Thermodynamic modelling of detonation H-N-O high explosives

Yu A Bogdanova¹, S A Gubin¹, A A Anikeev¹ and S B Victorov²

¹National Research Nuclear University MEPhI (Moscow Engineering Physics Institute) Kashirskoye shosse 31, Moscow 115409, Russia
²OpenSearchServer, Paris, France

E-mail: bogdanova.youlia@bk.ru

Abstract. The multiphase model of a detonation products based on the equations of state (EOS) of chemically reacting H-N-O systems which is used in the thermodynamic TDS code is presented. This model is applicable over a wide range of temperatures and density. This model consists of theoretically reasonable EOS for a multicomponent gas (fluid) phase. The calculations of detonation based on the presented model to be in good agreement with experimental data.

1. Introduction
The knowledge of thermodynamic properties of the chemical reactive systems consisting of elements H, N, O is necessary in solving of various practical problems in many fields of science and equipment. In particular, thermodynamic data of equilibrium conditions of such multicomponent systems at high pressures and temperatures are necessary in chemistry and physics of detonation and shocks [1-3]. Therefore development of reliable equation of state (EOS) models for such systems is of a great theoretical and practical interest.

In this work the multiphase EOS model for the chemical reacting H-N-O - systems which was realized into the thermodynamic TDS code [4] is presented. The model is applicable over a wide range of temperatures and density covering the area from normal pressure up to tens of gigapascals. This model includes theoretically reasonable EOS for a multicomponent gaseous (fluid) phase. The thermodynamic calculations based on the presented model allow to obtain the data of thermodynamic properties and chemical composition of the studied system. The examples presented in this work show that the offered EOS provide the exact thermodynamic description of conditions of H-N-O systems reached in static, dynamic (shock wave) and detonation experiments.

2. Equations of state
It is known that all thermodynamic properties of system, including product composition, can be found by differentiation of free Helmholtz energy.

In the present work it is supposed that the multicomponent gas (fluid) phase of products contains any combination of the following molecules and atoms: N₂, O₂, O, N, NO, N₂O, NO₂, H₂O, H₂, H and NH₃. It is assumed that molecules i and j of a multicomponent fluid phase interact via a spherically symmetric Exp-6 potential (modified Buckingham potential):
\[ \varphi_{ij}(r) = \frac{\varepsilon_{ij}}{\alpha_{ij}} - 6 \left[ \exp\left( \alpha_{ij} \left( \frac{1}{r_{min}} - \frac{r}{r_{ij}} \right) \right) - \alpha_{ij} \left( \frac{r_{min}}{r} \right)^6 \right], r \geq r_{ij} \quad (1) \]

\[ \varphi_{ij}(r) = +\alpha_{ij}, r \leq r_{ij} \quad (2) \]

where \( \varepsilon_{ij} > 0 \) and corresponds to the potential well depth (\( \min[\varphi_{ij}(r)] = -\varepsilon_{ij} \)), \( r_{min} \) is the distance between the centres of molecules at which the potential energy takes the minimum value (\( \varphi_{ij}(r_{min}) = -\varepsilon_{ij} \)), and \( \alpha_{ij} \) is the parameter determining the repulsive stiffness.

For polar molecules in [5, 6] the modified form of potential of Exp-6 considering electrostatic interactions of molecules in which well-depth depends on temperature was offered:

\[ \varepsilon_{ij}(T) = \varepsilon_{0,ij} \left( 1 + \frac{\lambda_{ij}}{T} \right) \quad (2) \]

where \( \lambda_{ij} \) – parameter which is responsible for the accounting of electrostatic effects.

In [7] it was shown that thermodynamic calculation of isotherms of ammonia and its mixtures with hydrogen with EOS on the basis of potentials (1)–(3) have better agreement with experimental data, than when using standard three-parametrical potential of Exp-6 (1)-(2).

Such potential (1)-(3) provides the realistic description of intermolecular forces in dense gases at high pressures and temperatures relevant to problems of detonation and shock waves.

In this work the improved version [8] of the perturbation theory KLRR is used. This version has the higher accuracy of calculation of thermodynamic parameters of a pure fluid at the high density, and especially for stiff potentials (\( \alpha > 14 \)), in comparison with the original version [9] and the BBH version [10] of the KLRR theory is used.

The potential parameters have been determined mostly by matching experimental Hugoniot data and available results of static experiments for the region of moderate pressures and temperatures. Potential parameters are defined in [8] and for the substances investigated in this work are presented in table 1.

| Molecule | \( \varepsilon_{0,ij}/k_B \) | \( r_{min} \) | \( \alpha_{ij} \) | \( \lambda_{ij} \) |
|----------|-----------------|---------|---------|---------|
| N2       | 100.6           | 4.25    | 12.3    | 0       |
| N        | 120.0           | 2.65    | 10.4    | 0       |
| O2       | 96.2            | 3.79    | 14.7    | 0       |
| O        | 277.0           | 2.57    | 11.5    | 0       |
| NO       | 140.2           | 3.70    | 13.9    | 0       |
| NO2      | 326.2           | 4.27    | 13.8    | 0       |
| N2O      | 234.3           | 4.27    | 13.8    | 0       |
| H2       | 36.9            | 3.67    | 10.6    | 0       |
| H        | 110.0           | 1.55    | 10.0    | 0       |
| H2O      | 195.0           | 3.22    | 13.4    | 640.0   |
| NH3      | 207.0           | 3.69    | 12.8    | 199.0   |

