the slightly divergent reactive flow theory of Kirby and Leiper [12], together with the reactive hydrocode DYNA2D. This method has the advantage of allowing accurate resolution of the reaction zone length in composite explosives by assuming a more realistic expression for the rate of energy release based on a sequence of decomposition reactions occurring on different time scales. Appropriate values for the time constants appearing in these equations are then obtained from experimental data on the variation of detonation velocity with charge diameter. The method also requires an estimate of the detonation velocity at infinite diameter, and this is obtained from a chemical equilibrium code, but in this application the need to restrict the degree of reaction of some of the constituents of the equilibrium composition is removed. In applying this approach however it has been found that the BKW code appears to overestimate the detonation velocity of some composite explosives. For ANFO-like explosives for example Kennedy has found that the JCZ3 equation of state in ICI's detonation code HEDEQ gives better estimates for the detonation velocity of these explosives [13], and Kennedy and Jones [14] have found that the detonation velocity of PBXN-111 is more accurately calculated using the

ICI chemical equilibrium code IDEX, which uses an intermolecular equation of state for the gaseous products.

Mader's BKW code employs the Becker-Kistiakowsky-Wilson equation of state for the gaseous detonation products [15], and the Cowan-Fickett equation of state for the solid products [16]. The BKW equation of state is a phenomenological expression containing several adjustable parameters which have been determined by fitting to a series of experimental results obtained on ideal explosives. More realistic equations of state based on intermolecular potentials and refined mixing rules are now available, but the effect of these different equations of state on the calculated detonation properties of highly non-ideal explosives such as PBXN-111 has not been extensively investigated. The BKW code is not easily modified however, and could not be used to study the effect of different equations of state on the detonation performance of PBXN-111.

Determination of the CJ state of an explosive requires the minimization of the free energy of the product composition. The BKW code uses the method of steepest descent to perform this calculation [17], and this method requires an initial estimate of the CJ state to be made. The method of steepest descent then finds the closest minimum to the initial guess, but is not guaranteed to find the global minimum. In actual practice, when dealing with CHNO explosives, the method invariably does find the global minimum because realistic initial estimates of the CJ state can be made. For highly non-ideal explosives this is not necessarily the case however, and a method of minimizing the free energy which was guaranteed to find the global minimum without the need to make an initial estimate of the CJ state would be highly desirable.

The above considerations have lead us to develop our own chemical equilibrium code for the determination of the CJ state of condensed phase explosives. The code is written in modular form and the equation of state has been incorporated as a subroutine so that it can easily be replaced by a new equation of state by rewriting this subroutine. Two numerical techniques have been used to minimize the free energy; we use the method of steepest descent as used by Mader, both because of its speed of execution, and the need to check agreement with Mader's calculations, and we also use a new probabilistic algorithm of Benke and Skinner [18], which is designed to find the global minimum without the need for an initial estimate of the equilibrium composition.

In Section 2 we outline the equations describing the thermodynamics of the equilibrium composition and their solution using the method of steepest descent and the BKW equation of state. In Section 3 we describe the probabilistic algorithm of Benke and Skinner and it's implementation into our chemical equilibrium code. Calculations of the CJ state of standard CHNO explosives using our code are in excellent agreement with Mader's BKW results when either the method of steepest descent or the probabilistic algorithm are used for the free energy minimization. In Section 4 we use our code to calculate the infinite diameter detonation velocity and pressure for PBXN-111, and also consider the effect of limiting the extent of reaction of some of the products on the calculated detonation properties. In Section 5 we describe the implementation of the JCZ3 intermolecular equation of state [19] into our chemical equilibrium code, and then discuss the effect which this has on the calculated detonation parameters of PBXN-111.

2. Determining the CJ State of Explosives

2.1 CJ Condition and Conservation Relation

The CJ state of an explosive can be determined by satisfying the following criteria [1,2]:

1. At the CJ point the slope of the Raleigh line is tangent to the isentrope, ie

$$\left.\frac{\partial P}{\partial V}\right|_S = \frac{P_0 - P}{V_0 - V} \tag{1}$$

2. Energy must be conserved across the shock front, ie the Hugoniot condition must be satisfied.

$$E - E_0 = \frac{1}{2}(P + P_0)(V_0 - V) \tag{2}$$

In order to apply these criteria we need to be able to compute the internal energy of the equilibrium composition of the detonation products. The equilibrium composition can be calculated by minimizing the free energy of the mixture of detonation products.

2.2 Computation of Chemical Equilibrium

For a complex mixture of reaction products the equilibrium composition is determined by minimizing the free energy of the products within the constraint of mass balance. The free energy of the mixture can be expressed as the sum of the free energy of the components:

$$F(X) = \sum_{i=1}^{N} f_i \tag{3}$$

where X represents the product composition vector. The free energy f_i is given by

$$f_i = F_i^* + ln\left(x_i^f\right) \tag{4}$$

where x_i^f is the mole fraction of the ith component. The expression for F_i^* will depend on the particular equation of state chosen to describe the detonation products.

To obtain the equilibrium composition, $X = (x_1, x_2 .....x_N)$ where x_i is the number of moles of the i^{th} product, then F(X) is minimized subject to the mass balance constraint. A commonly used method to achieve this is the method of steepest descent, as described by White et al. [17]. We start with any positive set of values $Y = (y_1, y_2....y_N)$ which satisfy the mass balance equation. The free energy is then expanded in a Taylor's series to second order about Y and gives Q(X), the quadratic approximation to F(X), as follows

$$Q(X) = F(Y) + \Delta_i \sum_i \frac{\partial F}{\partial x_i}\bigg|_{X=Y} + \frac{1}{2} \Delta_i \Delta_k \sum_i \sum_k \frac{\partial^2 F}{\partial x_i \partial x_k} \tag{5}$$

where $\Delta_i = x_i - y_i$. To minimize Q(X) subject to the mass balance constraint, ie.

$$\sum_{i=1}^{N} \alpha_{ik} x_i = b_k \tag{6}$$

we form the function G(X) defined by

$$G(X) = Q(X) + \sum_j \pi_j \left(-\sum_i \alpha_{ij} x_i + b_j \right) \tag{7}$$

where the π_j are Lagrange multipliers. To minimize G(X), we set $\partial G / \partial x_i = 0$ and find the following set of equations:

$$\frac{x_i}{y_i} - \frac{\overline{x}}{\overline{y}} + \sum_{k=1}^{M} \pi_k \alpha_{ik} = -f_i(Y) \tag{8}$$

where

$$\overline{x} = \sum_{i=1}^{N} x_i, \quad \overline{y} = \sum_{i=1}^{N} y_i \tag{9}$$

and M is the number of elements, N is the number of products, α_{ik} is the product elemental composition matrix, and b_k is the reactant elemental composition vector. Equations (8) and (6) are then used to construct a matrix equation which can be solved by one of the standard methods. We use the subroutine GAUSS as described in Press et al. [20]. The calculation of the equilibrium composition for a given P and T is an iterative procedure. An initial estimate of the composition vector ($Y = y_1, y_2 \ldots y_N$) is made and then equations (6) and (8) solved to provide the new estimate $X = (x_1, x_2 \ldots x_N)$. The free energy of the new composition is then calculated and equations (6) and (8) again solved with this new value to give a new estimate of the composition. This procedure is repeated until the difference between X and Y falls below some predetermined level.

2.3 Thermodynamic Functions for the BKW Equation of State

In order to determine the equilibrium composition, expressions for the free energy of the detonation products are required. Furthermore, expressions for the internal energy are also needed to test the conservation of energy relation (see equation 2). These expressions are dependent upon the equation of state chosen to represent the detonation products. Mader has derived the appropriate expressions for the BKW equation of state.

The BKW EOS has the following form [1];

$$\frac{PV_g}{RT} = 1 + xe^{\beta x} = \overline{F}(x) \tag{10}$$

where

$$x = \frac{\kappa k}{V_g (T+\theta)^{\alpha}} \tag{11}$$

and

$$k = \sum_{i=1}^{N} x_i^f k_i \tag{12}$$

In these expressions V_g is the molar volume of the gaseous products, x_i^f is the mole fraction of the i^{th} component of the equilibrium composition, and k_i is the co-volume of the i^{th} gaseous component (which is effectively an estimate of the molecular volume). α, β, κ and θ are equation of state parameters whose values depend on which particular model is adopted. Note that the BKW equation of state only applies to the gaseous detonation products. For solid products, such as carbon or Al_2O_3, we use the Cowan-Fickett equation of state, which has the form [16];

$$P = p_1(\eta) + a(\eta)T + b(\eta)T^2 \tag{13}$$

where $\eta = \rho / \rho_o$ is the compression of the solid material relative to its normal crystal density, and p_1 a and b are polynomial expressions in η.

For gaseous detonation products described by the BKW EOS F_i^* is given by

$$F_i^* = \left(\frac{F^o - H_o^o}{RT}\right)_i + \frac{(H_o^o)_i}{RT} + \ln\left(\frac{x_i^f P}{P_o}\right) + \frac{e^{\beta x} - 1}{\beta} - \ln\overline{F}(x) + \frac{k_i}{k}(\overline{F}(x) - 1) \tag{14}$$

In equation (14), $(F^o - H_o^o)_i$ is the free energy of species i if i is regarded as a perfect gas and N is the total number of gaseous products. The free energy term is calculated using the following expression:

$$\frac{F^o - H_o^o}{T} = -\left(a_g + \frac{b_g T}{2} + \frac{c_g T^2}{3} + \frac{d_g T^3}{4} + \frac{e_g T^4}{5}\right) + \frac{ric_g}{T} \qquad (15)$$

where a_g, b_g, c_g, d_g, e_g and ric_g are constants.

The expression for the free energy of the solid components is

$$F_s^* = \left(\frac{F^o - H_o^o}{RT}\right)_s + \frac{(H_o^o)_s}{RT} + \frac{F_s'}{RT} \qquad (16)$$

where

$$F_s' = M_r\left(PV_s - P_oV_o - \left[a_sV + b_s\ell nV - \frac{c_s}{V} - \frac{d_s}{2V^2} - \frac{e_s}{3V^3}\right.\right.$$
$$\left.\left. + (A_1V + A_2 \ln V)T_V + \left(C_1V + \frac{C_2V^2}{2} + \frac{C_3V^3}{3}\right)T_V^2\right]_{V_o}^{V_s}\right) \qquad (17)$$

where T_V is the temperature in volts, M_r is the molecular mass in g/mol, V_o is the S.T.P. volume of the solid in cm^3/g and V_s is the solid volume in cm^3/g at the relevant P and T. A_1, A_2, C_1, C_2, C_3, a_s, b_s, c_s, d_s and e_s are the Cowan equation of state constants specific for each solid product. $((F^o - H_o^o)/T)_s$ is computed as per equation 15.

