# Computer Code to Predict the Heat of Explosion of Non-ideal Aluminized Explosives

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## 1 Introduction

Since aluminum increases energy and raises reaction temperature of explosion, it is common ingredient in explosives. Heat of explosion is the quantity of heat released when high energy material undergoes detonation as an explosive (e.g., RDX, HMX, TNT, etc.,) or deflagration (burning)as a propellant (e.g., a rocket propellant)[1]. It is one of the most important thermodynamic parameters of aluminized explosives.

Extensive publications [2-5] are available in the literature on theoretical calculations to predict detonation behaviors of ideal explosives and detonation velocity and pressure of aluminized explosives. However, there is a general lack of information on predicating the heat of explosion for non-ideal aluminized explosives in the literatures.

Mohammad introduced a new pathway to predict detonation pressure of CHNO and CHNOAl explosives through molecular structure [6] and a simple method for prediction of detonation velocity of ideal and non-ideal explosives [7]. Keshavarz proposed an empirical formula for predicting detonation pressure and velocity of aluminized explosives [8-9].Eight adjustable parameters in the formula [8-9] need to be determined by experience. These adjustable parameters do not reflect the physical behavior of the aluminized explosives yet. Muthurajan et al. presented the computational approach to predict the heat of explosion of high energy materials which do not contain aluminum powder [10].

The Chapman-Jouguet detonation velocity and pressure predicted from existing thermodynamic computer codes were reported in the references [11-15]. The reported data showed that the Chapman-Jouguet detonation parameters of non-ideal explosives calculated from existing thermodynamic computer codes were significantly different from experimental results. Some investigators assumed that non-equilibrium effects in reaction zones may contribute to this confusion, and measured pressures may be higher than equilibrium calculations if the measurement is taken behind the von Neumann spike and in front of the C–J plane. In fact, aluminum powder needs to be excited for several $\mu$s before chemical reaction occurs. Therefore, it is impossible that aluminum powder participates in chemical reaction in reaction zones from high energy ingredients.

The main purpose of the present work is to develop a new approach to predicat the heat of explosion, based on the revised equation of state and thermodynamic detonation theory.

## 2 Computational approach

The two significant improvements in numerical calculations to predicate the behaviors of explosion of non-ideal aluminized explosives were completed in this work. One is that the chemical reaction between aluminum powder and C-J detonation product of high energy ingredients determined. Another is that the equation of state for detonation product of high energy ingredients was revised.

### 2.1 Revised equation of state for detonation products

Like some other reports [16], in this present work, one of parameters, k, in BKW equation of state was adjusted slightly. This is because aluminum particles as an inert material in reaction zones mean increase of solid products of C-J reaction. The value of k depends on the fractions of solid products in C-J reaction and it should be adjusted when the fractions of solid products in C-J reaction increase. The original value of k for the RDX type explosives in BKW equations of state was 10.91 and was adjusted into 9.2725 in this work by a series of trial calculation. The original value of k for

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the TNT type explosives in BKW equations of state was 12.685 and was adjusted into10.4017. Revised parameters in BKW equations of state are listed Table 1.

Table 1 Revised parameters in BKW equations of state

| *Parameters* | $\alpha$ | $\beta$ | $K$ | $\theta$ |
|---|---|---|---|---|
| RDX type aluminized explosives | 0.5 | 0.16 | 9.2735 | 400 |
| TNT type aluminized explosives | 0.5 | 0.09585 | 10.4017 | 400 |

2.2 Determination of chemical reaction of aluminum

The chemical reactions of aluminum and detonation products of high energy ingredients have three reaction channels:

$Al+1.125CO_2$——$0.5Al_2O_3+0.75CO+0.375C$ （Reaction 1） (1)

$Al+1.5CO$——$0.5Al_2O_3+1.5C$ （Reaction 2） (2)

$Al+1.5H2O$——$0.5Al_2O_3+1.5H_2$ （Reaction 3） (3)

The correlation between specific heat and temperature can be given as follows:

$$Cp(T) = a + bT + cT^2$$

Where Cp(T) is the specific heat of ingredient i in a chemical reaction; T is the instantaneous temperature; a, b and c are the constants which can be determined by experimental data fitting.