In multicomponent mixtures except like-pair interactions it is necessary to consider unlike-pair interactions. Potential parameters for unlike interactions \( (i \neq j) \) can be set in an obvious form (if these parameters are known), or formally expressed via like-pair potential parameters for the corresponding pairs of molecules:

\[ r_{min}^{ij} = \frac{k_{ij} r_{min}^{aa} + r_{min}^{ab}}{2} ; \ varepsilon_{ij} = l_{ij} \sqrt{\varepsilon_a \varepsilon_b} ; \ \alpha_{ij} = m_{ij} \sqrt{\alpha_a \alpha_b} \quad (3) \]

In expressions (4) \( k_{ij}, l_{ij} \) and \( m_{ij} \) – the correcting multipliers which values are usually close to unit. These multipliers can be defined if there is suitable theoretical information or experimental data.
Otherwise \( k_{ij} = l_{ij} = m_{ij} = 1 \) that reduces formulas (3) to classical Lorentz–Berthelot combination rules [11].

The unlike-pair Exp-6 parameters are additive in present work, i.e. they follow the Lorentz–Berthelot combination rules \( (k_{ij} = l_{ij} = m_{ij} = 1) \), for all pairs except for H\(_2\)O–N\(_2\), for which we found the best-fitting value of \( k_{H2O-N2} = 1.02 \).

To calculate the thermodynamic properties of a multicomponent fluid phase in [12] an improved van der Waals one fluid (vdW1f) model is proposed, which assumes a mixture of chemical species, interacting via potentials (1), to be a hypothetical one-component fluid with an effective Exp-6 potential. The composition-dependent parameters of the effective potential are given by

\[
 r_m = \left[ \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j r_{m,ij}^3 \right]^{1/3}; \quad \varepsilon = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \varepsilon_{ij} r_{m,ij}^6 \left( r_{m,ij} \right); \quad \alpha = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \alpha_{ij} \varepsilon_{ij} r_{m,ij}^3 \left( \varepsilon \cdot r_{m,ij} \right) \tag{4}
\]

where the summation extends over all \( ij \) pairs, \( n \) is the number of the components, and \( x_i \) is the mole fraction of species \( i \). The reliability of vdW1f in predicting the excess thermodynamic parameters of a multicomponent fluid has been shown by Ree [12], who is the author of the \( \alpha \)-mixing rule.

3. Results
The presented multicomponent model of detonation products based on EOS of dense gas was applied to calculation of thermodynamic properties and composition of detonation products of some H-N-O systems in the wide range of pressure and temperatures. Results of calculations are in good agreement with experimental data of shock Hugoniots (figure 1), static measurements (figure 2) and detonation experiments (table 2).

![Figure 1. Shock Hugoniots for liquid nitrogen in P-V. Symbols - experiments [16, 17] and MC simulation [18], lines – this work. Results of our calculations with potentials [13, 14] are showed also.](image)

![Figure 2. Shock Hugoniots for liquid oxygen in P-V. Symbols - experiments [17, 19] and MC simulation [18], lines – this work. Results of our calculations with potentials [13, 14] are showed also.](image)
Comparisons of results of calculations with experimental data showed that the developed EOS for dense gas provide more exact consent with experiments, than the theoretical models of other authors. It should be noted that for calibration of potential parameters experimental data on a detonation weren't used. Nevertheless, our model provided good consent with the measured detonation parameters in all considered cases. It is important to note that our model gives reliable forecasts of detonation parameters not only for HE considered above, but also for many other explosive systems. The last also HE in which detonation products besides gases significant amounts of the condensed substances are formed are among. The corresponding examples can be found in our works [1, 3, 8, 26].

Such success in a prediction of parameters of HE detonation having various temperatures, pressure and chemical compositions of detonation products was a consequence of physical validity of our model constructed on realistic intermolecular potentials and the exact theoretical EOS which is reliably reproducing data MC simulation in wide area of thermodynamic conditions of a fluid. The received results allow to conclude that our theoretical model reliably predicts thermodynamic properties of multicomponent gas mixes in the wide range of change of pressure, temperature and a chemical composition of mixtures, as provided successful forecasting of detonation characteristics of different HE with various density of charges.