The internal energy is given by [1]:

$$E_g = \sum_i\left(\frac{x_i}{\bar{x}}\left[\left(H^o - H_o^o\right)_i - RT + \left(\Delta H_f^o\right)_i\right]\right) + \frac{\alpha RT^2}{T+\theta}(\bar{F}(x) - 1) \qquad (18)$$

$$E_{si} = (H^o - H_o^o)_i + (\Delta H_f)_i^o + RE_s' \qquad (19)$$

$$H^o - H_o^o = \frac{b_gT^2}{2} + \frac{2c_gT^3}{3} + \frac{3d_gT^4}{4} + \frac{4e_gT^5}{5} + ric_g \qquad (20)$$

where $H^o - H_o^o$ is the enthalpy of the product in the standard state at T Kelvin minus the enthalpy of the product in the standard state at 0 Kelvin.

$$E_s' = M_r\left[\left(C_1V + \frac{C_2V^2}{2} + \frac{C_3V^3}{3}\right)T_V^2 - \left(a_sV + b_s\ell nV - \frac{c_s}{V} - \frac{d_s}{2V^2} - \frac{e_s}{3V^3}\right)\right]_{V_o}^{V_s} \qquad (21)$$

and

$$E_{total} = \bar{x}_gE_g + \sum_{solids} x_iE_s(i) \qquad (22)$$

2.4 The AMRL Code

Given the ability to:

(i) compute the equilibrium composition at a given P and T by minimizing the free energy.

(ii) compute the internal energy of this equilibrium mixture at P and T

then the Hugoniot equation and the CJ condition can be solved to yield the CJ point.

Use of the CJ condition in the form given by equation (1) is inconvenient when coupled with the form of equations (18) through (22) giving internal energy. By recalling that

$$\left(\frac{\partial P}{\partial V}\right)_S \equiv \left(\frac{\partial P}{\partial V}\right)_T \tag{23}$$

at the CJ point, we can use the CJ condition in the form

$$\left(\frac{\partial P}{\partial V}\right)_T - \left(\frac{P_o - P}{V_o - V}\right) = 0 \tag{24}$$

The CJ point is then determined via the following sequence:

(i) make an initial estimate of P, T, and the equilibrium composition.

(ii) minimize the free energy to obtain the correct composition for the given P and T.

(iii) at this stage the variables P, T do not necessarily lie on the Hugoniot, so equation (2) is solved to obtain a new value of T. The composition at this new value of T is incorrect now, and so the free energy must be minimized again to obtain the correct composition at the new value of T.

(iv) after the above iteration we have a value of P and T which lie on the Hugoniot and for which the composition is valid, but the variables do not necessarily satisfy the CJ condition. Hence equation (24) is now solved to determine a new value of P which satisfies the CJ condition. The equilibrium composition is now no longer valid at the new value of P, and so the sequence, (ii), (iii) and (iv) is repeated.

As can be seen from the above procedure, the calculation of the CJ state is an iterative process, and the iteration is continued until the difference between the current value of the variables and the previous values falls below some predetermined value.

Once the CJ state has been determined, the detonation velocity at the CJ point can be calculated using:

$$D_{CJ} = C_f V_o \sqrt{\frac{P_{CJ} - P_o}{V_o - V_{CJ}}} \tag{25}$$

where P_{CJ} and V_{CJ} are the pressure in Mbar and specific volume in cm^3/g respectively. C_f is a conversion factor (C_f=1.0x10^4) to give the detonation velocity in m/s. A computer program was written (called SDA•FOR) to implement the above equations and was used to calculate the detonation properties of a wide range of explosives and explosive compositions.

2.5 Code Validation

Table 1 contains a listing of the explosives and the calculated CJ states, as well as a comparison with the results obtained from Mader's BKW code. For these calculations a single set of BKW equation of state parameters was used. These values are α=0.5, β=0.16, κ=10.90978 and θ=400; this set is referred to as the RDX parameter set by Mader [1]. The agreement between SDA•FOR and BKW is excellent for all explosives and explosive compositions shown in Table 1. Typically the percentage difference between the BKW and SDA calculated detonation velocities is less than 0.5%. For the detonation pressure a percentage difference of 5% is obtained for PETN at a loading density of 0.5 g/cm³ and at a loading density of 1.0 g/cm³ the same explosive has a percentage difference of 3%. Apart from these two cases the percentage difference in the detonation pressure is less than 1%. Suceska [21] has written a code (EXPLO5) to perform calculations of detonation parameters using a BKW equation of state and has compared results of this code with results obtained from the Mader BKW program. In this comparison Suceska also observes small differences between the two programs and suggests that the differences could be due to the use of different values for the standard thermodynamic functions or due to a difference in the way EXPLO5 computes solid product thermodynamic functions. The minor variations observed between the SDA code and the Mader BKW code can be attributed to coding differences between the two programs. For example, in the SDA code an iterative technique is used to determine the CJ point whereas in the Mader BKW code the CJ point is determined by approximating the detonation velocity as a parabolic function in P and then finding the minimum of this parabola to give the minimum detonation velocity and hence the CJ state. This and other differences in numerical techniques can explain the minor variations noted above.

Table 1: Comparison of computed CJ parameters for selected explosives and explosives compositions. The values in the BKW columns were computed by the Mader BKW code (see Mader [1]) and the values in the columns headed by SDA were computed using the SDA.FOR code written for this work.

EXPLOSIVE	P_{CJ} (Mbar)		T_{CJ} (K)		D_{CJ} (m/s)	
	BKW	SDA	BKW	SDA	BKW	SDA
RDX $\rho = 1.8$	0.347	0.345	2587	2588	8754	8711
TNT $\rho = 1.64$	0.213	0.213	2829	2825	7197	7168
HMX $\rho = 1.9$	0.395	0.394	2364	2364	9159	9121
PETN $\rho = 1.67$	0.280	0.279	3018	3014	8056	8024
$\rho = 1.0$	0.101	0.0978	3970	3958	5947	5929
$\rho = 0.5$	0.0303	0.0286	4493	4599	4313	4308
TATB $\rho = 1.895$	0.326	0.325	1887	1890	8411	8365
PADP $\rho = 1.86$	0.300	0.298	3112	3112	7971	7931
HNS $\rho = 1.74$	0.241	0.241	3059	3057	7410	7377
RDX/TNT 64/36 (Comp B) $\rho = 1.713$	0.284	0.282	2763	2764	8084	8037
RDX/TNT/Wax 48.9/46.1/5 $\rho = 1.62$	0.237	0.236	2741	2738	7609	7576
TNT/PETN 50/50 $\rho = 1.65$	0.257	0.256	3239	3235	7740	7707

RDX=cyclotrimethylene trinitramine, TNT=2,4,6-trinitrotoluene, HMX=cyclotetramethylene tetranitramine, PETN=pentaerythritol tetranitrate, TATB=1,3,5-triamino-2,4,6-trinitrobenzene, PADP=2,6-bis(picrylazo)-3,5-dinitropyridine.

3. The Probabilistic Algorithm for Energy Minimization

One of the disadvantages of the method of steepest descent described in the previous section is the need to provide an initial estimate of the equilibrium composition which, in some cases, needs to be reasonably close to the "correct" equilibrium composition. A further problem is the need to ensure that all the x_i remain positive for each iteration. With the method of steepest descent it was found that if any of the assumed products was particularly unfavourable (ie. had a very large free energy) then the method would try to make the x_i of that product negative. This can be avoided by employing a scaling factor, but in some cases the scaling factor is so small that the composition barely changes from one cycle to the next and the true equilibrium composition cannot be obtained.

White et al. [17] described an alternative method for minimizing the free energy which is based on a linear programming technique and automatically ensures that all x_i remain positive during the course of the calculation. This method was considered for use in the SDA•FOR code but was found to be unsuitable because in the formulation of the problem it is necessary for the total free energy function to be expressed as a linear function of the product composition vector, and with BKW (and other complex EOS) this is not the case.

3.1 Description of Algorithm

An alternative approach to minimizing functions is to use a probabilistic or stochastic methodology. In this general approach, a composition with $x_i \geq 0$ is guessed and the free energy is computed. This process is continued until a pre-determined number of guesses has been achieved. At this stage the equilibrium composition is that composition amongst all the guesses that yielded the lowest free energy. More sophisticated versions employ a weighting function approach to improve convergence. The advantages of a stochastic method include the guarantee that $x_i \geq 0$, and that a global maximum/minimum will be found (deterministic algorithms such as the method of steepest descent find local maxima/minima and do not guarantee finding a global one). A potential disadvantage of a probabilistic approach is that the total computing time will be longer.

A stochastic method presented by Benke & Skinner [18] uses an 'adaptive probabilistic algorithm' for locating global optima of multivariate functions. Let f be a function of some vector X {in the application to an equilibrium code $f \equiv$ free energy and $X \equiv$ product composition vector }. The algorithm can then be represented by the following pseudo code {virtually identical to that shown by Benke & Skinner}.

```
1.    Generate X1 randomly within constraints
2.    f1 = function (X1)
3.    FOR number of guesses DO
          generate X2 randomly within constraints
          f2 = function (X2)
          X3 = (f1 X1 + f2 X2) / (f1 + f2)
          f3 = function (X3)
          IF f1 = min (f1, f2, f3) THEN
              do nothing
          ELSE
              IF f2 = min (f1, f2, f3) THEN
                  X1 = X2
                  f1 = f2
              ELSE
                  X1 = X3
                  f1 = f3
              ENDIF
          ENDIF
      ENDFOR
4.    X1 is optimum parameter vector
      f1 is optimum value
5.    END algorithm
```

The weighted mean X_3 is the adaptive part of the algorithm. X_1 is the current best guess at any stage of the algorithm.

3.2 Implementation in AMRL Code

In order to apply this algorithm to the problem of determining equilibrium compositions, we need a method of generating random composition vectors X that sample the allowed solution space of X evenly. The first attempt was based on the premise that allowed composition vectors can be obtained by taking linear combinations of basis vectors that span the allowed solution space. Unfortunately, although such basis vectors could be determined, it was found that linear combination of these vectors gave rise to $x_i < 0$.

Failing this, a new approach was implemented. Consider a list of n products $X = (x_1, x_2, \ldots x_n)$ where each product contains one or more of m elements. Let A be the product composition matrix where a_{ij} specifies the number of atoms of type j which are in product i. Let B be the initial or reactant vector where b_j specifies the initial amount of atom type j. Choose a product, number P, at random from the list and assign it a random composition, x_p, between 0 and an upper limit given by min (b_j/a_{pj}) thus ensuring that none of the b_j will go negative. Update the b_j values. Now select another product at random until all products have been processed. It is possible that at the end of the process not all of the $b_j = 0$; in this case the composition determined is invalid and is thus rejected. Another feature is added to the algorithm to reduce the number of rejected compositions. When a product is selected a check is made to see if it is the last product left that contains a particular element. If so then the product is assigned a composition such that all of the element in question is used up. The algorithm can be expressed as:

```
1.    Set up list of products
2.    Set up counters indicating number of products for each element
      ie count (j) = number of products containing j'th element.
3.    WHILE (more products in list) DO
            Select product at random.
            Determine maximum x for this product:
            xmax = min (tot(j)/prod(j); prod (j) ≠ 0)
            IF (not the last product containing any element)   then
                  x = random number between 0.0 and xmax
            ELSE
                  x = xmax
            ENDIF
            IF (x < 0) THEN start again {go to 1}
            FOR (each element) DO
                  IF (product contains element;  ie prod(j) ≠ 0) THEN
                        tot(j) = tot(j) - x • prod (j)
                        count (j) = count (j) - 1
                  ENDIF
            ENDFOR
            Remove product from the list
      ENDWHILE
4.    IF (any tot(j) ≠ 0) THEN start again {go to 1}
5.    Finished.
```

Note: prod(j) ≡ number of atoms of type j in the chosen product
tot(j) ≡ number of atoms of type j left; initially the tot(j) value reflect the reactant composition.