For a chemical reaction, the change of specific heats from reactants to products is

$$\Delta Cp = \sum v_i Cp(t) = \Delta a + \Delta bT + \Delta cT^2 \qquad (4)$$

Where $\Delta Cp$ is difference between the specific heats of products and those of reactants for a chemical reaction; $v_i$ is the number of mol for ingredient i which is positive for the products and is negative for the reactants;

$\Delta a = \sum v_i a\,; \Delta b = \sum v_i b\,; \Delta c = \sum v_i c\,. \Delta a = \sum v_i a_i\,; \Delta b = \sum v_i b_i\,; \Delta c = \sum v_i c_i\,.$

Relationship between with $\Delta H$ and $\Delta Cp$ is

$$\Delta H(T) = \int \Delta Cp(T) dT \qquad (5)$$

From Eqs.(4) and (5),there is

$$\Delta H(T) = \Delta H_0 + \Delta aT + \frac{1}{2}\Delta bT^2 + \frac{1}{3}\Delta cT^3 \qquad (6)$$

Where $T_0$ is the initial temperature; $\Delta H_0$ is the change of enthalpy under initial temperature $T_0$.

$$\Delta H_0 = -(\Delta aT_0 + \Delta bT_0^2 + \Delta cT_0^3) \qquad (7)$$

The van' t hoff equation is

$$\frac{d\ln K}{dT} = \frac{\Delta H\ (T)}{RT^2} \qquad (8)$$

From the van’t hoff equation, there is

$$\int d\ln K = \int \frac{\Delta H\ (T)}{RT^2} dT \qquad (9)$$

Where K is the balance constant for a chemical reaction; $\Delta H(T)$ is the change of enthalpy in a chemical reaction which is a function of instantaneous temperature T.

From Eqs.(6) ,(7) and (9), there is

$$\ln K(T) = -\frac{\Delta H_0}{RT} + \frac{\Delta a}{R}\ln T + \frac{1}{2R}\Delta bT + \frac{1}{6R}\Delta cT^2 + I \qquad (10)$$

where I is the integral constant which can be determined by $K$ at normal temperature.

The data for change of specific heats with temperature can be found in the reported literatures. The correlation between balance constant and instantaneous (current) temperature for the three chemical reactions can be obtained through data fitting, as shown in Table 2.

Table 2 Correlation between balance coinstant and temperature

| Reaction formula | Temperature range | Correlation between K and T |
|---|---|---|
| Al+1.125$CO_2$——0.5$Al_2O_3$+0.75CO+0.375C | 298K-2400K | $\ln K_p = 25.0764/T - 3.6790e-004\ln T + 0.1889$ |
| | 2400K-2800K | $\ln K_p = 20.3359/T + 8.1444e-004\ln T + 0.1900$ |
| | 2800K 以上 | $\ln K_p = 60.1298/T + 0.0027\ln T + 0.1727$ |
| Al+1.5CO——0.5$Al_2O_3$+1.5C | 298K-2400K | $\ln K_p = -48.0051/T + 8.3774e-004\ln T + 0.2840$ |
| | 2400K-2800K | $\ln K_p = -52.7457/T + 0.0020\ln T + 0.2851$ |
| | 2800K 以上 | $\ln K_p = -12.9517/T + 0.0039\ln T + 0.2677$ |
| Al+1.5$H_2O$——0.5$Al_2O_3$+1.5$H_2$ | 298K-2400K | $\ln K_p = 57.4704/T + 9.2795e-004\ln T + 0.1649$ |
| | 2400K-2800K | $\ln K_p = 52.7298/T + 0.0021\ln T + 0.1660$ |
| | 2800K 以上 | $\ln K_p = 92.5238/T + 0.0040\ln T + 0.1486$ |

The calculation results of the balance constants for the three chemical reactions showed that the balance constant for the reaction of aluminum and $H_2O$ is highest, that for the reaction of aluminum and CO2 is medium and that for the reaction of aluminum and CO is lowest.

Based on the detonation products calculated for the reaction zone of high energy ingredients, the initial ingredients for the three chemical reactions of aluminum and detonation products of high energy ingredients are given. Suppose that x is the number of mol of CO2 in the reactants of reaction 1, y is that of C in the products for reaction 2 and z is that of H2 in the products for reaction 3. The numbers of mol of the initial ingredients in the three chemical reactions and those at the balance state can be confirmed through calculation, as shown in Table 3.

Table 3 Ingredients of the three reactions

| *Ingredients* | *Al* | *$CO_2$* | *CO* | *C* | *$H_2O$* | *$H_2$* |
|---|---|---|---|---|---|---|
| Initial state | a | b | c | d | e | f |
| Balance state | a-1/1.125x-2/3y-2/3z | b-x | c+0.75/1.125x-y | d+0.375/1.125x+y | e-z | f+z |

Based on the definition of balance constants there is

$$K^{\Theta} = \Pi\left(\frac{p_B}{P^{\Theta}}\right)^{\nu_B} = \Pi\left(\frac{n_B}{\sum n_B}\times\frac{p}{P^{\Theta}}\right)^{\nu_B} = \left(\frac{p/p^{\Theta}}{\sum n_B}\right)^{\sum \nu_B}\Pi {n_B}^{\nu_B} \qquad (11)$$