### Table 2. Detonation parameters of different condensed high explosives.

| HE     | \( \rho \), kg/m\(^3\) | \( H_0 \), kcal/mole | \( D_{\text{exp}} \), m/s | \( T_{CJ} \), K | \( P_{CJ} \), GPa | \( D_{\text{calc}} \), m/s | \( \Delta D \), % |
|--------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| \( \text{H}_2\text{N}_2\text{O}_4 \) | 1050             | -87,28           | 4500             | 1667             | 5,56             | 4920             | 9,3              |
| \( \text{H}_2\text{N}_2\text{O}_5 \) | 1630             | -58,9            | 8690             | 2417             | 20               | 7913             | 8,9              |
| \( \text{H}_2\text{N}_3\text{O}_4 \) | 1620             | -6               | 8310             | 2481             | 28               | 8646             | 4,04             |
| \( \text{H}_{51.9}\text{N}_{29.1}\text{O}_{19.1} \) | 1420             | -27,7            | 8640             | 3200             | 27               | 9163             | 6,05             |
| \( \text{HN}_3 \) | 1127             | 64,4             | 7570             | 4631             | 16               | 7247             | 4,27             |
| \( \text{H}_2\text{N}_3 \) | 1260             | 40               | 7600             | 1890             | 17,8             | 8090             | 6,5              |
| \( \text{NO} \) | 1294             | 17               | 5620             | 2652             | 8,9              | 5436             | 3,3              |

**Figure 3.** Isotherms for ammonia. Symbols - experiments [21-23], lines – this work.

**Figure 4.** Isotherms for \( \text{NH}_3\)-\( \text{H}_2 \) mixture, mole fraction of \( \text{NH}_3 \):34.75%. Lines – this work. Symbols - experiment [24] and MC simulation [7].
4. Conclusion
One of the most significant results of work is the shown possibility of realistic thermodynamic modelling of complicate, multiphase and the multicomponent chemical reacting systems at high pressures and temperatures. It is shown that use of the developed technique of thermodynamic modelling and theoretically reasonable EOS of multicomponent fluid phases significantly increases reliability of thermodynamic modelling of difficult chemical systems at high pressures. Thus becomes possible to use results of thermodynamic calculations not only in the traditional field for this purpose connected with researches of shocks and detonation processes but also at the solution of a wide class of problems from other fields of science.

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References
[1] Gubin S A, Korsunskii B L, Pepekin V I, Bogdanova Yu A 2009 Comb. Expl. Sh. Waves 45 738.
[2] Shargatov V A, Bryakina U F, Gubin S A, Lyubimov A V 2012 Rus. J. Phys. Chem. B 6 261.
[3] Maklashova I V, Dolgoborodov A Yu et al 2014 J. Phys: Conf. Ser. 500 052010.
[4] Victorov S B, Gubin S A, Maklashova I V and Revyakin I I 2001 Proc. Energetic. Materials, Ignition, Combustion and Detonation 32nd Annual Conference of ICT (Karlsruhe, Germany) pp 69/1–69/15.
[5] Ree F H 1981 Proc. 7th Int. Sympos. on Detonation (Annapolis, Maryland) pp 646-661.
[6] Ree F H 1982 J. Chem. Phys. 76 6287.
[7] Bogdanova Yu A, Gubin S A, Anikeev A A, Victorov S B, Maklashova I V 2015 Rus. J. Phys. Chem. B 9 392.
[8] Victorov S B, Gubin S A 2006 Proc.13th Int. Detonation Symp. (Norfolk: Los Alamos National laboratory) p 13.1118.
[9] Kang H S, Lee C S, Lee T, Ree F H 1985 J. Chem. Phys. 82 414.
[10] Byers-Brown W, Horton T V 1988 Mol. Phys 63 125.
[11] Reed T M, Gubbins K E 1973 Applied Statistical Mechanics (New York: McGraw-Hill) 132 p.
[12] Ree F H 1983 J. Chem. Phys. 78 409.
[13] Fried L E, Howard W M J. Chem. Phys. 1998 109 7338.
[14] Van Thiel M, Ree F H J. Chem. Phys. 1996 104 5019 .
[15] Charlet F 1998 J. Appl. Phys. 84 4227.
[16] Nellis W J et.al. 1991 J. Chem. Phys. 94 2244.
[17] Nellis W J, Mitchell A C 1980 J. Chem. Phys. 73 6137.
[18] Anikeev A A, Bogdanova Yu A, Gubin S A, 2015 J. Phys: Conf. Ser. 653 012055.
[19] LASL Shock Hugoniot Data 1980 ed S. P. Marsh (University of California Press) p 653.
[20] Ross M, Ree F H 1980 J. Chem. Phys. 73 6146.
[21] Kasarnowsky I S 1940 Acta Physicochimica 12 513.
[22] Golubev I F, Kiyasheva V P, Perel’shtein I I, and Parushin E B 1978 Thermophysical Properties of Ammonia (Moscow : Izd-vo Standartov) 264 p[in Russian].
[23] Lichtblau I M, Bretton R H, Dodge B F 1964 A.I.Ch. E. Journal 10 486.
[24] Kasarnovskiy Ya S, Simonov G B, Aristov G Ye 1968 Technikal Translation 142 AD 843492.
[25] Gubin S A, Odintsov V V and Pepekin V I 1986 Thermodynamic calculations of condensed explosive detonations (Preprint. Chernogolovka: IChPh USSR Academy of Sciences).
[26] Victorov S B, El-Rabii H, Gubin S A, Maklashova I V, Bogdanova Y A 2010 J. En. Mat. 28 35.