A new program PEA•FOR (for Probabilistic Equilibrium Algorithm) was written to incorporate the minimization method of Benke & Skinner. The program uses the BKW EOS, a bisection method to solve the Hugoniot equation, and a VMS random number generator.

3.3 Code Validation

Table 2 shows a comparison of the results obtained with PEA•FOR and with the BKW code. Once again a single set of BKW parameters, the RDX parameters cited earlier, is used for the values quoted in Table 2. These results indicate that the program can determine CJ values for explosives that are in close accord with the results of Mader's BKW code. It is also evident that the code is much more time intensive (all runs were performed on a VAX 8700), but the location of a global minimum of free energy without a good initial guess is virtually guaranteed. In addition, no problems with x_i < 0 arise with this method.

Table 2: Comparison of computed CJ parameters calculated using the conventional method of steepest descent (BKW column) and a probabilistic algorithm for determining equilibrium compositions.

	Probabilistic Code					BKW		
Explosive	**P_{CJ} (Mbar)**	**D_{CJ} (m/s)**	**T_{CJ} (K)**	**CPU time**	**# of guesses**	**P_{CJ} (Mbar)**	**D_{CJ} (m/s)**	**T_{CJ} (K)**
Comp B $\rho = 1.713$	0.289	8081	2779	58 hr 29 min	100,000	0.284	8084	2763
PETN $\rho = 1.67$	0.285	8076	2898	2 hr 31 min	5,000	0.280	8056	3018
	0.285	8078	2957	5 hr 2 min	10,000			
	0.286	8081	3015	49 hr 55 min	100,000			
HMX $\rho = 1.90$	0.402	9197	2274	3 hr 11 min	5,000	0.395	9195	2364
	0.404	9207	2330	6 hr 5 min	10,000			
	0.402	9183	2366	61 hr 21 min	100,000			
TNT $\rho = 1.64$	0.246	7317	2949	2 hr 44 min	5,000	0.213	7197	2829
	0.216	7191	2866	4 hr 42 min	10,000			
	0.218	7222	2831	47 hr 13 min	100,000			
RDX $\rho = 1.8$	0.353	8790	2510	2 hr 23 min	5,000	0.347	8754	2587
	0.355	8853	2573	4 hr 42 min	10,000			
	0.353	8836	2588	51 hr 17 min	100,000			

4. Application to PBXN-111

4.1 The Method of Steepest Descent

Prior to computing detonation parameters of the non-ideal explosive formulation PBXN-111, a description of the formulation is required. In particular the equilibrium code SDA.FOR requires the elemental breakdown, heat of formation and density of the formulation. PBXN-111 comprises 20% RDX (cyclotrimethylene trinitramine), 43% AP (ammonium perchlorate), 25% Al (aluminium) and 12% of a HTPB based polyurethane binder. The binder can be broken down into its components; 47.7% HTPB (hydroxy terminated polybutadiene), 47.7% IDP (isodecyl pelargonate) and 4.6% IPDI (isophorone diisocyanate). The heat of formation of the formulation is calculated by summing the contribution of each of the components as shown in Table 3. The elemental composition is obtained in a similar fashion by summing the contribution of each component to the amount of each element as shown in Table 4. Given an explosive loading density of ρ=1.80 g/cm^3 for PBXN-111, the CJ parameters can be determined using the SDA code and an appropriate set of products.

Table 3: Nominal formulation of PBXN-111 and relevant heats of formation.

Component	ΔH_f(0 K) kcal/mol	Molecular Formula	M_R g/mol	Weight Fraction	Contribution to E_0 cal/mol
RDX	33.97	$C_3H_6N_6O_6$	222.11	0.20	3058.8
AP	-70.73	NH_4ClO_4	117.489	0.43	-25886.6
Al	0	Al	26.98	0.25	0
HTPB	-0.038*	$C_{7.33}H_{11}O_{0.083}$	100.0	0.0572	-2.2
IDP	212.8*	$C_{19}H_{38}O_2$	298.51	0.0572	4077.6
IPDI	-88.8*	$C_{12}H_{18}N_2O_2$	222.29	0.0056	-223.7
				Total	-18976.1

* heats of formation for these components are not available at 0 K so ΔH_f at 298 K is used instead. This is not expected to significantly alter the results.

The parameter set used in the BKW equation of state was obtained by adjusting the parameters to fit observed CJ values for a number of explosives. This procedure has been performed a number of times by different workers and thus different parameter sets are available. In Table 5 the calculated detonation properties of PBXN-111 are shown using SDA.FOR and different equation of state parameter sets. Although there are differences between the calculated detonation velocity and detonation pressure for the four parameter sets shown in Table 5, the calculated values are all significantly higher than those obtained from experimental observations. Forbes [5] has reported a CJ pressure for PBXN-111 of 12.2 GPa (0.120 Mbar), which is less than half the pressure calculated using SDA.FOR and any of the four parameter sets. The infinite diameter detonation velocity obtained by Forbes using a linear extrapolation technique is 6195 m/s, while Bocksteiner et al. [8], using the same linear extrapolation, report a lower value of 5913 m/s. Both experimental estimates are very much lower than the values shown in Table 5. Bocksteiner et. al. have shown that an elliptical fit of the detonation velocity data is superior to a linear fit. Using an elliptical extrapolation they obtain an infinite diameter detonation velocity of 5641 m/s for Australian PBXN-111 and a value of 5760 m/s for US PBXN-111.

Table 4: Elemental composition of PBXN-111.

Component	Atom					
	C	H	N	O	Cl	Al
RDX	0.270	0.540	0.540	0.540	-	-
AP	-	1.464	0.366	1.464	0.366	-
Al	-	-	-	-	-	0.927
HTPB	0.419	0.629	-	0.005	-	-
IDP	0.364	0.728	-	0.038	-	-
IPDI	0.030	0.045	0.005	0.005	-	-
Total	1.083	3.406	0.911	2.052	0.366	0.927

Two possibilities for the large discrepancy between calculated and experimental estimates of the CJ pressure and detonation velocity will be considered here. Firstly, it is well known that certain explosive formulations behave non-ideally [23], and thus calculations based upon the steady state theory developed by Chapmen and Jouguet cannot reproduce experimental values. Secondly, the parameters in the BKW equation of state are determined by fitting calculations to experimental results. Consequently the equation of state is "customized" for the particular explosives used in the fitting process. This being the case, one would expect to obtain reasonable results for explosives similar to the explosives used in the fit. However, if the explosive under consideration is very different then the reliability of the calculated results is reduced. A more general, non-parameterized equation of state would allow greater flexibility in predicting detonation parameters of new explosives/formulations.

Table 5: Calculated CJ state of PBXN-111.

	RDX parameters	TNT parameters	BKWR set [23]	Hobbs and Baer [22]
T (K)	5229	5291	5494	5823
P (Mbar)	0.294	0.299	0.305	0.289
D (m/s)	8186	8090	8337	7909
α	0.5	0.5	0.5	0.5
β	0.16	0.09585	0.176	0.174
θ	400	400	1850	5160
κ	10.90978	12.685	11.8	11.85

Mader [1] defines a non-ideal explosive as having a CJ pressure, velocity or expansion isentrope significantly different from those expected from equilibrium steady state calculations. PBXN-111 certainly satisfies this definition. There are a number of reasons why an explosive may behave non-ideally. For example the reaction of one or more components of the explosive may occur on a timescale too long to support the propagation of the shock front, the explosive geometry may lead to rarefactions that reduce the energy transferred to the shock front or the magnitude of the initiating pulse can affect the detonation state achieved by a non-ideal explosive. Using the chemical equilibrium code BKW, Johnson, Mader and Goldstein [10] have examined the influence of partial reaction of one of the reactants on the CJ parameters of Amatex 40. Their results showed that by assuming 50% of the AN (ammonium nitrate) remains inert then the BKW calculation closely matches the experimental value.

Using this idea, a series of calculations where the extent of reaction of one or more of the reactants is limited was undertaken with the SDA code. The aim of these calculations was to ascertain what degree of reaction of the Al and AP would reproduce experimental detonation velocity and pressure for PBXN-111. The first set of calculations involved taking RDX and successively adding an inert diluent to gauge the effect of this inert diluent on the RDX explosive performance. In these calculations Al was added as the inert diluent. Although Al is reactive, for the purpose of this exercise it was assumed to be inert. Figure I shows that both the detonation velocity and pressure decrease with increasing percentage of the Al diluent. Thus the addition of a component that is either unreactive or does not react on a timescale appropriate for sustaining a detonation will reduce the explosive performance as calculated by the equilibrium code.

Similar calculations were performed for a PBXN-111 like formulation. For these calculations the formulation was simplified by removing the binder, giving a mixture containing 20% RDX, 49% AP and 31% Al. In these calculations, the Al was assumed to be inert and the amount of AP that participated in the reaction was varied. The inert AP was assumed to behave similarly to inert AN (ammonium nitrate). This assumption was necessary since appropriate thermodynamic and solid equation of state parameters were not available for AP but were readily available for AN. The results of these calculations are shown in Figure 2. Once again the calculations reveal that both the detonation velocity and detonation pressure decrease as the amount of inert material is increased. The result obtained when all of the AP is assumed to be inert gives D_{CJ}=6475 m/s and P_{CJ}=0.143 Mbar. This result is still somewhat higher than the values obtained by Forbes [5]; D_{CJ}=6195 m/s and P_{CJ}=0.120 Mbar. Based on the comparison of the experimental results and the results of the calculations presented in Figure 2, it appears that RDX is the major driving force in the detonation of PBXN-111 and that AP and Al provide very little, if any, contribution to the propagation of the shock wave.

4.2 The Probabilistic Algorithm

The previous section has shown that attempts to predict the detonation velocity and pressure of PBXN-111 using the BKW EOS and the method of steepest descent minimization algorithm lead to values which are significantly higher than the experimental values. One possible cause of this discrepancy, which was discussed in the previous section, is that the BKW EOS has been parametrised on a data base containing primarily ideal explosives, and hence is unsuited for use with highly non-ideal explosives. The previous section showed that restricting the extent of reaction of both the AP and Al considerably reduced both the detonation velocity and pressure, but the best estimates obtained were still significantly higher than the experimental results. If the minimization algorithm is finding the global minimum in the free energy, then the above results suggest that use of a more appropriate equation of state is required. We consider this possibility in the next section.

Another possible cause of the discrepancy, which was mentioned in the Introduction, is that the algorithm which finds the minimum in the free energy is failing to find the true free energy minimum. To investigate this possibility we now use the probabalistic algorithm in the AMRL code to calculate the CJ state of PBXN-111. Unfortunately the amount of computer time required to perform this calculation is considerably higher than the time needed for the simpler CHNO explosives . PBXN-111 contains two extra elements, namely Cl and Al, in comparison to standard CHNO explosives. Consequently there are more products in the composition and this considerably increases the computer time required to find the equilibrium composition. Table 6 summarise the results obtained when the PEA•FOR program was used to predict the CJ state of PBXN-111 using the RDX set of parameters. The composition and CJ parameters are shown for a number of initial guesses, varying from 1,000 to 100,000. Comparing the results for 100,000 guesses with the CJ parameters calculated using the method of steepest descent and the RDX parameters shows an approximate 2% difference in CJ pressure, 4% difference in CJ velocity, and 1.5% difference in CJ temperature. This indicates that the probabalistic algorithm is finding a different minimum to the one found by the method of steepest descent. However, the differences between the results predicted by the two algorithms are small compared to the differences between the experimental values and the results calculated by either of the minimization algorithms, and so we conclude the BKW EOS is inappropriate for the description of the CJ state of explosives such as PBXN-111.