Where $K^{\Theta}$ is the balance constant; $p$ is the full pressure of gas products; $p_i$ is the fractional pressure of species I; $p_i = p(\frac{n_i}{\sum n_i})$ ; $p^{\Theta}$ is the standard atmosphere ($10^5$Pa); $\sum \nu_i$ is the summation of numbers of mol of reactants in every reaction equation; $\nu_i > 0$ for products and $\nu_i < 0$ for reactants. For example, reaction 3 (Eq.(3 )), $\sum \nu_i$ =1.5+0.5-1-1.5= -1.

$\sum n_B$ is the summation of numbers of mol of all gas products including reactions 1,2 and 3, which can be expressed by x, y and z.. $K_1^{\Theta}, K_2^{\Theta}, K_3^{\Theta}$ and $p/p^{\Theta}$ are known. Therefore, three non linear equations including x, y, and z can be obtained. Through numerical calculation of the three nonlinear equations, the values of x, y and z can be found. Take the calculated values of x, y, and z into formulae in table 3, the final ingredients in products can be obtained.

After the mol number of every ingredient in reactions between aluminum and detonation products from high energy ingredients the heat produced by reactions between aluminum and detonation products from high energy ingredients can be calculated by use of following equation:

$$Q = -[H(T_p) - H(T_{CJ})] = \int_{T_{CJ}}^{T_p} \sum \mathrm{n}_i Cp_i(t)dt \qquad (12)$$

where $H(T_{CJ})$ is the summation of enthalpy of every ingredients at the CJ temperature.

$$H(T_{CJ}) = \sum n_i H_i(T_{CJ}) \qquad (13)$$

Where $n_i$ is the mol number of ingredient i; $H_i(T_{CJ})$ is the enthalpy of ingredient *i* at the CJ temperature; $T_p$ is the parameter to be found. By use of iteration method, the solution of Eq.(7) can obtained until $T_p$ meets the need of calculation precisions.

Under the calculated temperature $T_p$, the heat of explosion of aluminized explosive can be obtained:

$$Q_p = -\sum n_i H_i(T_p) - \mathrm{Q}_{ef} \qquad (14)$$

where $Q_{ef}$ is the heat of formation of aluminized explosive.

2.3 Numerical approach

The logic for the computation is shown in Fig.1.

# 3 Empirical method estimating heat of explosion of mixed explosive

To validate the calculation method and the code in this work, the previous empirical method was used to estimate the heats of explosion for aluminized explosives. The heats of explosion estimated were used to compare the results calculated in this work.

For a mixed explosive consisting of several ingredients, the heat of explosion is estimated generally by use of following approach. Suppose $Q_{oi}$ to be the heat of explosion for every ingredient in the mixtures at the theoretical density. It can be obtained from the reported data. The heats of explosion for the mixed explosives at the theoretical density, $Q_o$ ,can be obtained by the summation of $Q_{oi}$ and $m_i$ (mass fraction of every ingredients) by a weighted method:

$$Q_o = \sum m_i Q_{oi} \qquad (15)$$

Because the heat of explosion for lean oxygen explosive increases with the density, the heat of explosion at the density $\rho$ can be obtained by the following equation:

$$Q_v = Q_o - B(\rho_o - \rho) \qquad (16)$$

Where $\rho_0$ is the theoretical density of explosive; $Q_v$ is the heat of explosion for the mixed explosive at the density $\rho$; $B$ is the revision coefficient for the mixed explosive which is the summation of $B_i$ (the revision coefficients for every ingredients) and the mass fractions by a weighted method.