Table 6: Comparison of computed CJ parameters and compositions calculated for PBXN-111 with different number of guesses using the probabilistic algorithm for determining equilibrium compositions.

	Number of guesses				
Composition	**1000**	**2000**	**3000**	**10,000**	**100,000**
H_2O	0.6435	0.6435	0.6480	0.6432	0.6481
CO_2	0.0023	0.0023	0.0011	0.0013	0.0004
N_2	0.1606	0.1606	0.1603	0.1600	0.1595
NH_3	0.5898	0.5898	0.5904	0.5909	0.5920
CO	0.0135	0.0135	0.0110	0.0157	0.0126
HCl	0.3497	0.3497	0.3622	0.3467	0.3337
Cl_2	0.0081	0.0081	0.0139	0.0097	0.0161
$C_{(s)}$	1.0673	1.0673	1.0709	1.0660	1.0700
$Al_2O_{3(s)}$	0.4635	0.4635	0.4635	0.4635	0.4635
CJ parameters					
P_{CJ} (Mbar)	0.257	0.257	0.290	0.258	0.300
T_{CJ} (K)	5202	5202	5286	5203	5309
D_{CJ} (m/s)	7822	7822	7861	7821	7884
CPU time	2hrs 44 min[1]	8hrs 3 min[2]	9hrs 37 min[2]	39hrs 11min[2]	322hrs 48min[2]

1: Run on a HP 715/75   2: Run on a HP 715/50

5. The Effect of Intermolecular Equations of State

5.1 The JCZ3 Equation of State

As discussed in the Introduction, previous work has shown that highly non-ideal composite explosives are best described using an EOS based on an intermolecular potential. The JCZ3 equation of state, as described by Cowperthwaite and Zwisler [19], satisfies this criterion, and has been shown to be applicable to several non-ideal explosives [13,14]. The advantage of JCZ3 over BKW, for example, is that it does not contain any parameters which must be determined from an empirical fit. JCZ3 would therefore be expected to be equally applicable to a wide range of explosives, whereas BKW is only useful for those classes of explosives used in the fitting process. Hence, in this section, we describe the implementation of JCZ3 in the SDA•FOR code

5.2 Implementation of JCZ3 EOS in the AMRL Code

Incorporating the JCZ3 equation of state into the SDA code involves deriving expressions for the free energy and internal energy of a mixture of gaseous products. For a mixture of n moles of s fluid species:

$$P = p_o(V) + G(V,T)\frac{nRT}{V} \qquad (26)$$

where $p_o(V)$ = lattice pressure along the zero degree isotherm, G(V,T) is the factor that accounts for the thermal contribution to the pressure from intermolecular forces, and R is the universal gas constant.

$p_o(V)$ has the form [19]

$$p_o(V) = -\frac{dE_o}{dV}$$

where $E_o(V)$ is the volume potential of a face-centered cubic lattice, given by:

$$E_o(V) = \frac{27e_o}{5}\left\{\frac{B_l}{l}\exp\left[l - l\left(\frac{V^*}{V}\right)^{-\frac{1}{3}}\right] - \frac{B_m}{m}\left(\frac{V^*}{V}\right)^{\frac{m}{3}}\right\} \qquad (27)$$

where

$$e_o = \frac{1}{n}\sum_i\sum_j n_i n_j e_{ij} \qquad (28)$$

$$e_{ij} = R\sqrt{\frac{\varepsilon_i \varepsilon_j}{k^2}} \tag{29}$$

$$V^* = \frac{1}{n}\sum_i \sum_j n_i n_j v_{ij}^* \tag{30}$$

$$v_{ij}^* = \frac{N\left(r_{ij}^*\right)^3}{\sqrt{2}} \tag{31}$$

$$r_{ij}^* = \frac{r_i + r_j}{2} \tag{32}$$

and B_l = 13.99166, B_m = 14.45392, l ≡ repulsive exponent = 13.5, m ≡ attractive exponent = 6, ε_i ≡ potential well depth, r_i ≡ equilibrium distance, and N ≡ Avogadro's number. The G factor is given by:

$$G(V,T) = 1 - \frac{V}{f}\left(\frac{\partial f}{\partial V}\right)_T \tag{33}$$

where

$$f = f_g + f_s \tag{34}$$

$$f_s = 2\left[\frac{e_o}{nRT}\left(\frac{m}{l-m}\right)\frac{l}{\pi}\left(\frac{V^*}{V}\right)^{-\frac{1}{3}}\left(l\left(\frac{V^*}{V}\right)^{-\frac{1}{3}} - 2\right)\exp\left\{l - l\left(\frac{V^*}{V}\right)^{-\frac{1}{3}}\right\}\right]^{\frac{3}{2}} \tag{35}$$

$$f_g = 1 + a_1 y + a_2 y^2 + a_3 y^3 \tag{36}$$

$$y = \frac{V^*}{V}\left(\frac{F}{l}\right)^3 \tag{37}$$

$$F = c_1 - \ln\left[\frac{T(l-m)}{m(e_o / nR)}\right] \tag{38}$$

$$c_1 = c + l \tag{39}$$

and c ≡ Euler's constant = 0.57722. The chemical potential of the i'th species can be obtained using:

$$\mu_i = \frac{\partial A}{\partial n_i} \tag{40}$$

where A is the Helmholtz free energy for n moles of s species. This is given by [19]:

$$A = A_{ideal} + E_o(V) + nRT\,ln f(V,T) \tag{41}$$

so

$$\mu_i = \frac{\partial A_{ideal}}{\partial n_i} + \frac{\partial E_o(V)}{\partial n_i} + \frac{\partial}{\partial n_i}\left\{nRT\,ln f(V,T)\right\} \tag{42}$$

The ideal part of the chemical potential can be taken as [1]:

$$\mu_i(\text{ideal}) = \frac{\partial A_{ideal}}{\partial n_i} = (F^o - H_o^o)_i + (H_o^o)_i + RT\,ln\left(\frac{x_i P}{P_o}\right) \tag{43}$$

The second term in the expression for the chemical potential can be written as:

$$\frac{\partial E_o}{\partial n_i} = \frac{\partial E_o}{\partial e_o}\frac{\partial e_o}{\partial n_i} + \frac{\partial E_o}{\partial V^*}\frac{\partial V^*}{\partial n_i} \tag{44}$$

where

$$\frac{\partial E_o}{\partial e_o} = \frac{E_o}{e_o} \tag{45}$$

$$\frac{\partial E_o}{\partial V^*} = \frac{27e_o}{5}\left\{\frac{B_l}{3V^*}\left(\frac{V^*}{V}\right)^{-\frac{1}{3}}\exp\left[l - l\left(\frac{V^*}{V}\right)^{-\frac{1}{3}}\right] - \frac{B_m}{3v}\left(\frac{V^*}{V}\right)\right\} \tag{46}$$

$$\frac{\partial e_o}{\partial n_i} = \frac{2\sum_j n_j e_{ij}}{n} - \frac{e_o}{n} \tag{47}$$

$$\frac{\partial V^*}{\partial n_i} = \frac{2\sum_j n_j v_{ij}^*}{n} - \frac{V^*}{n} \tag{48}$$

The final term in the expression for the chemical potential can be written as:

$$\frac{\partial}{\partial n_i}(nRT\,ln f) = nRT\frac{1}{f}\frac{\partial f}{\partial n_i} + RT\,ln f \tag{49}$$

where

$$\frac{\partial f}{\partial n_i} = \frac{\partial f}{\partial e_o}\frac{\partial e_o}{\partial n_i} + \frac{\partial f}{\partial V^*}\frac{\partial V^*}{\partial n_i} + \frac{\partial f}{\partial n}\frac{\partial n}{\partial n_i} \tag{50}$$

Let

$$\sigma_1 = \frac{6e^{c_1}}{7.5nRT} \quad \text{and} \quad \sigma_2 = \frac{54e^{l}}{5\pi nRT} \tag{51}$$

then

$$\frac{\partial f}{\partial e_o} = a_1\left(\frac{v^*}{vl^3}\right)\frac{3(\ln\sigma_1 e_o)^2}{e_o} + a_2\left(\frac{v^*}{vl^3}\right)^2 \frac{6(\ln\sigma_1 e_o)^5}{e_o} + a_3\left(\frac{v^*}{vl^3}\right)^3 \frac{9(\ln\sigma_1 e_o)^8}{e_o}$$

$$+3\sigma_2\sqrt{\sigma_2 e_o}\left[\left(l\left(\frac{v^*}{v}\right)^{-\frac{2}{3}} - 2\left(\frac{v^*}{v}\right)^{-\frac{1}{3}}\right)\exp\left(-l\left(\frac{v^*}{v}\right)^{-\frac{1}{3}}\right)\right]^{\frac{3}{2}} \tag{52}$$

Now,

$$\frac{\partial f}{\partial n} = \frac{\partial f}{\partial \sigma_1}\frac{\partial \sigma_1}{\partial n} + \frac{\partial f}{\partial \sigma_2}\frac{\partial \sigma_2}{\partial n} \tag{53}$$

where

$$\frac{\partial \sigma_1}{\partial n} = -\frac{\sigma_1}{n} \tag{54}$$

$$\frac{\partial \sigma_2}{\partial n} = -\frac{\sigma_2}{n} \tag{55}$$

$$\frac{\partial f}{\partial \sigma_1} = a_1\left(\frac{v^*}{vl^3}\right)\frac{3(\ln\sigma_1 e_o)^2}{\sigma_1} + a_2\left(\frac{v^*}{vl^3}\right)^2 \frac{6(\ln\sigma_1 e_o)^5}{\sigma_1} + a_3\left(\frac{v^*}{vl^3}\right)^6 \frac{9(\ln\sigma_1 e_o)^8}{\sigma_1} \tag{56}$$

and

$$\frac{\partial f}{\partial v^*} = \frac{a_1(\ln\sigma_1 e_o)^3}{l^3 v} + \frac{2a_2 v^*(\ln\sigma_1 e_o)^6}{\left(l^3 v\right)^2} + \frac{3a_3\left(v^*\right)^2(\ln\sigma_1 e_o)^9}{\left(l^3 v\right)^3}$$

$$+3(\sigma_2 e_o)^{\frac{3}{2}}\left[\left(l\left(\frac{v^*}{v}\right)^{-\frac{2}{3}} - 2\left(\frac{v^*}{v}\right)^{-\frac{1}{3}}\right)\exp\left(-l\left(\frac{v^*}{v}\right)^{-\frac{1}{3}}\right)\right]^{\frac{1}{2}} \exp\left(-l\left(\frac{v^*}{v}\right)^{-\frac{1}{3}}\right) x$$

$$\left\{\frac{l^2}{3}\left(v^*\right)^{-2} v + \frac{2}{3}\left(v^*\right)^{-\frac{4}{3}} v^{\frac{1}{3}} - 18\left(v^*\right)^{-\frac{5}{3}} v^{\frac{2}{3}}\right\} \tag{57}$$

The internal energy can be derived using the same approach adopted by Mader with the BKW equation of state:

$$E(T,v) = nE(T,\infty) + nRT^2 \int_{\infty}^{v} \frac{1}{v}\left(\frac{\partial G}{\partial T}\right) dv + E_o(v) \tag{58}$$

where

$$\begin{aligned} E(T,\infty) &= \sum_i x_i \left(E_T^o\right)_i \\ &= \sum_i x_i \left(E_T^o - H_0^o\right)_i + \sum_i x_i \left(H_0^o\right)_i \end{aligned} \tag{59}$$

The G factor can be written as:

$$G(T,v) = 1 + \frac{\overline{u}}{\overline{v}} \tag{60}$$

where

$$\overline{u} = \alpha_1\tau^3 + 2\alpha_2\tau^6 + 3\alpha_3\tau^9 - \frac{\alpha_6\alpha_7 v}{T^{\frac{3}{2}}} \tag{61}$$

$$\overline{v} = 1 + \alpha_1\tau^3 + \alpha_2\tau^6 + \alpha_3\tau^9 + \frac{\alpha_5}{T^{\frac{3}{2}}} \tag{62}$$

$$\alpha_1 = a_1\left(\frac{v^*}{v l^3}\right) \tag{63}$$

$$\alpha_2 = a_2\left(\frac{v^*}{v l^3}\right)^2 \tag{64}$$

$$\alpha_3 = a_3\left(\frac{v^*}{v l^3}\right)^3 \tag{65}$$

$$\alpha_4 = \left[l\left(\frac{v^*}{v}\right)^{-\frac{2}{3}} - 2\left(\frac{v^*}{v}\right)^{-\frac{1}{3}} \right] x_3 \tag{66}$$

$$\alpha_5 = 2x_2\alpha_4\sqrt{\alpha_4} \tag{67}$$

$$\alpha_6 = \frac{4}{3} x_2 \sqrt{\alpha_4} \tag{68}$$

$$\alpha_7 = x_3 \left[\frac{117}{4} \left(v^*\right)^{-\frac{2}{3}} (v)^{-\frac{1}{3}} - \frac{l^2}{3v^*} - \frac{2}{3} \left(v^*\right)^{-\frac{1}{3}} (v)^{-\frac{2}{3}} \right] \tag{69}$$

$$x_1 = \frac{6 e_0 e^{c_1}}{7.5R} \tag{70}$$

$$x_2 = \left(\frac{54 e_0 e^{l}}{5 \pi R} \right)^{\frac{3}{2}} \tag{71}$$

$$x_3 = \exp\left\{ -l \left(\frac{v^*}{v} \right)^{-\frac{1}{3}} \right\} \tag{72}$$

$$\tau = ln\left(\frac{x_1}{T} \right) \tag{73}$$

then

$$\frac{\partial G}{\partial T} = \frac{\bar{v} \frac{\partial \bar{u}}{\partial T} - \bar{u} \frac{\partial \bar{v}}{\partial T}}{\bar{v}^2} \tag{74}$$

where

$$\frac{\partial \bar{u}}{\partial T} = -\frac{3\alpha_1 \tau^2}{T} - \frac{12\alpha_2 \tau^5}{T} - \frac{27\alpha_3 \tau^8}{T} + \frac{3\alpha_6 \alpha_7 v}{2T^{\frac{5}{2}}} \tag{75}$$

$$\frac{\partial \bar{v}}{\partial T} = -\frac{3\alpha_1 \tau^2}{T} - \frac{6\alpha_2 \tau^5}{T} - \frac{9\alpha_3 \tau^8}{T} - \frac{3\alpha_5}{2T^{\frac{5}{2}}} \tag{76}$$

The integral in equation 58 is evaluated numerically.

5.3 Code Validation

The equations outlined in the previous section were programmed into SDA•FOR and the code was then used to calculate the CJ state of 11 representative CHNO explosives using the JCZ3 EOS. Table 7 shows the computed CJ pressure, velocity and temperature for these explosives, and compares the results with values obtained by other authors using the same equation of state and different codes (primarily the TIGER code).

Table 7 shows that there is considerable disagreement between the results obtained by different authors using the same equation of state. For RDX for example three calculated values of the CJ pressure vary from 0.308 Mbar to 0.322 Mbar, a range of 5%, while for TNT four different authors obtain values varying from 0.177 Mbar to 0.190 Mbar for the CJ pressure, which is a range of 7%. Our computed CJ pressure for RDX of 0.311 Mbar is within the range obtained by other authors, and our value of 0.176 Mbar for TNT is less than 0.5% outside the range quoted by others. For PETN and NM our calculated CJ pressures are also within the range of values calculated by other authors, while for DATB and NQ our results differ by no more than 2% from other literature values. Our least accurate results appear to be obtained for TATB, NG and TETRYL, where our computed CJ pressures differ by 5% to 7% from values quoted in the literature. Even these differences are still within the limits of the disagreements found by other authors however. Variations in computed CJ velocities are much less, and our values are generally within 2% of those obtained by other authors. There is much less data on CJ temperature, but our computed values are also in good agreement with the available data.

The values presented in Table 7 suggest that the JCZ3 EOS has been implemented correctly into our code and we are now able to consider its application to the CJ state of PBXN-111. Before doing so however it is instructive to consider some of the possible sources of the disagreements shown in Table 7.

One potential source of error in the calculations is the use of a polynomial fit to the thermodynamic functions of the gases and solids (that is, F^O and H^O_O in equation (43)). Historically this fit was used to save space and time in the calculation, but with the development of computer hardware there is no restriction on calculating the thermodynamic functions exactly. The exact thermodynamic functions for gases specified in Mader [1] (appendix F) have been incorporated into the program. It is not expected that the polynomial fit to the solid thermodynamic functions will have much effect on the calculations.

The results for several explosives are shown in Table 8, where F refers to $\left(F^{o}-H_{o}^{o}\right)/T$ and H refers to $\left(H^{o}-H_{o}^{o}\right)$. For most of the explosives the CJ pressures generally show only a small deviation between the exact thermodynamic calculation and the approximate polynomial fit, although for one of the compositions (PETN) the difference is as high as 7%, and others (PETN, NG, TETRYL) show differences of the order of 3% to 4%. The CJ velocities show much less variation than the CJ pressures, most differences are on the order of 1% to 2%, with the largest difference of 2.5% occurring for HNS. The CJ temperatures show greater discrepancies, with PETN and NG both showing differences of the order of 4%. Given that differences of this order can arise due to differences in the way the ideal quantities are parametrised, the differences observed in Table 7 are less surprising.

Another aspect of the code which may have had a significant effect on the final result was the method used to compute the CJ point. With this in mind, we included an alternative algorithm based on the method described by Mader (see [1], p 442). In this approach the detonation velocity is calculated at three different pressure values and a parabola is fitted to the data. The minimum of the parabola then defines the CJ point. Values calculated using this method however showed no discernible difference from the results calculated using the previous method of calculating the C-J point, that is, equation (23).

Table 7: Computed CJ Pressure (Mbar), Velocity (m/s) and Temperature (K) for the JCZ3 EOS from the AMRL code compared with calculated values obtained by other authors.

Explosive	Density	AMRL JCZ3			OTHERS JCZ3			REFS
	(g/cm³)	P	D	T	P	D	T	
RDX	1.8	0.311	8741	4145	0.322	8806	4012	27
					0.343	8813		28
					0.308	8670		25
PETN	1.77	0.281	8220	4615	0.288	8210	4237	23
					0.280	8200		25
HMX	1.89	0.349	9133	3976	0.356	9110	3726	23
					0.352	9160		25
TNT	1.64	0.176	6786	3799	0.181	6790	3501	23
					0.190	6912	3647	24
					0.177	6911	3692	26
					0.188	6910		25
NM	1.13	0.121	6182	3755	0.119	6110	3467	23
					0.121	6245	3515	24
					0.117	6120		25
HNS	1.69	0.198	7050	4300	0.205	7140		25
TATB	1.85	0.254	7955	3033	0.267	8053	2957	24
DATB	1.79	0.240	7748	3653	0.238	7624	3269	24
					0.237	7700		25
TETRYL	1.70	0.223	7476	4242	0.240	7607	4065	24
NQ	1.55	0.187	7384	2581	0.191	7453	2474	24
NG	1.60	0.230	7715	4927	0.217	7535	4445	24

Table 8: Computed CJ Pressure, Velocity and Temperature using Mader's parametrisation to the thermodynamic functions and the exact thermodynamic functions

CJ Pressure (Mbar)

Explosive	Density	Exact F	Exact F	Approx. F
	(g/cm³)	Exact H	Approx. H	Approx. H
RDX	1.8	0.310	0.312	0.311
	1.0	0.099	0.103	0.095
PETN	1.77	0.270	0.276	0.281
HMX	1.89	0.350	0.351	0.349
TNT	1.64	0.173	0.173	0.176
NM	1.13	0.117	0.117	0.121
HNS	1.5	0.145	0.148	0.156
TATB	1.85	0.257	0.256	0.254
DATB	1.79	0.241	0.241	0.240
TETRYL	1.70	0.217	0.219	0.223
NQ	1.55	0.189	0.189	0.187
NG	1.60	0.222	0.229	0.230

CJ Velocity (m/s)

Explosive	Density	Exact F	Exact F	Approx. F
	(g/cm³)	Exact H	Approx. H	Approx. H
RDX	1.8	8709	8763	8741
	1.0	5903	6017	6010
PETN	1.77	8106	8190	8220
HMX	1.89	9118	9159	9133
TNT	1.64	6745	6775	6786
NM	1.13	6044	6084	6182
HNS	1.5	6294	6363	6454
TATB	1.85	7983	7982	7955
DATB	1.79	7744	7765	7748
TETRYL	1.70	7403	7461	7476
NQ	1.55	7422	7420	7384
NG	1.60	7642	7731	7715

CJ Temperature (K)

Explosive	Density (g/cm^3)	Exact F Exact H	Exact F Approx. H	Approx. F Approx. H
RDX	1.8	4046	4167	4145
	1.0	4624	4836	4680
PETN	1.77	4432	4620	4615
HMX	1.89	3896	3990	3976
TNT	1.64	3779	3834	3799
NM	1.13	3739	3788	3755
HNS	1.5	4313	4452	4388
TATB	1.85	3045	3041	3033
DATB	1.79	3628	3672	3653
TETRYL	1.70	4153	4277	4242
NQ	1.55	2591	2589	2581
NG	1.60	4743	4962	4927

5.4 Application to PBXN-111

We now consider the CJ state of PBXN-111 using the JCZ3 equation of state. The intermolecular potential parameters (ie r_i and ε_i) used for the gas phase species are listed in Table 9. Values for these parameters are the same as those used by Cowperthwaite and Zwisler [19] with the exception of HCl and Cl_2. For these two molecules values of r_i and ε_i are not available, so the values shown in Table 9 were estimated. The estimation was based on the difference between the intermolecular parameters for the exponential-6 potential and a Lennard-Jones potential. Values of r_i and ε_i for the Lennard-Jones potential are available for a large number of species including HCl and Cl_2 [29]. The average difference in r_i and e_i between the exponential-6 and Lennard-Jones potentials for a number of molecules (H_2O, CO_2, N_2, CO, H_2, NO, O_2 and CH_4) was used to adjust the Lennard-Jones parameters of HCl and Cl_2 to obtain estimates of the exponential-6 parameters for these molecules. It should be noted that the NH_3 parameters shown in Table 9 are assumed to be the same as those for the isoelectronic molecule, H_2O. This assumption was used by Cowperthwaite and Zwisler [19], and it could influence the amount of NH_3 in the equilibrium composition. The Cowan-Fickett equation of state was used for the solid products.