$$B = \sum m_i B_i \qquad (17)$$

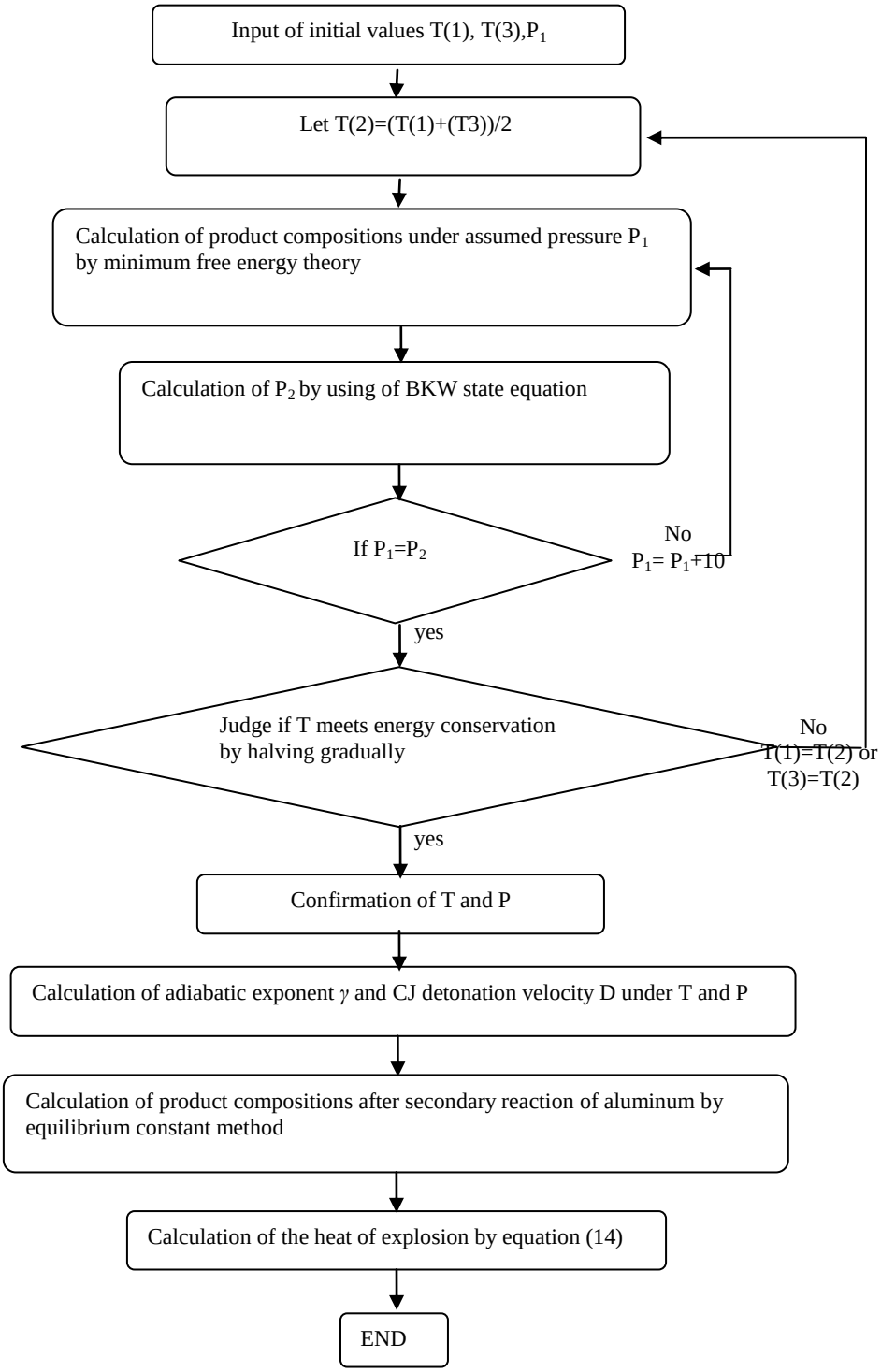


**Fig. 1.** Logic for computation of C-J detonation pressure and velocity of aluminized explosives by thermodynamic detonation theory

By use of above equation the heat of explosion for a mixed explosive at any density can be obtained by the heat of explosion ( $Q_{oi}$ ) and the revision coefficients ( $B_i$ ) for every ingredients. The characteristic heats of explosion ( $Q_{oi}$ ) and the revision coefficients ( $B_i$ ) for some explosives are listed Table 4

Table 4 $Q_{oi}$ and $B_i$ for some explosives

| Ingredient | $Q_{oi}$ (kJ/kg) | $B_i$ (kJ/(kg*g/cm$^3$)) |
|---|---|---|
| TNT | 4554.4 | 1340 |
| RDX | 5986.0 | 712 |
| HMX | 6040.4 | 712 |
| Al | 11930.1 | 2093 |

# 5 Conclusions

（1）This work presents a new code to predicate the heat and temperature of explosion for aluminized explosives. The new approach is based on the least free energy theory, successive approximation methods and judgment of reactions between aluminum and detonation products from high energy ingredients.

（2）Aluminum powder added into high energy explosives(ingredients) impacts the state of detonation in C-J reaction zones. Therefore, the equation of state calculating C-J detonation parameters (BKW equation) should be revised. The constant in the BKW equation has been revised to obtain the perfect results to predicate the C-J parameters from high energy ingredients and the heat and temperature from reactions of aluminum powder and detonation products.

（3）the predicated results show that the heats and temperatures of aluminized explosives get maximal values when the mass fractions of aluminum powder are 30%, which has good agreement with the results obtained by the empirical formulae.

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