Table 9: Intermolecular potential parameters.

Molecule	r_i (10^{-10}m)	ε_i (K)
H_2O	3.350	138.0
N_2	4.050	120.0
CO_2	4.200	200.0
CO	4.050	120.0
O_2	3.730	132.0
H_2	3.340	37.0
NH_3	3.350	138.0
NO	3.970	105.0
CH_4	4.290	154.0
HCl	3.385	370.6
Cl_2	4.495	367.6

The results of the performance calculations are summarised in Tables 10 and 11, along with the results obtained using the BKW equation of state, and the ICI IDEX code [14]. The IDEX code uses the THEOSTAR EOS [30], which is also based on an intermolecular potential. Table 10 shows that both equations of state based on intermolecular potentials provide a CJ state in better agreement with the experimental observations, while the parametrised BKW EOS overestimates both the CJ velocity and pressure significantly. There is good agreement between the detonation velocity calculated using the AMRL implementation of the JCZ3 EOS (6606 m/s) and the IDEX THEOSTAR EOS (6661 m/s), the difference between them being less than 1%, while the detonation pressures agree to within approximately 10% (0.201 Mbar for JCZ3, 0.222 Mbar for THEOSTAR). Clearly, there are significant differences in the composition (and temperature) calculated by each EOS, but there is no experimental data available to assess the accuracy of the different compositions.

Table 10: CJ parameters for PBXN-111 calculated with different equations of state.

Detonation Parameter	BKW	IDEX	AMRL
Pressure (Mbar)	0.294	0.222	0.201
Velocity (m/s)	8153	6661	6606
Temperature (K)	5229	5297	5864

While the agreement between the detonation velocity and pressure calculated from the two different equations of state based on intermolecular potentials is reasonable, there is still a significant difference from the experimentally determined values. Forbes et al. have reported the detonation pressure of PBXN-111 as 0.120 Mbar, with an infinite diameter detonation velocity of 6195 m/s [5], while Bocksteiner et al. have reported the infinite diameter detonation velocity of (Australian) PBXN-111 to be 5650 m/s. Comparison between calculated and measured detonation parameters for highly non-ideal explosives requires considerable care however. The calculated detonation velocities should be compared with experimental values determined on cylindrical charges having infinite diameter. In practice, the experiments have been carried out on charges having diameters no greater than twice their respective failure diameters. The infinite diameter results have then been found by extrapolation using either a liner [5] or elliptic [8] fitting procedure. This is a relatively small diameter range for non-ideal explosives such as PBXN-111 however, and experience with commercial composite explosives has shown that diameters up to twenty times the failure diameter need to be used before reliable estimates of the infinite diameter detonation velocity can be made [31].

Table 11: CJ composition (moles per 100 g of explosive) for PBXN-111 calculated with different equations of state.

Product	BKW	IDEX	JCZ3
H_2O	0.6121	0.2681	0.3620
H_2	0.6787	0.2775	0.0432
CH_4	0.0877	0.1556	0.0298
CO_2	0.0019	0.0067	0.0883
CO	0.0455	0.3436	0.1227
N_2	0.4239	0.2197	0.1055
NH_3	0.0633	0.4661	0.7000
NO	-	0.0009	-
O_2	0.0000	0.0000	0.0001
HCl	0.2839	0.2591	0.3650
Cl_2	0.0411	0.0534	0.0005
C(graphite)	0.9478	0.0000	0.8393
C(diamond)	-	0.6338	-
Al_2O_3	0.4635	0.4632	0.4635

The detonation pressure reported by Forbes is based on measurements of the underwater shock velocity obtained from a standard aquarium test conducted on PBXN-111 [32]. The pressure is then calculated from the velocity measurement using a procedure which was derived for explosives having ideal detonation behaviour. Forbes notes that this procedure is questionable, and may result in errors of up to 30% in the reported detonation pressure. Kennedy and Jones [14], and more recently Kennedy [33], have discussed the behaviour of non-ideal explosives such as PBXN-111 in more detail, and have shown that the concept of a unique "detonation pressure" (or C-J pressure) has little significance for such explosives.

The detonation parameters for PBXN-111 recorded in Table 10 were calculated using the method of steepest descent algorithm. Use of the probabalistic algorithm would have required considerably more computational time, and in view of the results obtained in Section 4, and the accuracy of some of the potential parameters used in the calculation, this was considered to be unnecessary.

6. Discussion and Conclusion

This report has described the development and application of a chemical equilibrium computer code to calculate the detonation parameters of condensed phase explosives. The code is based on the Chapman-Jouguet theory of detonation, incorporates two different equations of state to describe the detonation products, and offers a choice of two different algorithms to minimize the free energy of the product composition.

Using the BKW EOS and either the method of steepest descent or the probabalistic algorithm to minimise the free energy the code accurately reproduces the detonation parameters of ideal CHNO explosives. The method of steepest descent is inherently faster, but is not guaranteed to find the global minimum. The probabalistic algorithm is considerably slower but has the advantage of not requiring an initial estimate of the equilibrium composition, and is guaranteed to find the global minimum. Either minimization method can be used, depending on the particular application, and the amount of computer time available.

As well as BKW the code also employs the JCZ3 equation of state. BKW contains four adjustable parameters, and these have been optimized to provide good agreement with detonation parameters for ideal CHNO explosives. JCZ3 is based on an intermolecular potential and contains no adjustable parameters, other than the well depth and equilibrium bond distance for each interaction. JCZ3 was found to be considerably better than BKW in predicting the detonation parameters of the underwater explosive PBXN-111, and we expect that in general JCZ3 will be the more appropriate equation of state to use for highly non-ideal explosives.

The results obtained here show that considerable care should be exercised when attempting to use the code to calculate detonation parameters for a particular explosive. The code is based on the Chapman-Jouguet theory of detonations, and as such is only applicable to explosives which behave ideally. When used to model explosives which behave non-ideally the predicted detonation velocity and pressure require careful interpretation.

7. Acknowledgements

We thank Michael Cowperthwaite for very helpful correspondence, and for running his TIGER code for us. We also thank Jerry Forbes for communicating his experimental results on PBXN-111, and David Kennedy for many useful discussions on the behaviour of non-ideal explosives. We are also grateful to Dan Whelan and Gunter Bocksteiner for many stimulating discussions on PBXN-111.

8. References

1. C.L. Mader (1979) Numerical Modeling of Detonations. University of California Press.

2. R. Cheret (1993) Detonation of Condensed Explosives, Springer-Verlag, New York, Inc.

3. C.L. Mader (1967) FORTRAN BKW: A Code for Computing the Detonation Properties of Explosives, Los Alamos Scientific Laboratory Report LA-3704.

4. G.J. Jenks, J. J. Masinskas and D.A. Price (1983) Detonation Parameters for Australian High-Explosives Composition, DSTO Technical Report MRL-R-882.

5. J.W. Forbes, E.R. Lemar and R.N. Baker (1989) "Detonation Wave Propagation in PBXW-115". Ninth Symposium (International) on Detonation, Office of the Chief of Naval Research, OCNR 113291-7, pp. 806-815.

6. J.W. Forbes, E.R. Lemar, G.T. Sutherland and R.N. Baker (1992) "Detonation Wave Curvature, Corner Turning and Unreacted Hugoniot of PBXN-111", Naval Surface Warfare Center (Maryland) Technical Report, NSWC -TR-92-164.

7. G. Bocksteiner and D.J. Whelan (1993) A Comparison of the Explosive Properties and Performance of Underwater Explosives, PBXW-115 (Aust.), PBXW-115(USA) / PBXN-111, Composition H6 and Torpex 4D/TF, Materials Research Laboratory (Melbourne) Technical Report, MRL TR-93-45 (Restricted).

8. G. Bocksteiner, M.G. Wolfson and D. Whelan (1994) The Critical Diameter, Detonation Velocity and Shock Sensitivity of Australian PBXW-115, DSTO Technical Report DSTO)-TR-94-76.

9. G. Bocksteiner, M.G. Wolfson and D.J. Whelan, The Velocity of Detonation of Confined and Unconfined Charges of Australian-made PBXW-115, DSTO Technical Report, in preparation.

10. J.N. Johnson, C.L. Mader and S. Goldstein (1983) Performance Properties of Commercial Explosives. Propellants, Explosives, Pyrotechnics **8**, 8-18.

11. D.A. Jones and D.L. Kennedy (1991) Application of the CPEX Non-Ideal Explosive Model to PBXW-115. MRL Technical Report, MRL-TR-91-40.

12. I.J. Kirby and G.A. Leiper (1985) "A small divergent detonation theory for intermolecular explosives", Proceedings of the Eigth Symposium (International) on Detonation, Albuquerque, pp. 176-185.

13. D.L. Kennedy, personal communication, 1993.

14. D.L. Kennedy and D.A. Jones (1993) "Modelling Shock Initiation and Detonation in the Non-Ideal Explosive PBXW-115" Proceedings of the Tenth International Detonation Symposium, Office of Naval Research, ONR 38395-12, pp. 665-674.

15. G.B. Kistiakowsky and E.B. Wilson (1941) "The Hydrodynamic Theory of Detonation and Shock Waves", Office of Scientific Research and Development Report OSRD-114.

16. R.D. Cowan and W. Fickett (1956) "Calculation of the Detonation Products of Solid Explosives with the Kistiakowsky-Wilson Equation of State", J. Chem. Phys. **24**, 932.

17. W.B. White, S.M. Johnson and G.B. Dantzig (1958) "Chemical Equilibrium in Complex Mixtures". J. Chem. Phys. **28**, 751.

18. K.K. Benke and D.R. Skinner (1991) "A direct search algorithm for global optimisation of multivariate functions". Aust. Comp. J. **23**, 73.

19. M. Cowperthwaite and W.H. Zwisler (1976) "The JCZ Equations of State for Detonation Products and their Incorporation into the TIGER Code", Sixth Symposium (International) on Detonation, White Oak, MD, Office of Naval Research ACR-221, pp. 162-172.

20. W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling (1989) Numerical Recipes (FORTRAN Version). Cambridge University Press.

21. M. Suceska (1991) "Calculation of the Detonation Properties of C-H-N-O Explosives", Propellants, Explosives, Pyrotechnics **16**, 197.

22. M.L. Hobbs and M.R. Baer (1992) "Nonideal Thermoequilibrium Calculations Using a Large Product Species Data Base". Shock Waves **2**, 177.

23. M. Finger, E. Lee, F.H. Helm, B. Hayes, H. Hornig, R. McGuire, M. Kahara and M. Guidry (1976) " The Effect of Elemental Composition on the Detonation Behaviour of Explosives". Sixth Symposium (International) on Detonation, White Oak, MD, Office of Naval Research, ACR 221, pp. 710-722.

24. K.K. Feng, W.K. Chung and B.C.-Y. Lu (1985) "Calculation of Detonation Products by means of the CS Hard-Sphere Equation of State", Proceedings of the Eigth Symposium (International) on Detonation, Albuquerque, NSWC MP 86-194, pp. 805-813.

25. D.R. Hardesty and J.E. Kennedy (1977) "Thermochemical Estimation of Explosive Energy Output", Combustion and Flame, **28**, 45-59.

26. L.H. Sentman, R.A. Strehlow, B. Haeffele and A. Eckstein (1981) "Development of a Single Species Equation of State for Detonation Products suitable for Hydrocode Calculations", Proceedings of the Seventh Symposium (International) on Detonation, Annapolis, MD, NSWC MP 82-334, pp. 721-732.

27. M. Cowperthwaite, (1993) Personal communication.

28. R. Chirat and G. Pittion-Rossillon (1974) "Detonation Properties of Condensed Explosives calculated with an Equation of State based on Intermolecular Potentials", UCRL-51319.

29. P.W. Atkins (1982) "Physical Chemistry", 2nd Edition, Oxford University Press.

30. M. Braithwaite, T. Farran, I. Gladwell, P.M. Lynch, A. Minchinton, I.B. Parker and R.M. Thomas (1990) "A detonation problem posed as a differential/algebraic boundary value problem", Math. Engng. Ind., **3**, No. 1, pp. 25-57.

31. D.L. Kennedy, personal communication, 1993.

32. J.W. Forbes, personal communication, May, 1991.

33. D.L. Kennedy, (1995) "The Challenges of Non-Ideal Detonation", Journal de Physique IV, Colloque C4, Supplement au Journal de Physique III, Vol. 5, Mai 1995, pp. C4-191 to C4-207.

This page intentionally left blank

9. Appendix: Running SDA.FOR and PEA.FOR

This appendix describes the actual usage of the two new programs for computing CJ properties of explosives, SDA.FOR and PEA.FOR. Firstly the input file for these codes will be described followed by a description of the output that each of the codes produces. The final section will reveal a number of useful hints for achieving successful results from these codes.

INPUT DESCRIPTION

Since the input files for SDA.FOR and PEA.FOR are virtually identical we will only describe the file once with a clear indication of the minor differences where applicable. The input file is mostly free format and Table 12 describes each line of input in detail.

There are two differences in this input for the SDA and PEA programs. In card 8 and card 15 an initial estimate of the number of moles of each product is entered. Both SDA and PEA read in this input but only the SDA program actually uses it. The PEA program ignores initial guesses. The second difference occurs in card 17. Only the PEA program requires this input card, the SDA program does not read in the nlim value.

OUTPUT DESCRIPTION

Table 13 shows a sample of the output from a run of the SDA.FOR program. The output of the PEA.FOR program is identical. The output below represents the last three cycles in the calculation of the detonation parameters of pure RDX at a loading density of 1.8 g/cm^3. Each cycle represents a further refinement of P and T as described earlier in the four step iterative process for determining the CJ point (see just below equation 28). The output at each cycle prints the current value of the temperature and pressure followed by a list of each product, the current number of moles of that product and the amount each product was changed by during the last step of the equilibrium composition determination. The last line of output of each cycle reprints the pressure and a value called fvp. The fvp value is a measure of how close equation 28 actually is to being zero. When fvp falls below a specified tolerance then equation 28 is deemed to be satisfied and the program will terminate. Prior to terminating, the program calculates the detonation velocity and finally prints out the detonation temperature, pressure and velocity as shown at the very bottom of the sample output.

RUNNING HINTS

There are a number of points that should be kept in mind when using the SDA.FOR and the PEA.FOR programs. Experience has shown that under certain circumstances the program(s) will fail to give a successful result unless these points are carefully considered when preparing the input file. In most cases when the program fails to produce a result, the output it does produce usually indicates the nature of the problem and the following hints describe the approach that has proved successful in overcoming the original problem.

1) The fvp value is diverging away from zero.
Under certain circumstances the program will adjust P in such a way that the fvp value does not tend to zero as it should. This usually happens if the initial guess of the detonation pressure is very poor and the problem seems to be worse for explosives with a low loading density. The remedy is simple, restart the calculation with a different estimate of the detonation pressure.

2) Solid products with a large free energy.
If any of the solid products has a large free energy then the equilibrium composition of that product will tend towards zero. If the equilibrium composition of a solid product becomes zero the calculation will fail. This will be evident as the program will print the word "solid" followed by a number which indicates which solid is causing the trouble. This is followed by a message which reads "rlam = 0". If this occurs the only solution is to remove that solid from the product list and restart the calculation. In general it may be prudent to start a calculation with no solid products and then add each solid product one at a time to see if any of the solid products is going to cause a problem.

3) Initial guess of equilibrium composition.
This is only relevant for the SDA.FOR program since the PEA.FOR program does not require an initial estimate of the equilibrium composition. In general it is best to assume that, for CHNO explosives, the major detonation products will be H_2O, CO_2, CO and N_2. The initial guess of the equilibrium composition should then comprise appropriate amounts of these products. Thus all of the H in the explosive formulation will become H_2O, all of the N will become N_2 and the amounts of CO and CO_2 will be determined by the oxygen balance of the explosive formulation. If the explosive is particularly oxygen deficient then more CO will be required to maintain mass balance. Other gaseous products can still be included in the list of possible products and can be given a very small initial value for y(i). Solid products can also be included with a small initial value of y(i). It is not necessary to have an initial guess that satisfies mass balance although it is suggested that the initial guess should not be too far away from mass balance to avoid potential problems in the determination of the correct equilibrium composition.

Table 12:

Line	Variable Name(s)	Type	Format	Description
1	nelem	integer	free	number of unique elements in explosive formulation
2	react(i)	real	free	for each element in the explosive formulation this array holds the amount of that element present
3	hfe,rmme, dens	real	free	hfe is the explosive formulation heat of formation at 0K in cal/formula weight, rmme is the formula weight of the explosive and dens is the density of the explosive.
4	ngprod	integer	free	number of gaseous detonation products
5	gases(i)	string	a5	label description for gaseous product
6	prodg(i,j), j=1 to nelem	real	free	specifies amount of each element in this gaseous product
7	ag(i),bg(i), cg(i),dg(i), eg(i),ricg(i), hf(i)	real	free	ag,bg,cg,dg,eg and ricg are the constants used in equation 8 and hf is the heat of formation of the gaseous product at 0 K.
8	y(i),rk(i)	real;	free	y is the initial guess of the number of moles of the gaseous product and rk is the co-volume of the gaseous product (see equations 2 and 3)
Cards 5 to 8 are repeated for each gas species (ie ngprod times)				
9	nsprod	integer	free	number of solid detonation products
10	solids(i)	string	a5	label description for solid product
11	prods(i,j), j=1 to nelem	real	free	specifies amount of each element in this solid product
12	as(i).bs(i), cs(i),ds(i), es(i)	real	free	these are the Cowan solid equation of state parameters (see for example equation 10)
13	a1s(i),a2s(i),c1s(i) ,c2s(i),c3s(i)	real	free	these are the remaining Cowan solid equation of state parameters
14	ase(i),bse(i),cse(i) ,dse(i),ese(i),rics(i),hfs(i)	real	free	ase,bse,cse,dse,ese and rics are the solid product equivalent of the constants used in equation 8 and hfs is the heat of formation of the solid product at 0 K.
15	ys(i),rmm(i),vo(i)	real	free	y is the initial guess of the number of moles of the solid product, rmm is the molecular mass of the solid product and vo is the initial volume (in cm^3/g).
Cards 10 to 15 are repeated for each solid species (ie nsprod times)				
16	press,temp	real	free	starting values for the pressure and temperature
17	nlim	real	free	number of guesses used in the probabilistic algorithm, this input is only required for the PEA.FOR program.

Table 13:

Tcj=	2587.792968750000	Pcj=	0.3451171875000000
H2O	2.998805060393444		2.0324615110367539E-08
CO2	1.489432550814017		1.6185742568453065E-07
N2	2.999984618027165		2.9389973510429712E-10
H2	1.1487936880493267E-03		-1.9442915771799424E-08
CO	2.2324121316814211E-02		-3.4390013300231604E-07
NH3	3.0763945670919224E-05		-5.8779959834121635E-10
O2	2.8583308535342730E-06		-6.9666778548661276E-11
SOLC	1.488243327869169		1.8204270731819738E-07
p	0.3451171875000000	fvp	2.9294807983619442E-04
Tcj=	2587.792968750000	Pcj=	0.3450976562500000
H2O	2.998804735844558		2.0336275741161813E-08
CO2	1.489430558980391		1.6193195202102162E-07
N2	2.999984612673078		2.9410318902467480E-10
H2	1.1491021746754503E-03		-1.9453966329874089E-08
CO	2.2328430423178673E-02		-3.4406089971365274E-07
NH3	3.0774653844636130E-05		-5.8820624758797982E-10
O2	2.8578857408429585E-06		-6.9639988203416170E-11
SOLC	1.488241010596430		1.8212894770663901E-07
p	0.3450976562500000	fvp	2.8134827164343762E-04
Tcj=	2587.792968750000	Pcj=	0.3450878906250000
H2O	2.998804573543107		2.0444491077853400E-08
CO2	1.489429562965963		1.6268356730908540E-07
N2	2.999984609995493		2.9605989049219516E-10
H2	1.1492564433704240E-03		-1.9556311564429096E-08
CO	2.2330585198497803E-02		-3.4567291897485020E-07
NH3	3.0780009014973331E-05		-5.9211970592613272E-10
O2	2.8576632343753382E-06		-6.9353458803125902E-11
SOLC	1.488239851835539		1.8298935164640096E-07
p	0.3450878906250000	fvp	1.2516557871852102E-04
Tcj=	2587.792968750000 K	Pcj=	0.3450781250000000 Mbar
Dcj=	8711.452096205158 m/s		

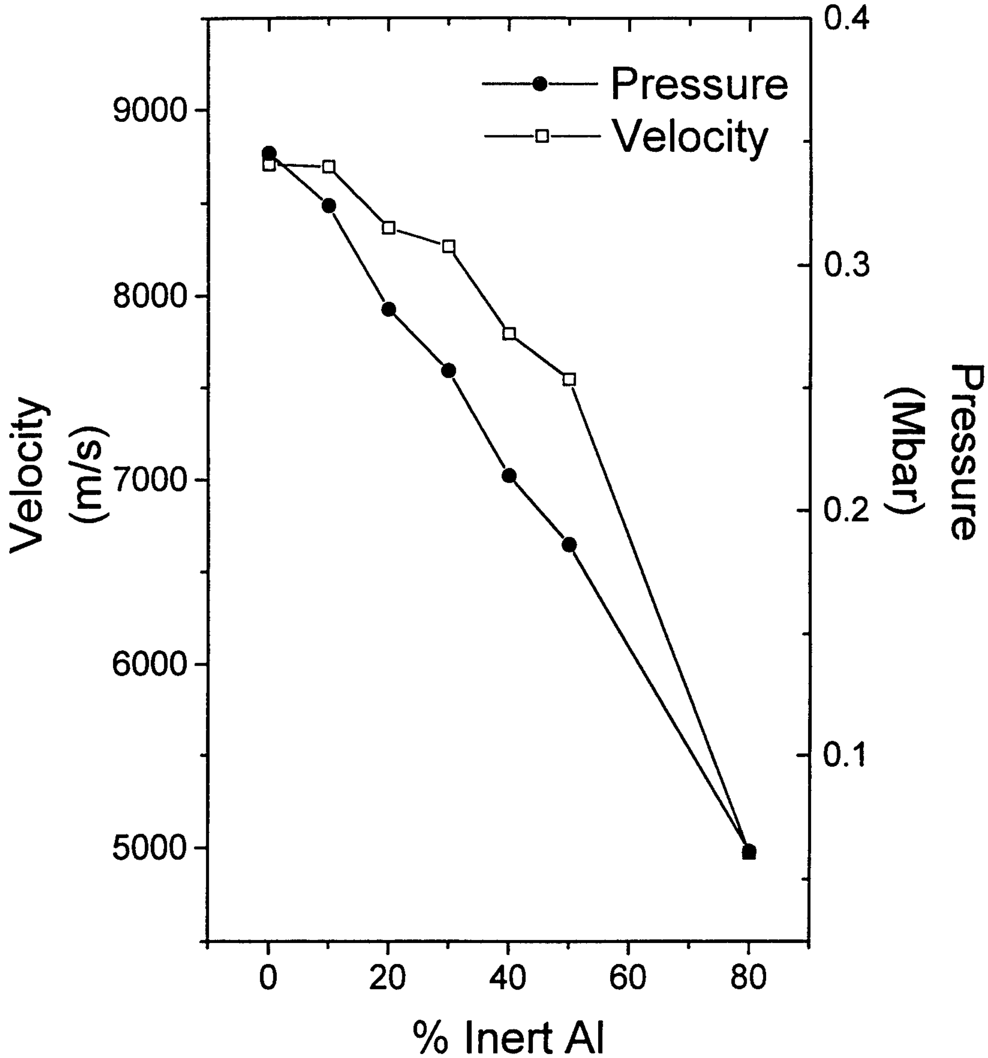


Figure 1: Influence of an inert diluent (aluminium) on the calculated performance of RDX.

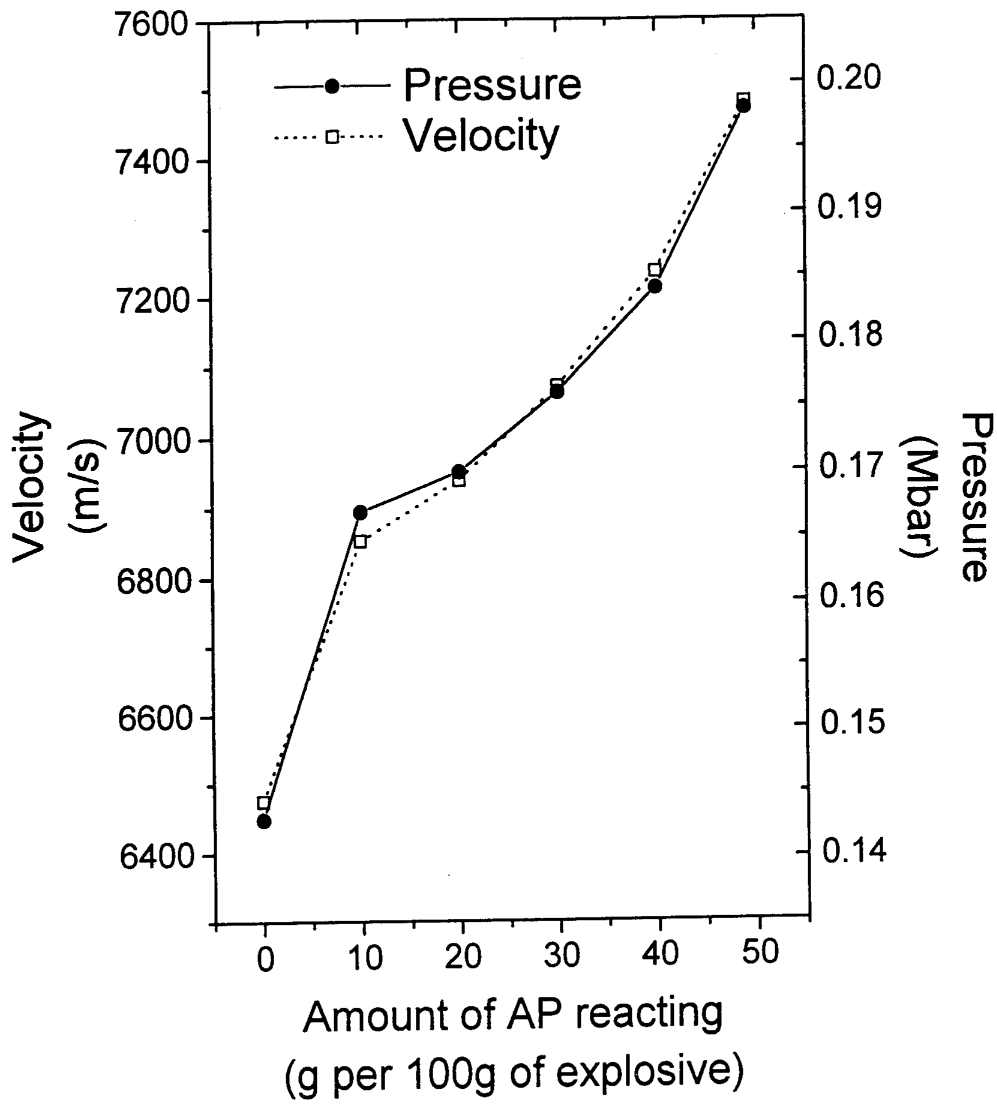


Figure 2: Effect of extent of reaction of ammonium perchlorate (AP) on the calculated performance of PBXN-111.

Chemical Equilibrium Calculations for Detonation Products

Rodney A.J. Borg, Gary Kemister and David A. Jones

(DSTO-TR-0226)

DISTRIBUTION LIST

DEFENCE ORGANISATION

Defence Science and Technology Organisation

Chief Defence Scientist
FAS Science Policy
AS Science Corporate Management } shared copy
Counsellor Defence Science, London (Doc Data Sheet only)
Counsellor Defence Science, Washington (Doc Data Sheet only)
Scientific Adviser to Thailand MRD (Doc Data Sheet Only)
Scientific Adviser to the DRC (Kuala Lumpur) (Doc Data Sheet Only)
Senior Defence Scientific Adviser/Scientific Adviser Policy and Command (shared copy)
Navy Scientific Adviser
Scientific Adviser - Army (Doc Data Sheet only)
Air Force Scientific Adviser
Director Trials

Aeronautical and Maritime Research Laboratory

Director
Chief. Weapons Systems Division
Dr B.W. Thorpe
Dr D. Whelan
Dr R.A.J. Borg
Dr G. Kemister
Dr D.A. Jones
Dr G.J. Jenks
Mr D.V. Ritzel
Dr K.K. Benke

DSTO Library

Library Fishermens Bend
Library Maribyrnong
Main Library DSTOS (2 copies)
Library, MOD, Pyrmont (doc data sheet only)

Defence Central

OIC TRS, Defence Central Library
Officer in Charge, Document Exchange Centre, 1 copy
DEC requires, as permitted by the release limitations, the following copies to meet exchange agreements under their management:
*US Defence Technical Information Centre, 2 copies
*UK Defence Research Information Centre, 2 copies
*Canada Defence Scientific Information Service, 1 copy
*NZ Defence Information Centre, 1 copy
National Library of Australia, 1 copy
The Director, Qinghua University, Beijing, 1 copy
The Librarian, Beijing University of Aeronautics, 1 copy
The Librarian, Institute of Mechanics, Chinese Academy of Sciences, 1 copy

DISTRIBUTION LIST
(Continued)

(DSTO-TR-0226)

Defence Intelligence Organisation
Library, Defence Signals Directorate (Doc Data Sheet only)

Army

Director General Force Development (Land) (doc data sheet only)
ABCA Office, G-1-34, Russell Offices, Canberra (4 copies)

Navy

ASSTASS, APW2-1-OA2, Anzac Park West, Canberra

UNIVERSITIES AND COLLEGES

Australian Defence Force Academy
Library
Head of Aerospace and Mechanical Engineering
Deakin University, Serials Section (M list)), Deakin University Library, Geelong, 3217,
Senior Librarian, Hargrave Library, Monash University

OTHER ORGANISATIONS

NASA (Canberra
AGPS

ABSTRACTING AND INFORMATION ORGANISATIONS

INSPEC: Acquisitions Section Institution of Electrical Engineers
Library, Chemical Abstracts Reference Service
Engineering Societies Library, US
American Society for Metals
Documents Librarian, The Center for Research Libraries, US

INFORMATION EXCHANGE AGREEMENT PARTNERS

Acquisitions Unit, Science Reference and Information Service, UK
Library - Exchange Desk, National Institute of Standards and Technology, US

ADDITIONAL DISTRIBUTION

Dr Jerry Forbes, NSWC, White Oak, MD
Dr David Kennedy, ICI Australia, NSW
Dr Michael Cowperthwaite, SRI, CA
Dr Elaine Oran, NRL, Washington, DC
Dr Paul Thibault, Combustion Dynamics Ltd.
Dr Craig Tarver, Lawrence Livermore National Laboratory

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION DOCUMENT CONTROL DATA	1. PAGE CLASSIFICATION UNCLASSIFIED 2. PRIVACY MARKING/CAVEAT (OF DOCUMENT)

3. TITLE	4. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION)
Chemical equilibrium calculations for detonation products	Document (U) Title (U) Abstract (U)
5. AUTHOR(S)	6. CORPORATE AUTHOR
Rodney A.J. Borg, Gary Kemister and David A. Jones	Aeronautical and Maritime Research Laboratory PO Box 4331 Melbourne Vic 3001

7a. DSTO NUMBER	7b. AR NUMBER	7c. TYPE OF REPORT	8. DOCUMENT DATE
DSTO-TR-0226	AR-009-359	Technical Report	October 1995

9. FILE NUMBER	10. TASK NUMBER	11. TASK SPONSOR	12. NO. OF PAGES	13. NO. OF REFERENCES
510/207/0310	NAV 91/173	DARMENG	48	33

14. DOWNGRADING/DELIMITING INSTRUCTIONS	15. RELEASE AUTHORITY
	Chief, Weapons Systems Division

16. SECONDARY RELEASE STATEMENT OF THIS DOCUMENT

Approved for public release

OVERSEAS ENQUIRIES OUTSIDE STATED LIMITATIONS SHOULD BE REFERRED THROUGH DOCUMENT EXCHANGE CENTRE, DIS NETWORK OFFICE, DEPT OF DEFENCE, CAMPBELL PARK OFFICES, CANBERRA ACT 2600

17. DELIBERATE ANNOUNCEMENT

Announcement of this report is unlimited

18. CASUAL ANNOUNCEMENT YES/NO (Cross out whichever is not applicable)

19. DEFTEST DESCRIPTORS

Detonation; Chemical equilibrium; Explosives; Computer program design; Chemical reactions; RDX; TNT

20. ABSTRACT

We present a detailed description of the development, implementation, and application of a computer program to calculate the detonation parameters of condensed phase explosives. The code is based on Mader's BKW chemical equilibrium code, but contains important new features. A new algorithm to calculate the minimum in the free energy of the product composition has been included. This is a probabilistic algorithm, based on the method of Benke and Skinner, and its inclusion ensures that the true global minimum in the free energy will always be found. As well as the BKW equation of state to describe the detonation products, the new code also includes the JCZ3 equation of state. This is an intermolecular equation of state containing no adjustable parameters, and hence should be applicable to a wider range of explosives than could be considered using the BKW code. We have validated the code on a wide range of military explosives, using both the new probabilistic minimisation algorithm as well as the original method of steepest descent, for both the BKW and JCZ3 equations of state. We also present a detailed description of the application of the code to the non-ideal underwater explosive PBXN-111, and show that the performance of the explosive is best described using the JCZ3 equation of state.